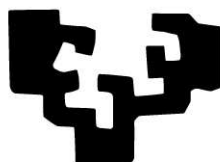


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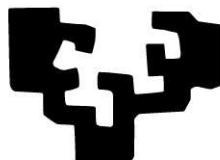
**Quantum rate coefficients
for triatomic and tetratomic reactions**

Memoria para optar al grado de Doctor con mención "Doctor Europeus"
por la Universidad del País Vasco / Euskal Herriko Unibertsitatea
presentada por:

Amaia Saracibar Ruíz de Ocenda

Julio 2007

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ERNESTO GARCIA PARA, Catedrático del Departamento de Química Física de la Universidad del País Vasco - Euskal Herriko Unibertsitatea,

CERTIFICA

que el trabajo **Quantum rate coefficients for triatomic and tetratomic reactions** ha sido realizado bajo su dirección por la Lda. **Amaia Saracibar Ruíz de Ocenda** para optar al grado de Doctor con mención "Doctor Europeus".

En Vitoria-Gasteiz, a dos de Julio de dos mil siete

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Chapter 1

Introduction

Among the most familiar characteristics of matter is its ability of undergoing chemical changes. Everyone can remember a chemistry lecture, where the demonstrator used to mix two clear liquids and obtained a colored solid precipitate. Living organisms are born, grow, reproduce, and die. Even the formation of planetary rocks, oceans, and atmospheres consists of a set of chemical reactions. The time scale for these reactions may vary from a few femtoseconds to geologic eras.

Probably, one of the main goals of chemical reaction studies is the acquisition of quantitative data, such as the reaction heat, the reaction yield or, more generally, the influence of relevant variables on the behaviour of reactive systems. This goal is usually achieved under the framework of two chemistry disciplines, thermodynamics and kinetics.

The science of thermodynamics provides us information about the sense in which the reaction will take place or not. The well-known general criterion for spontaneity is that the free energy variation between reactants and products at a given pressure and

temperature has to be negative. It is worth pointing out that this measure is expressed by means of state functions; whose variation associated to the process depends only on the features of initial and final states. However, thermodynamics cannot provide information about the rate with which the reaction will occur (there can be, for example, cases in which the evolution of a spontaneous process will not be appreciable). It can be said, therefore, that for the complete study of a chemical process chemical kinetics (the branch of chemistry that studies the time dependence of the rate of a reactions) are needed. However, since both thermodynamics and kinetics observations are based on macroscopic measurements, they are not able to provide an explanation of chemical processes based on atomic and molecular interactions and their predictive capability remains confined to phenomenological correlations. Given the enormous variety of behaviours that can be found in the chemical world, an effort to extract the fundamental trends that characterize them appears as essential. These trends have to be obtained from the microscopic study of the chemical species and the further connection to the macroscopically measurable information through statistical mechanics, including both equilibrium (partition functions, etc) and non-equilibrium disciplines (microcanonical and canonical rate coefficients, correlation functions, etc). In this connection is where the Molecular Reaction Dynamics takes place. Being more specific, Molecular Reaction Dynamics gives us an initial path to find out the connection between the experimental behaviour, macroscopically observed, and the corresponding microscopical findings. Thus, an usual result from a macroscopic kinetics study of a particular reaction is the plot of the concentration variation with time for each of the chemical species involved. The study of these variations leads to establishing empirically the rate equation, for a given reaction $aA + bB + cC + \dots \longrightarrow mM + nN + \dots$, as:

$$v = k(T)[A]^{\alpha}[B]^{\beta}[M]^{\mu}[N]^{\nu} \dots$$

where $k(T)$ is the (usually T dependent) rate coefficient and $\alpha, \beta, \dots$ are generally positive or negative, integer or half-integer exponents.

The main characteristic of the rate equations corresponding to each individual elementary stages of any mechanism is that their mathematical form corresponds to a simple case, since only reactants concentrations appear in them and their exponents coincide with their respective stoichiometric coefficients. This allows us to deduce that the reaction rate is due to a common factor, non intrinsic to the system, namely concentrations, and an intrinsic factor, the rate coefficient. If there would be no rate coefficients in the rate equation, the rate of all elementary reactions with identical stoichiometry would be the same, disregarding the nature of the chemical species undertaking the reaction. Nevertheless, experience tells us the contrary. Therefore, if the concentration term plays the role of modifying the number of collisions in a unit of time, the rate coefficient is found to characterize the effectiveness of these collisions. The explicit quantification of how different factors modify the value of the rate coefficient requires a microscopic explanation of the collisions between the chemical species. As just mentioned, this is the domain of the Molecular Reaction Dynamics or Chemical Dynamics.

Two good examples of the importance in Chemical Dynamics field are the Nobel Prize in Chemistry to Herschbach, Polanyi and Lee "for their contributions concerning the dynamics of chemical elementary processes" in 1986 [1] and to Zewail "for his studies of the transition states of chemical reactions using femtosecond spectroscopy" in 1999 [2].

The theoretical study of elementary collision processes involving atomic and molecular systems, reactive or not, can be carried out using several methodologies which find their origin in the field of Atomic and Molecular Physics. The many methodologies nowadays available are usually classified in three main categories: classical, quantum and semiclassical. A good review of these methodologies can be found in ref. [3]. Obviously, the microscopic behaviour of matter can only be rigorously reproduced using the description provided by Quantum Mechanics. (In this

work, the dynamical study has been made using mainly quantum approaches.) The quantum-mechanical treatment (either time-independent and time-dependent formulations) of the reaction dynamics has historically presented two main difficulties. The first one is that the complexity of the rearrangement processes demands a careful selection of the coordinates to be used in order to describe a realistic wavefunction during the whole scattering process. The second one arises from the fact that a chemical reaction can involve a large number of rovibrational states of both reactants and products. Fortunately, the evolution of computing platforms and the related increase of computational performances have provided powerful tools which have made feasible rigorous reactive dynamical calculations.

The early history of quantum dynamics was largely concerned with the development of methods describing atom-diatom reactions. In addition, there was much interest in the early generation of two dimensional (2D) and three dimensional (3D) quantum scattering applications to the most simple triatomic reactions, $\text{H}+\text{H}_2$ and $\text{F}+\text{H}_2$ [4]. For instance, the first full-dimensional quantum dynamical calculation was carried out by Kuppermann and coworkers for the $\text{H}+\text{H}_2$ reaction in 1976 [5, 6].

In the 1980s there was much interest in developing reduced dimensionality calculations in which two degrees of freedom (sometimes higher) calculations were embedded in higher dimensionality calculations [7]. A number of new approaches to quantum reactive scattering appeared in the late 1980s, namely hyperspherical coordinate coupled channel methods, numerical integration methods, variational methods, wavepacket methods, ... More recently, methodologies for four-atom and five-atom reactions begun to appear.

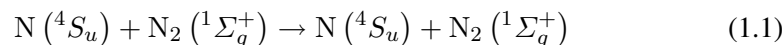
There are several experiments in Molecular Reaction Dynamics which can provide detailed information about the reactive system from a molecular viewpoint. It is worth to mention the molecular cross beams techniques [8]. It can be said that thanks

to the cross beam experiments several important paradigms in reactive dynamics have been established. They can provide the main product of the reaction, determine the dynamic of the reaction, estimate the energy of the transition state and the life time of the intermediate complex when it exists. They also allow to calculate the reactive cross section and its dependence with the collision energy, with the reactants internal energy and with the molecular orientation. They can also specify how the energy is distributed once the collision has occurred and the angular distribution of products. In addition, infrared chemiluminescence (pioneered by Polanyi and coworkers [9]) and chemical laser measurements (see for example ref. [10]) provide vibrational and rotational distributions (which in some cases are important to chemical laser performance). These and other experiments such as laser-induced fluorescence (LIF), femtosecond spectroscopy and transition state spectroscopy provide a wealth of data which interpretation has taken decades. Ultimate experiments in Molecular Reaction Dynamics result in a high level of sophistication in our understanding of the intricate details of reactive collisions including such issues as the characteristics of potential energy surfaces, nonadiabatic effects, direct collisions dynamics, quantum tunneling, resonances and other interference effects, etc. A consequence of this understanding is that our ability to use theory as a tool for predicting gas phase reaction rate processes is now quite advanced and the generation of thermal rate coefficients with chemical accuracy has been recently achieved for the simplest triatomic systems. However, the list of reactions for which this level of understanding, or at least something close to it, exists is not very long and many challenges still remain in developing theory that will be more widely applicable.

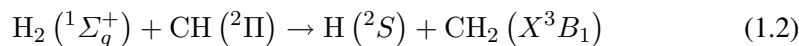
The fact that the experimental environment can be described in a relatively simple way does not mean that the information to be extracted, or the corresponding theoretical calculations, have to be simple as well. Nevertheless, the absence of external disturbing factors makes that, wishing to have theory and experiment at the same level, the theoretical methodology and the experimental technique become compli-

cated to really high limits. When this is achieved, the theoretical treatments can predict the experimental behaviour and advances in the experiment can confirm or discard the validity of the theoretical models. On the other hand, when the acquaintance of experimental data is complicated, theory can appear as a valuable a priori source of data. This mutual interaction can only be found in those fields of science where theory and experiment are at comparable levels, being this the case in many of the Molecular Reaction Dynamics applications.

The present Thesis is all part of the Molecular Reaction Dynamics area and reports on the progress made in the theoretical study of an atom-diatom reaction and a diatom-diatom reaction. The first one is the atom-diatom exchange reaction between a nitrogen atom and a nitrogen molecule:



The second one is the reaction between the methylidyne radical and a hydrogen molecule to form, through a very stable complex (the methyl radical, $\text{CH}_3(X^3A_2'')$), the methylene radical and a hydrogen atom:



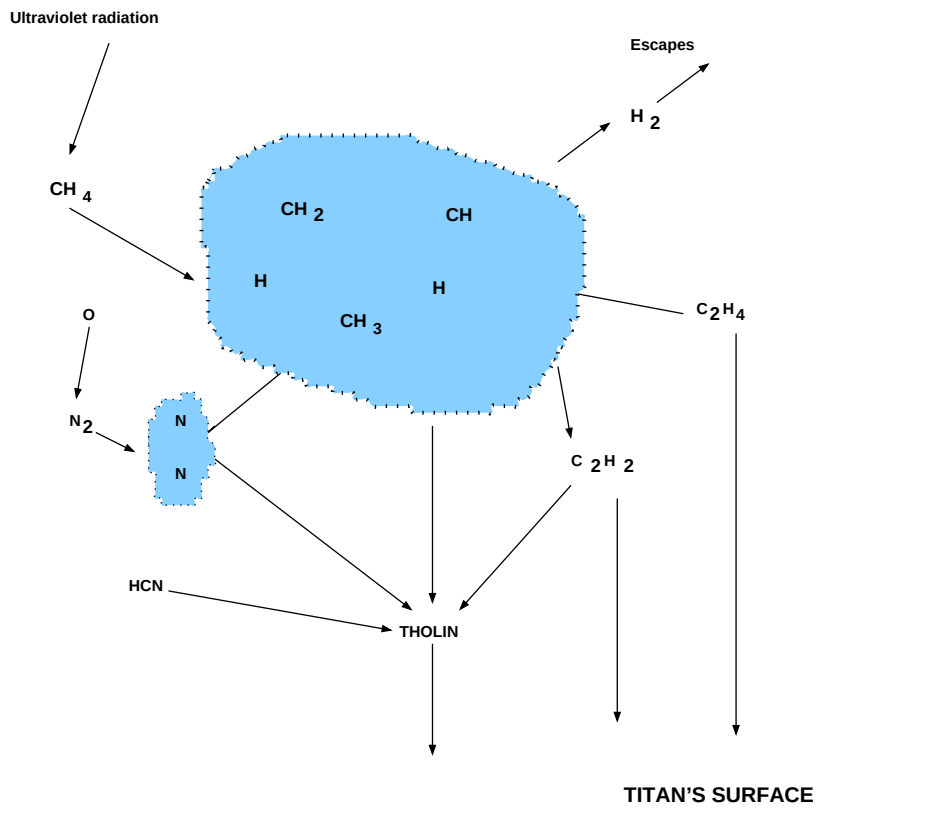
For both reactions, only the (adiabatic) ground electronic potential energy surface (PES) will be considered. Before fixing the detailed objectives of this work, the importance of these two reactions as well as some previous theoretical and experimental studies on them are described.

Chemical reactions of nitrogen atoms are significant in a variety of high temperature environments, such as shock tube experiments, comet/meteor entry into Titan's atmosphere and spacecrafts reentering into Earth's atmosphere.

In shock tube experiments, at first, the idea of the activation of nitrogen molecule represented a problem. As a matter of fact, the original idea was that the reactivity

shown by a gaseous mixture containing molecular nitrogen under electrical discharge could not be attributed to the N_2 molecule due to its high inactivity (the bond energy is 9.76 eV). After, experiments performed using a mixture of nitrogen molecules and hydrocarbons (in which the formation of cyanide acid was observed) led to suggest that some type of "active nitrogen" is intervening [11]. Molecular nitrogen under electrical discharge can be excited to a higher molecular electronic state or can dissociate into atoms. More in detail, the nitrogen atoms obtained from the dissociation process can be produced in one of the three electronic states 4S , 2D and 2P . Kinetics studies demonstrated that the electronic state 2D was the responsible for the reaction [12]. At the same time, the ground state 4S was found instead scarcely reactive especially with the N_2 singlet molecule because $N(^4S)$ adiabatically correlates with quartet intermediates that are characterized by high energies. On the other hand, the other nitrogen atom excited state, 2P , is mainly involved in quenching processes and does not show a considerable reactivity.

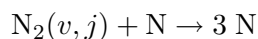
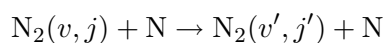
The exchange reaction (1.1), apart from its relevance in dissociation phenomena just mentioned, plays a key role in modelling the composition of the air both under equilibrium conditions [13] and typical non equilibrium conditions [14], like the ones occurring around reentering spacecrafts. Moreover, nitrogen-atom nitrogen-molecule reactions are important in high temperature environments, such as in the Titan (the largest moon of Saturn) atmosphere. Titan's atmosphere is 95% nitrogen and 5% methane. Ultraviolet light from the Sun breaks nitrogen molecules to form nitrogen atoms. Also the methane molecules are dissociated into various radicals (in the figure of page 8 radicals are enclosed by the blue contour). These radicals recombine into various organic molecules, the most abundant of which are C_2H_2 and C_2H_4 which can react with other hydrocarbon radicals and nitrogen atoms to form more complex materials. Since astrophysical and astronomic observations have revealed the presence of organic compounds containing C-N bounds, the importance of the exchange reaction $N + N_2$ is also related to the understanding of the formation of



organic molecules of fundamental importance for life.

The high speed entry of a spacecraft into the Earth's atmosphere releases a large amount of heat to the ambient gas. This large heat load excites, dissociates, and ionizes the atoms and molecules in the atmosphere. The radicals and ions so formed are chemically reactive and subsequent reactions can proceed rapidly under the high temperature conditions. Both the heat load and the reactivity of the species produced are important data for heat shield design. Since the major component of Earth's atmosphere is N_2 , the exchange and dissociation reactions of nitrogen play a primary role in flow-field modelling and in determining the heat load of spacecraft surfaces [15].

Temperatures in the spacecraft reentering can reach 20000 K. Since at these extreme temperatures practically all N_2 dissociates, the simulations of this reentering conditions requires a good characterization of nitrogen plasmas [16]. Their characterization can be performed by using methods of non equilibrium plasma kinetics which generally present strong deviation from equilibrium distributions. To solve the appropriate master equation strong attention has to be devoted to the elementary processes involved in the state-to-state vibrational kinetics. In particular V-V (vibration-vibration) and V-T (vibration-translation) energy transfer processes largely determine the shape of the vibrational distribution. Still now the V-T processes involving atomic nitrogen as well as dissociation processes induced by atoms from each vibrational states of N_2 , i.e., the processes:



where v and j (v' and j') are the vibrational and rotational quantum numbers of the reactant (product) internal states, represent a formidable problem. Some simplified methods have been developed in order to cope with this problem [17].

Experimental measurements for these high temperatures (~ 20000 K) reactions are difficult and extrapolations from lower temperature data are generally unreliable. One of the most relevant experiments that can reproduce some of these conditions are the shock-tube experiments. Unfortunately, these experiments are rather expensive and time consuming. On the contrary, progress in computer technologies has fostered the rapid development of their theoretical counterpart. In fact, the difficulty of obtaining good experimental information is more and more favouring the development of realistic theoretical models for describing accurately and from a molecular viewpoint the exchange and the dissociation processes at high temperatures.

The experimental information about the exchange reaction $N + N_2$ is quite scarce

and limited to thermal rate coefficients. Unfortunately, there are not crossed beam molecular experiments on this system since the production of a supersonic beam of nitrogen atoms intense enough to allow the study of the reactive process is extremely difficult.

The first determination of $\text{N} + \text{N}_2$ rate coefficient (at 1273 K) was done in 1962 by Back and Mui in an attempt to observe the reaction $^{14}\text{N} + ^{30}\text{N}_2 \rightarrow ^{29}\text{N}_2 + ^{15}\text{N}$ [18]. They injected $^{30}\text{N}_2$ into a stream of active nitrogen flowing through a hot tube but no formation of $^{29}\text{N}_2$ was detected. As a matter of fact, they estimated an upper limit for the exchange reaction of $k(1273 \text{ K}) < 6.6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

A further kinetic experiment was carried out in 1967 by Bar-Nun and Lifshitz who investigated the kinetic at 3400 K of the homogeneous exchange in an environment of molecular nitrogen highly diluted in argon in a single-pulse shock tube [19]. The value obtained for the rate coefficient was $k(3400 \text{ K}) = 5.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Moreover, assuming an Arrhenius factor between 10^{11} and $10^{14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, an activation energy of 1.5 eV was estimated.

The latest experimental investigation (at 1273 K) was carried out in 1972 by Lyon using a different and more sensitive molecular radiation method, the measurement of the formation of $^{29}\text{N}_2$ during the ^{30}Co gamma irradiation of $^{28}\text{N}_2$ and $^{30}\text{N}_2$ mixtures [20]. Again, just an upper limit of the rate coefficient was estimated, $k(1273 \text{ K}) < 1.3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The most extended theoretical studies of the $\text{N} + \text{N}_2$ reaction have been carried by Laganà (University of Perugia, Italy) and Garcia (University of the Basque Country, Spain). The first global potential energy function for the $\text{N} + \text{N}_2$ reaction was formulated in 1987 as a LEPS PES [21]. The LEPS PES is clearly collinearly dominant and shows a smooth monotonic approach to the saddle. The saddle height was set to be 1.55 eV, the activation energy suggested from the results of the experiment

of ref. [20]. On this surface, massive quasiclassical trajectory(QCT) and quantum reactive infinite order sudden (RIOS) computational campaigns of the vibrational state-to-state cross sections and rate coefficients of the exchange reaction (1.1) were carried out over a whole range of collision energies and temperatures [22–24]. More recently also rate coefficients for the dissociation process were calculated by Capitelli and coworkers (University of Bari, Italy) using the same LEPS PES [25, 26].

In 1997, the PES of the exchange reaction $\text{N} + \text{N}_2$ was reformulated using a LAGROBO (largest angle generalization of rotating bond order) functional [27–29] mainly in order to reproduce the non-linear geometry of the transition state suggested by the MRD-CI ab initio calculations by Petrongolo [30, 31]. Due to the flexibility of the LAGROBO model four potential energy surfaces, called L0, L1, L2 and L3 were developed [27, 32]. QCT and quantum RIOS calculations performed on both the LEPS and the LAGROBO PESs allowed to study the effect of varying the geometry of the transition state singling out a clear different dynamics of the system on the different PESs [32].

Until recently, there was not an accurate quantum dynamics study for the $\text{N} + \text{N}_2$ reaction. Three dimensional quantum calculations performed on the above mentioned LEPS only for zero total angular momentum and low translational energies were reported for the first time in the year 2004 [33]. More recently a semiclassical initial value representation (SC-IVR) method was applied to compute on the same PES the thermal rate coefficient [34].

In 2003, a new global PES was proposed [35]. This WSHDS (Wang-Stallcop-Huo-Dateo-Schwenke-Patridge) PES was based on more than three thousand ab initio points calculated using high-level methods and basis sets. Ab initio points were then fitted using a function with 68 parameters. This PES is drastically different from the LEPS and the LAGROBO ones. It exhibits a double barrier (i.e., two saddle points

connected by a shallow well), besides a higher transition state. On the WSHDS surface (and on the previous LEPS) the authors carried out zero total angular momentum quantum time-dependent calculations to compute the reaction probabilities. From these values the rate coefficients were computed employing the J -shift model [36]. Significant differences were found in the calculated rate coefficients on both surfaces. Further theoretical work on the WSHDS PES was focused to the study of the resonances [37, 38]. Unfortunately, the difficulty of reconstructing the WSHDSP PES from the information given in ref. [35] and of obtaining a copy of the related routine from the authors, did not allow us to carry out calculations on that surface.

The tetratomic reaction considered in this Thesis is, as already mentioned, the $\text{CH} + \text{H}_2$ one. It involves the simplest carbon-based molecular radical, the methylidyne one. The reactions of the methylidyne radical are important in the chemistry of the combustion [39] and of the planetary atmospheres [40, 41].

In general, the kinetics of radical reactions in gas phase is of central importance in pyrolysis combustion chemistry [42]. A wide variety of hydrocarbons, mostly in the form of complex mixtures, is used as practical fuels. The basic chemical features of their combustion reactions vary little from one hydrocarbon to another, except methane. The main differences are found to arise from the relative amounts of aliphatic, olefinic and aromatic hydrocarbons. There are important differences however in the chemistry of hydrocarbon oxidation at low (hundreds of Kelvins) and high (over 1000 K) temperatures. Hydrocarbon oxidation shows a particular self-acceleration and induction periods. While induction periods alone suggest that some form of branched chain reaction is involved, simple branched chain mechanisms cannot explain the induction behaviour observed in hydrocarbon-oxygen mixtures at low temperatures: (a) the self-acceleration rates are much lower than in explosive chain branching reactions, and (b) very large fractions of the fuel are converted to stable partially oxidized intermediate species long before any significant energy release.

Explaining these observations in chemical detail is one of the main goals of basic combustion chemistry research as soon as quantitative data were available. Semenov (Nobel Prize in Chemistry 1956 together with Hinshelwood "for their researches into the mechanism of chemical reactions" [43]) suggested that during low temperature hydrocarbon oxidation, the chain branching process requires "secondary" reactions of the partially oxidized intermediate products that are formed early in the reaction in the course of an essentially unbranched chain mechanism. Such intermediates would be relatively stable products able to undergo further transformations to give the active centers that eventually lead to "degenerate" chain branching. Gradual accumulation of intermediate products in significant amounts eventually leads to exponential growth of radical concentrations and fuel oxidation rates. Roles like these for intermediate products are indeed a general feature of hydrocarbon oxidation. Applications of progress in this area affect fields such as automotive engineering, energy production, process design and many others.

The reactions of the methylidyne radical are especially important in the atmospheres of Titan and Jupiter [40, 41] where, apart from nitrogen, methane is a major component. Methane gas is easily dissociated by solar photons generating various radicals such as CH, CH₂ and CH₃, (displayed in the blue area of the figure of page 8). The methane photochemistry in Titan is in general similar to that seen on the giant planets, although it is more efficient since there is far less free atomic hydrogen, as it readily escapes Titan's gravity field.

Furthermore, CH radicals were the first molecular species detected in deep space and they play a role in the chemistry of interstellar clouds. For this latter purposes, the knowledge of reaction rates at low and very low (10–100 K) temperatures is required. Nice experiments have been made possible at these low temperatures thanks to the CRESU apparatus [40]. The CRESU ("Cinétique de Réaction en Ecoulement Supersonique Uniforme" or Reaction Kinetics in Uniform Supersonic Flow) tech-

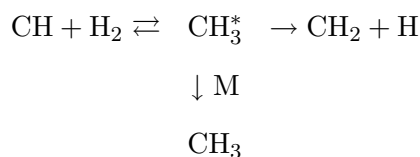
nique involves the expansion of a gas or mixture of gases through a Laval nozzle from a high pressure reservoir into a vacuum chamber. As it expands, the nozzle collimates the gas into a uniform supersonic beam which is essentially collision free. Each nozzle produces a characteristic temperature; in this way any temperature between room temperature and about 10 K can routinely be achieved. There are relatively few CRESU apparatus around the world. Two of the leading centres for this technique are the University of Rennes (France) and the University of Birmingham (UK). CRESU experiments have been used to show deviations from Arrhenius kinetics at low temperatures: as the temperature is reduced, the rate coefficient actually increases. This feature can explain why chemistry is so prevalent in the interstellar medium, where many different polyatomic species have been detected (by radio astronomy), but where temperatures are so low that conventional wisdom might suggest that chemical reactions would not occur.

The reaction $\text{CH} + \text{H}_2 \rightarrow \text{H} + \text{CH}_2$ and its reverse, playing an important role in hydrocarbon combustion, have been the focus of a large number of experimental and theoretical efforts [44–68]. The forward reaction is endothermic by only 0.145 eV [69], has no barrier to reaction and involves a deep well corresponding to the methyl radical. The formation of rovibrationally excited CH_3 complexes and their stabilization due to collisions make the kinetics of the system very interesting.

From the theoretical point of view, there is a special interest in the reaction $\text{CH} + \text{H}_2$ due to its electronic simplicity. Thus, a comparison between the results of experiments and of accurate quantum theories becomes a realistic possibility.

Berman and Lin [60] were the first to realize that the reaction between CH and H_2 can proceed via an energized $\text{CH}_3^*(X^2A_2'')$ intermediate which correlates adiabatically with both $\text{CH}(X^2\Pi) + \text{H}_2(X^1\Sigma_b^+)$ and $\text{CH}_2(X^3B_1) + \text{H}(^2S)$. Also the energized intermediate can be deexcited collisionally to form the CH_3 radical. The mechanism

proposed may be written as:



There has been several experimental studies on the reaction between CH and H₂ and its isotopic variants [47–54]. On the contrary, there has been only one attempt to measure rate coefficients for the removal of CH(*v* = 1) in collisions with H₂ [48] and only one direct determination of the rate coefficient for reverse reaction, between CH₂ and H atoms [53]. The large value of the rate coefficient for the (exothermic) reaction of H atoms with CH₂ provided strong confirmatory evidence for the theoretical prediction that there is no barrier to this reaction [46, 59]. At the same time, it is worth to mention the elegant molecular beam study of the CH + D₂ reaction [52].

The last experiment was carried out in 1997 [61]. This CRESU experiment provided rate coefficients for reactions of CH radicals over a range of temperatures not covered previously [55–58]. This work constitutes the most complete study yet reported on the kinetics of the interaction between CH radicals and H₂ and D₂. Measurements on the systems CH(*v*=0) + D₂, CH(*v*=1) + H₂, and CH(*v*=1) + D₂ demonstrated that the collision dynamics is dominated by the formation of CH₃^{*} (CHD₂^{*}) complexes over an entirely attractive PES. For these reactions, the rate coefficients were measured over a very wide range of temperature (13–584 K) allowing to infer values for the limiting high pressure rate coefficient for association of CH with H₂. More relevant to our work is the investigation on the kinetics of CH(*v*=0) and H₂ in the range of temperatures 53–744 K.

The first theoretical study on the CH + H₂ reaction was published in 1977 by Brooks and Schaefer [44]. In that work, the minimum energy path was found to be somewhat unusual because the two diatomic reactants are oriented parallel to each

other as they approach and only at a short separation they adopt the more intuitive C_{2v} insertion geometry.

Further theoretical work was done in 1990 by Wagner *et al.* [46]. These calculations confirmed the correctness of the mechanism proposed by Berman and Lin [60] regarding the role played by the energized CH_3^* complex. They indicate also that there are no potential barriers neither in the entrance channel nor in the exit channel.

Quite recently, Marquardt and Quack presented an ab initio PES for the CH_3 system in the framework of a global hypersurface for CH_4 [64, 65].

The last and most accurate (and used in the present work) PES of the $CH + H_2$ reaction was developed in 2006 by Medvedev *et al.* [67]. This PES was validated by obtaining a good agreement between the vibrational levels of the methyl radical calculated on it and the recent theoretical [70] and experimental results [71–74]. Our group has collaborated in the first dynamical test of this PES [68], where reaction probabilities for the total angular momentum $J = 0$ limit has been calculated using a four-atom quantum wavepacket approach and compared with quasiclassical trajectory and statistical theory results.

The main objective of this Thesis has been to calculate accurate rate coefficients for both the triatomic reaction $N + N_2$ and the tetratomic reaction $CH + H_2$ using a quantum time-dependent method. The full-dimensional quantum evaluation of rate coefficients is a so highly demanding computational task to make it unfeasible. For this reason, we have appealed to approximate methods after testing approximations employed.

From the theoretical point of view, the difficulty of studying the $N + N_2$ reaction comes from the fact that three non hydrogen atoms are involved and, therefore, the separation between its quantum states (the rovibrational states and also the total

angular momentum states) is significantly smaller than that of reactions involving hydrogen atoms. Accordingly, the number of initial rovibrational states to be included in the calculation of the rate coefficient at relatively high temperatures (like those involved in the spacecraft reentering) may sum up to about one thousand. At the same time, a large number of total angular momentum states is expected to contribute to the reaction.

In this Thesis we have braved and tackled the problem of determining the rate coefficient of the $\text{N} + \text{N}_2$ reaction by carrying out extended three dimensional quantum calculations using the RWAVEPR code developed by Skouteris and Laganà (University of Perugia, Italy) [75, 76]. In particular, exact $J = 0$ state-to-state quantum reactive probabilities have been calculated for the ground rotational level of the first six vibrational states of the reactant N_2 molecule on several potential energy surfaces and the effect of both the vibrational excitation and the surface topology has been analysed. The $J = 0$ calculations have been also performed to investigate the effect of the rotational excitation at $v = 0, 1, 2$ and 3 on the reactive probability and to calculate the rate coefficients in the range of temperatures $1000\text{--}4000$ K using the J -shift approximation by considering the lowest 242 rovibrational states. A more rigorous approximation (the Centrifugal Sudden (CS) one) has also been used. In spite of the high computational effort spent, we could not attack the problem of carrying out the calculation of the CS rate coefficients at relatively high temperatures. In fact, the CS calculation of the probability for a single rovibrational state and total angular momentum increases linearly with the total angular momentum. For this reason we have calculated only the CS cross sections for the most populated rovibrational states at the two temperatures of the experiment and we have compared the results obtained with the ones calculated using the J -shift approximation. At the same time, the contribution of each projection of the total angular momentum and of each total angular momentum to the reactive probability has been also analysed. The study of the dynamics of the reaction $\text{N} + \text{N}_2$ has finished by calculating "exact"

reactive probabilities for a limited number of quantum states. "Exact" means that the coupling among the quantum states, neglected in the CS approximation, has been included implying as a consequence a (limited) validation of the CS results.

Another important objective of this work has been the construction a new potential energy surface for the reaction $\text{N} + \text{N}_2$ according to the characteristics shown in recent ab initio calculations [35]. Thus, we have carried afresh ab initio calculations using, as in ref. [35], the open shell CCSD(T)/aug-cc-pVTZ method. Then, a new surface has been generated using the LAGROBO methodology. Indeed, we have had to reformulate the LAGROBO functional to describe the more structured topology of the new surface. On this new surface time-dependent quantum calculations have been performed to investigate its dynamical properties. In particular, cross sections using both the J -shift and the CS approximations have been calculated and compared each other. The results obtained have also been compared with the values obtained on the previous PESs.

It is worth noting at this point the huge computational effort needed to performed the above mentioned calculations. This computational burden has been alleviated by the use of the production grid infrastructure of EGEE [77,78]. To this end, significant efforts have been spent to implement the programs on these platforms.

As to the tetratomic reaction $\text{CH} + \text{H}_2$, the accurate calculation of the rate coefficients is favoured by the fact that three hydrogen atoms are involved despite the larger number of degrees of freedom (the two collision partners diatoms have an internal structure). To reduce the dimensionality of the problem, it was assumed that the initial CH bond does not break. Moreover, a capture statistical model is applied. In this model, the probability to form the CH_3 intermediate (i.e., the capture probability) is calculated using a real wavepacket code developed by Goldfield (Wayne State University, Detroit). Both $J = 0$ and $J > 0$ quantum calculations have been

performed. In the case of $J > 0$, the CS approximation is also adopted. The capture probability is then multiplied by the probability of the decay of the complex to calculate the rate coefficient.

At the same time, our work on the CH + H₂ reaction, besides to the calculation of the rate coefficients, includes the investigation of the effect of the initial orientation of the diatoms and its rotational excitation on the capture probability. Furthermore, a rationale of the dynamical behaviour of the reaction based on quasiclassical trajectory calculations has been proposed.

In spite of our interest in calculating the rate coefficients at relatively low temperatures (200–580 K) and of the fact that the calculations were restricted to reactants in their ground vibrational state, not all the initial quantum states were considered. In fact, a sampling procedure to select the initial quantum states has been developed in order to facilitate the convergence. Moreover, the number of total angular momentum quantum values considered has been clearly lower than that used in the heavier N + N₂ reaction. Finally, the calculated rate coefficient has been compared with the experimental results and with the results provided by a more standard statistical approach in which the capture probability is estimated considering unidimensional centrifugal barriers.

The Thesis is, therefore, articulated as follows. Chapters 2 and 3 deal with the exchange N + N₂ reaction while Chapters 4 and 5 deal with the reaction CH + H₂. In particular, Chapter 2 describes the time-dependent wavepacket approach used to calculate the reaction probabilities as well as the approximations formulated to obtain the quantum rate coefficients. This Chapter ends with the description of the potential energy surfaces used. Chapter 3 presents the time-dependent calculations performed and discusses the results (reaction probabilities, cross sections and rate coefficients) obtained. In this Chapter also the development of a new PES is presented

and dynamical calculations carried out on it are discussed. Chapter 4 describes the time-dependent real wavepacket approach used to calculate the capture probabilities and the procedure to estimate the rate coefficients from them. In this Chapter, also a description of the used potential energy surface is given. The calculated capture probabilities and rate coefficients are discussed in Chapter 5. Finally, Chapter 6 collects the main conclusions of this work.

Chapter 2

The N+N₂ reaction: Theoretical approach

2.1 Quantum dynamics

The general expression of the (non relativistic) hamiltonian describing the evolution from reactants to products for a reactive system with M nuclei and N electrons is given by:

$$\begin{aligned}\hat{H} = & -\sum_{i=1}^N \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_{A=1}^M \frac{\hbar^2}{2M_A} \nabla_A^2 \\ & - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A e^2}{r_{iA}^*} + \sum_{i=1}^N \sum_{j>i}^N \frac{e^2}{r_{ij}^*} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B e^2}{R_{AB}^*}\end{aligned}\quad (2.1)$$

where $\hbar = h/2\pi$ (with h being the Planck's constant), m_e is the mass of the electron, M_A is the mass of the nucleus A, e is the charge of the electron, $Z_A e$ is the charge of the nucleus A, r_{iA}^* is the distance between the electron i and the nucleus A, r_{ij}^* is the distance between the electrons i and j , and R_{AB}^* is the distance between the

nuclei A and B. In eq. 2.1 the first term represents the electronic kinetic energy, the second the nuclear kinetic energy, the third the Coulombic attraction potential energy between the electrons and the nuclei, the fourth the Coulombic repulsion potential energy between electrons and the last one is the Coulombic repulsion potential energy between nuclei.

At any instant, the reactive system is described by its wavefunction $\Psi(\mathbf{R}^*, \mathbf{r}^*, t)$ which is solution of the time-dependent Schrödinger equation:

$$\hat{H}\Psi(\mathbf{R}^*, \mathbf{r}^*, t) = i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{R}^*, \mathbf{r}^*, t) \quad (2.2)$$

where $\mathbf{R}^*$ and $\mathbf{r}^*$ represent collectively the nuclear and the electronic coordinates, respectively, referred to an arbitrary system of reference.

The solution of the equation 2.2 is extremely complicated and it would be almost hopeless to attempt an exact solution. Because of this, it is convenient to simplify the equation by considering some particular cases which may imply, sometimes, specific approximations. Accordingly, one first separates the center of mass of the system. Second, one exploits the fact that the nuclei are much heavier than the electrons and separates of the nuclear from the electronic motion (Born-Oppenheimer approximation). Then one can restrict the problem to time-independent hamiltonian. (In this Thesis, only time-dependent formulations have been used.)

The first simplification consists in the separation of equations for the center of mass. Its evolution in time, in fact, only depends on the relative distances of the colliding partners. Therefore, the motion of center of mass of the system remains unaltered and the hamiltonian can be expressed as a sum of terms referred to it and terms associated with the relative motion of the particles. To this end a new system of coordinates can be defined [79]:

$$\mathbf{S} = \frac{1}{M_{\text{tot}}} \left(\sum_{A=1}^M M_A \mathbf{R}_A^* + \sum_{i=1}^N m_e \mathbf{r}_i^* \right) \approx \frac{1}{M_0} \sum_{A=1}^M M_A \mathbf{R}_A^*$$

$$\begin{aligned}\mathbf{r}_i &= \mathbf{r}_i^* - \mathbf{S} & i &= 1, \dots, N \\ \mathbf{R}_A &= \mathbf{R}_A^* - \mathbf{S} & A &= 1, \dots, M\end{aligned}$$

where M_0 represents the total mass of the nuclei, $M_0 = \sum_{A=1}^M M_A$, and M_{tot} is the total mass of the system, $M_{\text{tot}} = M_0 + Nm_e$. Since the mass of the system is in practice almost entirely localized in the nuclei, the position vector of the center of mass, $\mathbf{S}$, can be approximated by the position vector of the center of mass of the nuclei.

The new $\mathbf{S}$ vector defines the position of the center of mass of the whole system with respect to the initial reference axes of coordinates, the $\mathbf{r}_i$ vector indicates the position of the electron i with respect to the center of mass and the $\mathbf{R}_A$ vector indicates the position of the nucleus A with respect to the center of mass. By taking the center of mass as the origin of the coordinate system one has that the coordinate of one of the atoms of the system (say C) is related to the position of all the other atoms ($A \neq C$) as follows:

$$\mathbf{R}_C = -\frac{1}{M_C} \sum_{A=1, A \neq C}^M M_A \mathbf{R}_A$$

Using these new coordinates, the hamiltonian operator can be written as:

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2M_{\text{tot}}} \nabla_{\mathbf{S}}^2 - \frac{\hbar^2}{2} \left(\frac{1}{m_e} + \frac{1}{M_0} \right) \sum_{i=1}^N \nabla_i^2 - \frac{\hbar^2}{2M_0} \sum_{i=1}^N \sum_{i>j}^N \nabla_i \nabla_j \\ &\quad - \frac{\hbar^2}{2} \sum_{A=1, A \neq C}^M \left(\frac{1}{M_A} + \frac{1}{M_0} \right) \nabla_A^2 + \frac{\hbar^2}{2M_0} \sum_{A=1, A \neq C}^M \sum_{B>A, B \neq C}^M \nabla_A \nabla_B \\ &\quad - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A e^2}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{e^2}{r_{ij}} + \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B e^2}{R_{AB}}\end{aligned}\tag{2.3}$$

Since the electrostatic interaction between nuclei and electrons depends on their relative distance, the last three terms of this expression coincide with those of eq. 2.1. The only term dependent on the center of mass coordinates is the first one which rep-

resents the translational motion of the whole system and therefore is simply adding a constant to the total energy of the reactive system.

The most important approximation is the well known Born-Oppenheimer (or adiabatic) approximation. It is again based on the fact that the mass of the nuclei is much larger than that of the electrons. Accordingly, the nuclei move far slower than the electrons, and the electrons carry out "many cycles" of motion in the time it takes the nuclei to move a short distance. On this ground the hamiltonian of eq. 2.3 (after separating the center of mass motion) can be rewritten as:

$$\hat{H} = \hat{T}_N + \hat{T}_e + U_{eN} + U_{ee} + U_{NN} = \hat{T}_N + \hat{H}_e \quad (2.4)$$

where $\hat{H}_e = \hat{T}_e + U_{eN} + U_{ee} + U_{NN}$ with

$$\begin{aligned} \hat{T}_N &= -\frac{\hbar^2}{2} \sum_{A=1}^M \left(\frac{1}{M_A} + \frac{1}{M_0} \right) \nabla_A^2 + \frac{\hbar^2}{2M_0} \sum_{A=1}^M \sum_{B>A}^M \nabla_A \nabla_B \\ \hat{T}_e &= -\frac{\hbar^2}{2} \left(\frac{1}{m_e} + \frac{1}{M_0} \right) \sum_{i=1}^N \nabla_i^2 - \frac{\hbar^2}{2M_0} \sum_{i=1}^N \sum_{j>i}^N \nabla_i \nabla_j \\ U_{eN} &= -\sum_{i=1}^N \sum_{A=1}^M \frac{Z_A e^2}{r_{iA}} \quad U_{ee} = \sum_{i=1}^N \sum_{j>i}^N \frac{e^2}{r_{ij}} \quad U_{NN} = \sum_{A=1}^M \sum_{B>A}^M \frac{Z_A Z_B e^2}{R_{AB}} \end{aligned}$$

In this approach, the time-dependent Schrödinger equation 2.2 is solved by expanding the total wavefunction as a linear combination of the electronic functions $\Phi_n(\mathbf{r}; \mathbf{R})$ as follows:

$$\Psi(\mathbf{R}, \mathbf{r}, t) = \sum_n \chi_n(\mathbf{R}, t) \Phi_n(\mathbf{r}; \mathbf{R}) \quad (2.5)$$

where the coefficients of the expansion, the nuclear functions $\chi_n(\mathbf{R}, t)$, depend on the nuclear coordinates only, while the electronic functions $\Phi_n(\mathbf{r}; \mathbf{R})$ depend on the electronic coordinates and parametrically on the nuclear coordinates. The electronic functions used for the expansion in the adiabatic representation are eigenfunctions of the electronic hamiltonian $\hat{H}_e$:

$$\hat{H}_e \Phi_n(\mathbf{r}; \mathbf{R}) = E_n \Phi_n(\mathbf{r}; \mathbf{R}) \quad (2.6)$$

Therefore, if one replaces eq. 2.5 in the Schrödinger equation 2.2 obtains:

$$\left(\hat{T}_N + \hat{H}_e\right) \sum_n \Phi_n(\mathbf{r}; \mathbf{R}) \chi_n(\mathbf{R}, t) = i\hbar \sum_n \Phi_n(\mathbf{r}; \mathbf{R}) \frac{\partial}{\partial t} \chi_n(\mathbf{R}, t) \quad (2.7)$$

Multiplying this expression by $\Phi_{n'}^*$, integrating over electronic coordinates and considering the orthonormality of the basis functions ($\langle \Phi_n | \Phi_{n'} \rangle = \delta_{nn'}$), eq. 2.7 can be written for a given electronic state n as:

$$\left[E_{nn} + \hat{a}_{nn} + \hat{b}_{nn} + \hat{T}_N\right] \chi_n(\mathbf{R}, t) + \sum_{n' \neq n} \hat{c}_{nn'} \chi_{n'}(\mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} \chi_n(\mathbf{R}, t) \quad (2.8)$$

being

$$\begin{aligned} \hat{c}_{nn'} &= E_{nn'} + \hat{a}_{nn'} + \hat{b}_{nn'} \\ E_{nn'} &= \langle \Phi_n(\mathbf{r}; \mathbf{R}) | \hat{H}_e | \Phi_{n'}(\mathbf{r}; \mathbf{R}) \rangle \\ \hat{a}_{nn'} &= -\frac{\hbar^2}{2} \sum_{A=1}^M \left(\frac{1}{M_A} + \frac{1}{M_0} \right) \langle \Phi_n | \nabla_A^2 | \Phi_{n'} \rangle + 2 \langle \Phi_n | \nabla_A | \Phi_{n'} \rangle \nabla_A \\ \hat{b}_{nn'} &= \frac{\hbar^2}{2M_0} \sum_{A=1}^M \sum_{B>A}^M \langle \Phi_n | \nabla_A \nabla_B | \Phi_{n'} \rangle + 2 \langle \Phi_n | \nabla_A | \Phi_{n'} \rangle \nabla_B \end{aligned}$$

This expression contains non-diagonal terms. The non-diagonal terms $\hat{c}_{nn'}$ represent the coupling between different adiabatic electronic states, the non-diagonal terms $E_{nn'}$ represent the interactions between electronic states while $\hat{a}_{nn'}$, $\hat{b}_{nn'}$ are the electronic state coupling elements associated with nuclear motion. The diagonal terms $E_{nn}(\mathbf{R})$ (or simply $E_n(\mathbf{R})$) are the energies of the electronic states for different nuclear positions, that is, the adiabatic potential energy surface (PES) for the electronic state n .

Equation 2.8 formulates rigorously the coupled Schrödinger equation for the nuclear wavefunction in the adiabatic representation. The direct calculation of the nonadiabatic coupling, however, is a very difficult task in quantum chemistry and the strenght of the adiabatic representation lies in neglecting the off-diagonal $\hat{c}_{nn'} (n \neq 0)$ coupling terms. Moreover the diagonal terms $\hat{a}_{nn}$ and $\hat{b}_{nn}$ are usually small and

are generally negligible. As a result one lands into the following decoupled set of differential equations:

$$\left[\hat{T}_N(\mathbf{R}) + E_n(\mathbf{R}) \right] \chi_n(\mathbf{R}, t) = i\hbar \frac{\partial}{\partial t} \chi_n(\mathbf{R}, t) \quad n = 0, 1, 2, \dots \quad (2.9)$$

where each n equation describes the nuclear motion on a single potential energy surface $E_n(\mathbf{R})$. In the remainder of the Thesis we shall consider only reaction on the ground electronic state and this will allow us to drop the electronic state index.

The physical meaning of the adiabatic approximation is clear: the slow nuclear motion only leads to the deformation of the electronic states but not to transitions between different electronic states. The electronic wavefunction deforms instantaneously to adjust to the slow motion of nuclei. The general criterion for the validity of the adiabatic approximation is that the nuclear kinetic energy be small with respect to the energy gap between electronic states such that the nuclear motion does not cause transitions between electronic states. This approximation is good enough when one is dealing with low translational energy collisions and in this case it is possible to study the dynamics of the collisions in a single adiabatic potential energy surface. However, sometimes, there are some regions in the PES where the nonadiabatic coupling are not negligible and it is necessary consider the influence of those electronic states in the adiabatic treatment.

All the formalism described before refers to M nuclei and N electrons systems. However, since the object of this Section is limited to atom-diatom reactive processes the following developments will refer only to triatomic systems. All quantum treatments of the (adiabatic) reactive dynamics start with the Schrödinger equation formulated in eq. 2.9. To solve this Schrödinger equation one needs to take into account the following steps: (1) the coordinate system for the hamiltonian representation, (2) the reference system for the hamiltonian representation, and (3) the scattering amplitudes calculated by solving the coupled differential equations. The two first points are general and will be described in detail in this Section. The last point depends on

the quantum approach used to solve the Schrödinger equation and will be discussed in Section 2.7.

In a generic triatomic reaction $A + BC$ the available channels are three: $A + BC \rightarrow A + BC$, $A + BC \rightarrow B + AC$ and $A + BC \rightarrow C + AB$. The first case involves elastic and inelastic non reactive collisions and the two last ones involve reactive collisions. Each possibility is known as rearrangement channel and, using the free atom notation, are referred as a , b and c , respectively.

Once the separation of the center of mass is performed, the relative motion of the three atoms can be defined using three Jacobi coordinate systems. These three coordinate systems are displayed in Figure 2.1. As apparent from the Figure, the definition of the vectors in it is cyclical with respect to the A, B and C atom positions. Therefore, hereafter, instead of a specific a , b and c rearrangement channel the indices λ , ν and κ will be used to represent anyone of these cyclical exchanges. The definition of the Jacobi coordinate systems is given by:

$$\mathbf{R}_\lambda = \mathbf{x}_\lambda - \frac{M_\nu \mathbf{x}_\nu + M_\kappa \mathbf{x}_\kappa}{M_\nu + M_\kappa} \quad \mathbf{r}_\lambda = \mathbf{x}_\kappa - \mathbf{x}_\nu \quad (2.10)$$

where M and $\mathbf{x}$ are, respectively, the atomic masses and the atom position vectors referred to the center of mass of the system.

The $\mathbf{R}_\lambda$ Jacobi vector represents the vector between the atom λ and the center of mass of the molecule $\nu\kappa$ and the $\mathbf{r}_\lambda$ vector corresponds to the internuclear vector between the atom ν and the atom κ . The angle between the Jacobi vectors is given by:

$$\Theta_\lambda = \arccos \frac{\mathbf{R}_\lambda \cdot \mathbf{r}_\lambda}{|\mathbf{R}_\lambda| |\mathbf{r}_\lambda|} \quad (2.11)$$

Obviously, when $|\mathbf{R}_\lambda| \rightarrow \infty$ and $|\mathbf{r}_\lambda|$ remains finite, the rearrangement channel is λ . The relationship between the three Jacobi coordinate systems comes from a transfor-

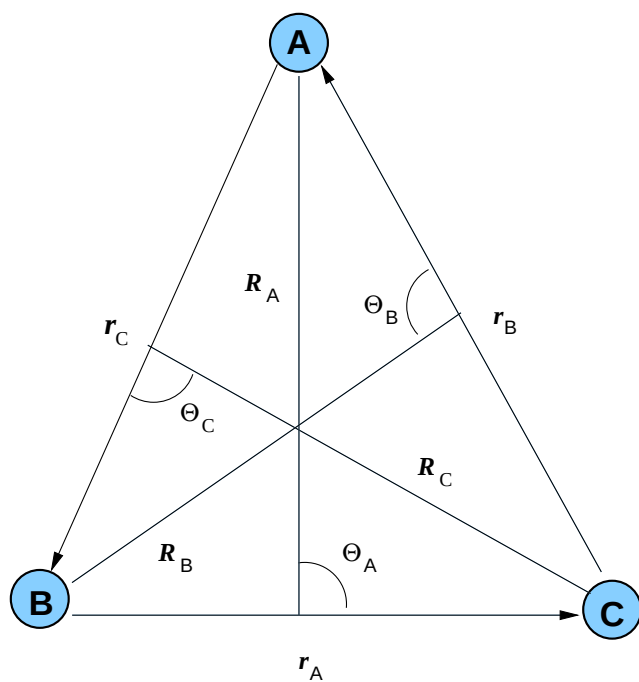


Figure 2.1: Definition of the Jacobi coordinates.

mation (kinematic rotation) which is function only of the atomic masses:

$$\begin{pmatrix} \mathbf{R}_\nu \\ \mathbf{r}_\nu \end{pmatrix} = \begin{pmatrix} \cos \beta_{\nu\lambda} & -\sin \beta_{\nu\lambda} \\ \sin \beta_{\nu\lambda} & \cos \beta_{\nu\lambda} \end{pmatrix} \begin{pmatrix} \mathbf{R}_\lambda \\ \mathbf{r}_\lambda \end{pmatrix} \quad (2.12)$$

where

$$\begin{aligned} \cos \beta_{\nu\lambda} &= \left[\frac{M_\lambda M_\nu}{(M_\lambda + M_\kappa)(M_\nu + M_\kappa)} \right]^{1/2} \\ \sin \beta_{\nu\lambda} &= \left[\frac{M_\kappa (M_\lambda + M_\nu + M_\kappa)}{(M_\lambda + M_\kappa)(M_\nu + M_\kappa)} \right]^{1/2} \end{aligned}$$

In chemical reaction dynamics the angle $\beta_{\nu\lambda}$ is known as skewing angle and represents the rotational angle between the Jacobi vectors in the different rearrangement channels.

Using the Jacobi coordinates the Schrödinger equation 2.9 of the nuclei is formulated as:

$$\left[-\frac{\hbar^2}{2\mu_{\lambda,\nu\kappa}} \nabla_{\mathbf{R}_\lambda}^2 - \frac{\hbar^2}{2\mu_{\nu\kappa}} \nabla_{\mathbf{r}_\lambda}^2 + V(\mathbf{R}_\lambda, \mathbf{r}_\lambda) \right] \Psi^\lambda(\mathbf{R}_\lambda, \mathbf{r}_\lambda, t) = i\hbar \frac{\partial}{\partial t} \Psi^\lambda(\mathbf{R}_\lambda, \mathbf{r}_\lambda, t) \quad (2.13)$$

where $\mu_{\lambda,\nu\kappa}$ is the reduced mass for the triatomic $\lambda + \nu\kappa$ system and $\mu_{\nu\kappa}$ is the reduced mass for the diatomic $\nu\kappa$ system. The index λ in the wavefunction of the system indicates the rearrangement channel. Obviously, the wavefunction representation according to the different rearrangement channels is equivalent. Nevertheless, the effectiveness of each representation to describe the global wavefunction varies for the various channels. For that reason, in reaction dynamics the procedure to obtain the wavefunction is to determine the wavefunctions for each rearrangement channel using the corresponding representation to that channel and, later, match properly these functions.

The choice of a reference system is another key element of a rigorous quantum treatment of reactive collisions. The choice a proper spatial orientation of the axis system is important for the exploitation of the angular momentum algebra. In fact,

in an atom-diatom system, the total angular momentum, $\mathbf{J} = \mathbf{l}_\lambda + \mathbf{j}_\lambda$, is conserved. However, both the orbital angular momentum, $\mathbf{l}_\lambda$, (corresponding to the motion of the atom around the diatom) and the rotational angular momentum, $\mathbf{j}_\lambda$, (corresponding to the rotation of the $\nu\kappa$ diatom) vary significantly especially in the regions where the rearrangement of reactants and products occurs. Therefore, a suitable formulation of the angular momentum problem can provide great advantages in the global treatment.

The two common formulations in quantum dynamics are the space fixed (SF) and the body fixed (BF) formalisms [80–85]. Figure 2.2 shows the two reference systems; the SF reference system is denoted as $OX^\#Y^\#Z^\#$ and BF axes as $OXYZ$. Both reference frames are centered in the center of mass of the global system. In the SF frame the axes always lay in fixed directions in space. In the BF frame the direction of the axes varies following the molecular motion in such a way that, for example, the Z axis always coincides with the Jacobi vector $\mathbf{R}$. Therefore, in the SF frame the quantization axis for the angular momentum remains fixed whereas in the BF frame the quantization axis follows the motion of the $\mathbf{R}$ vector.

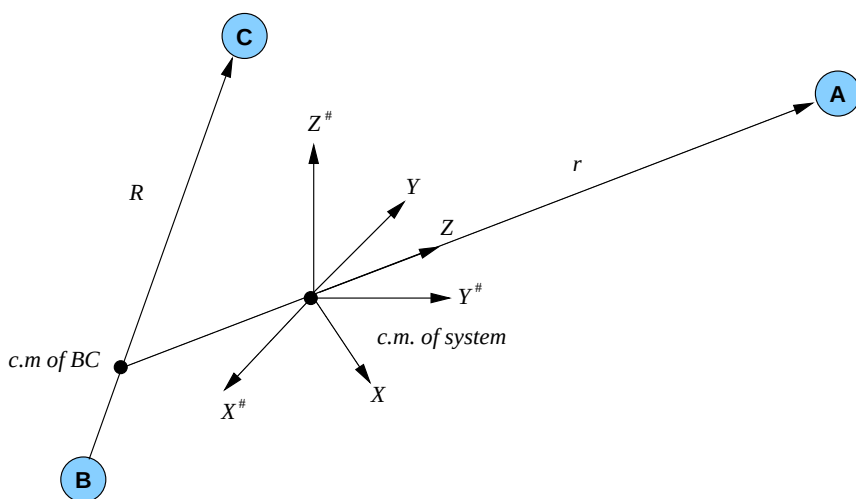


Figure 2.2: Space fixed (primed axes) and body fixed (unprimed axes) reference frames.

In the SF representation the coordinates used to describe the Jacobi vectors $\mathbf{R}_\lambda^\#$ and $\mathbf{r}_\lambda^\#$ are $R_\lambda^\#, \theta_{R_\lambda}, \varphi_{R_\lambda}, r_\lambda^\#, \theta_{r_\lambda}$ and φ_{r_λ} , where $R_\lambda^\#$ and $r_\lambda^\#$ are the vector moduli and $\theta_{R_\lambda}, \varphi_{R_\lambda}, \theta_{r_\lambda}$ and φ_{r_λ} are the associated polar and azimuthal angles.

In the BF representation the coordinates used to describe the Jacobi vectors are the vector moduli R_λ and r_λ , the angle Θ_λ between the $\mathbf{R}_\lambda$ and $\mathbf{r}_\lambda$ vectors and three angles, $\varphi_\lambda, \theta_\lambda$ and ψ_λ , which describe the Z axis orientation and are called Euler angles. For simplicity, the three atoms are placed onto the $X^\#Z^\#$ plane (i.e., the Euler angle ψ_λ is set to zero).

The choice of the reference frame allows to write the Schrödinger equation 2.13 in a more explicit way. In the SF frame it results:

$$\left[- \left(\frac{1}{2\mu_{R_\lambda}} \frac{\partial^2}{\partial R_\lambda^{\#2}} + \frac{1}{2\mu_{r_\lambda}} \frac{\partial^2}{\partial r_\lambda^{\#2}} \right) + \frac{\hat{l}_\lambda^2}{2\mu_{R_\lambda} R_\lambda^{\#2}} + \frac{\hat{j}_\lambda^2}{2\mu_{r_\lambda} r_\lambda^{\#2}} \right] \Psi^\lambda(\mathbf{R}_\lambda^\#, \mathbf{r}_\lambda^\#, t) = i\hbar \frac{\partial}{\partial t} \Psi^\lambda(\mathbf{R}_\lambda^\#, \mathbf{r}_\lambda^\#, t) + V(R_\lambda, r_\lambda, \Theta_\lambda) \quad (2.14)$$

and in the BF frame it results:

$$\left[- \left(\frac{1}{2\mu_{R_\lambda}} \frac{\partial^2}{\partial R_\lambda^2} + \frac{1}{2\mu_{r_\lambda}} \frac{\partial^2}{\partial r_\lambda^2} \right) + \frac{(\hat{J} - \hat{j}_\lambda)^2}{2\mu_{R_\lambda} R_\lambda^2} + \frac{\hat{j}_\lambda^2}{2\mu_{r_\lambda} r_\lambda^2} \right] \Psi^\lambda(\mathbf{R}_\lambda, \mathbf{r}_\lambda, t) = i\hbar \frac{\partial}{\partial t} \Psi^\lambda(\mathbf{R}_\lambda, \mathbf{r}_\lambda, t) + V(R_\lambda, r_\lambda, \Theta_\lambda) \quad (2.15)$$

where the reduced mass for the triatomic $\lambda + \nu\kappa$ system is represented by μ_{R_λ} and the reduced mass for the diatomic $\nu\kappa$ system by μ_{r_λ} and atomic units are used ($\hbar = 1$).

The main difference between the SF and BF Schrödinger equations is that the orbital angular momentum, $\mathbf{I}_\lambda$, cannot be used in the BF representation because the $\hat{l}^2$ operator does not commute with the hamiltonian operator. Therefore in the BF equation the orbital angular momentum $\mathbf{I}_\lambda$ is rewritten as $\mathbf{J} - \mathbf{j}_\lambda$. In other words, in the SF formulation the wavefunctions are eigenfunctions of the $\hat{J}^2, \hat{J}_{Z^\#}, \hat{j}^2$ and $\hat{l}^2$ operators, being $J_{Z^\#}$ the projection of the total angular momentum onto the $Z^\#$ axis.

In the BF representation the wavefunctions are eigenfunctions of $\hat{J}^2$, $\hat{J}_{Z^\#}$, $\hat{j}^2$ and $\hat{J}_Z$, where $\hat{l}^2$ is replaced by the projection of $\mathbf{J}$ onto the Z axis (usually called helicity) and their quantum numbers are denoted by Ω_λ . Since $\mathbf{I}_\lambda$ and $\mathbf{R}_\lambda$ are perpendicular, the quantum number Ω_λ also represents the quantum number for the projection of the rotational angular momentum $\mathbf{j}_\lambda$ onto the BF Z axis.

In both SF and BF formulations the potential energy surface is represented as a function of R_λ , r_λ and Θ_λ because it depends only on the relative positions of the atoms. For this reason, three variables are enough for describing the surface. Other coordinates, such as the three internuclear distances, can be instead used for the potential energy surface representation.

The quantum formulation of reactive collisions in both SF and BF frames are obviously formally equivalent and the relationships between the wavefunction in both approaches is an unitary transformation. Nevertheless, the practical suitability of each formulation depends on the nature of the considered process. Thus, while the BF frame is more adequate for close collisions and strong interaction processes, the SF one results more convenient for the description of weak interactions and long distance processes.

To solve the Schrödinger equations 2.14 or 2.15, the general approach used in reaction dynamics is to expand the overall wavefunction in terms of partial waves. In the SF representation the total angular momentum operators, $\hat{J}^2$, and its $Z^\#$ component, $\hat{J}_{Z^\#}$, commute between each other and with the hamiltonian. Therefore they are a constant of the motion. Thus, the eigenfunctions of $\hat{J}^2$ and $\hat{J}_{Z^\#}$, with eigenvalues $J(J+1)$ and M , can be used to form the basis to form the expansion basis:

$$\Psi^\lambda(\mathbf{R}_\lambda^\#, \mathbf{r}_\lambda^\#, t) = \sum_{J=0}^{\infty} \sum_{M=-J}^J C_\lambda^{JM} \Psi_\lambda^{JM}(\mathbf{R}_\lambda^\#, \mathbf{r}_\lambda^\#, t) \quad (2.16)$$

where the coefficients C_λ^{JM} are the Clebsch-Gordan coefficients.

Then the partial waves Ψ_λ^{JM} are further expanded in terms of the BF wavefunctions $\psi_\lambda^{J\Omega_\lambda}$ as:

$$\Psi_\lambda^{JM}(\mathbf{R}_\lambda^\#, \mathbf{r}_\lambda^\#, t) = \sum_{\Omega_\lambda=-J}^J D_{M\Omega_\lambda}^J(\varphi_\lambda, \theta_\lambda, 0) \psi_\lambda^{J\Omega_\lambda}(R_\lambda, r_\lambda, \Theta_\lambda, t) \quad (2.17)$$

where the $D_{M\Omega_\lambda}^J(\varphi_\lambda, \theta_\lambda, 0)$ coefficients are the Wigner rotation matrix elements performing the transformation from the SF reference system to the BF one (please notice that we deal with a BF representation in which $\psi_\lambda = 0$).

At this point is convenient to indicate that the wavefunctions $\psi_\lambda^{J\Omega_\lambda}$ have a parity $(-1)^p = (-1)^{(j_\lambda + J_\lambda - \Omega_\lambda)}$ with respect to the inversion in the space. Moreover, only the wavefunctions with the same parity couple between each other. For this reason, it is possible to separate the coupled equations in two groups, one for the even parity wavefunctions and the other for the odd parity wavefunctions. This feature contributes further to simplify the quantum treatment of the reactive collisions.

In conclusion, the goal of the quantum dynamics methods is to solve the Schrödinger equation in order to obtain the BF wavefunctions $\psi_\lambda^{J\Omega p}$.

2.2 Time-dependent quantum dynamics

The time-dependent wavepacket approach has rapidly emerged as a powerful tool for performing reaction dynamics calculations in the last decade. This approach allows to solve in a single run the Schrödinger equation for a given initial state of the reactants and a range of energies and to work out the properties of the products from the shape of wavepacket at the related asymptote. Wavepackets have been used for quantum scattering calculations since the late 1960's [86–88]; however they did not become popular until the late 1980's due to computer limitations [89]. Recent reviews

of the wavepacket approach has been given by Sathyamurthy *et al.* [90], Zhang [91] and Althorpe and Clary [92]. A wavepacket method propagating only the real part of the wavepacket and resulting in a significant memory saving has been developed by Gray and Balint-Kurti [93]. In most cases, the wavepacket approach has only been used to calculate reaction probabilities and integral cross sections, i.e. quantities depending only on the modulus of the $\mathbf{S}$ matrix elements (see for example refs. [94–99]) However, Althorpe used a novel way to finesse the coordinate problem and thus used the time-dependent method to calculate $\mathbf{S}$ matrix elements and differential cross sections for the H + H₂ system [100]. Very recently, Balint-Kurti *et al.* developed a new quantum wavepacket computer code (DIFFREALWAVE) to compute state-to-state reactive differential cross sections for the H + H₂ reaction on five different potential energy surfaces [101].

In the time-dependent (TD) quantum dynamics, the overall solution strategy involves the following three steps. First, one chooses an initial ($t=0$) wavefunction $\psi(\mathbf{R}, \mathbf{r}, t)$ that describes the range of energies and initial conditions that one wants to simulate. The wavefunction is usually called wavepacket. Typically the wavepacket is formulated in Jacobi coordinates, $\mathbf{R}$ and $\mathbf{r}$ (either of the reactants or of the products or initially of the reactants coordinates and at certain time of the products). Second, one solves the TD Schrödinger equation:

$$i\hbar \frac{\partial \psi(\mathbf{R}, \mathbf{r}, t)}{\partial t} = \hat{H} \psi(\mathbf{R}, \mathbf{r}, t) \quad (2.18)$$

for a sufficient length of time to describe the scattering process of interest. When $\hat{H}$ is explicitly time-independent, as the scattering case is, the formal solutions of eq. 2.18 is obtained as the evolution of the wavepacket along the collision time:

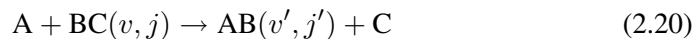
$$\psi(\mathbf{R}, \mathbf{r}, t + \tau) = e^{-i\hat{H}\tau/\hbar} \psi(\mathbf{R}, \mathbf{r}, t) \quad (2.19)$$

Third, one calculates the desired scattering information, such as the outgoing flux. This calculation usually implies an expansion of the wavefunction in the product

basis functions and the imposition of boundary conditions. One aspect of method which virtues have been realized only recently is the fact that the the hamiltonian $\hat{H}$ in eq. 2.18 can be replaced by any (single valued) function of $\hat{H}$ leading to the same solution [93,102]. If this function is chosen to be $\arccos(\hat{H})$, then the resulting solution using the Chebyshev integration method is exact and exceptionally simple.

The initial wavepacket is often chosen to be a Gaussian function of the translational coordinate, with mean velocity and width chosen to describe the range of interest. In making this choice, one needs to consider how the spatial part of the Schrödinger equation is to be handled, i.e., whether the dependence of the wavepacket on spatial coordinates has to be represented on a grid or in terms of basis functions.

For the present study we have used the quantum wavepacket code RWAVEPR developed by Skouteris and Laganà (University of Perugia, Italy) [33, 75, 76]. The code integrates the TD Schrödinger equation for the generic atom-diatom reaction:



where v and j are the vibrational and rotational quantum numbers of the reactants (the analogous quantities for products are primed). The related numerical procedure propagates the complex wavepacket in time using product coordinates. Thus, state-to-state probabilities are calculated.

2.3 Wavepacket representation

A key problem of quantum dynamical treatments is the selection of a suitable set of coordinates to give an appropriate representation of the wavefunction. This selection is associated with several aspects of the calculations. Namely, the definition of a continuity variable to use for integrating the Schrödinger equation, the expansion

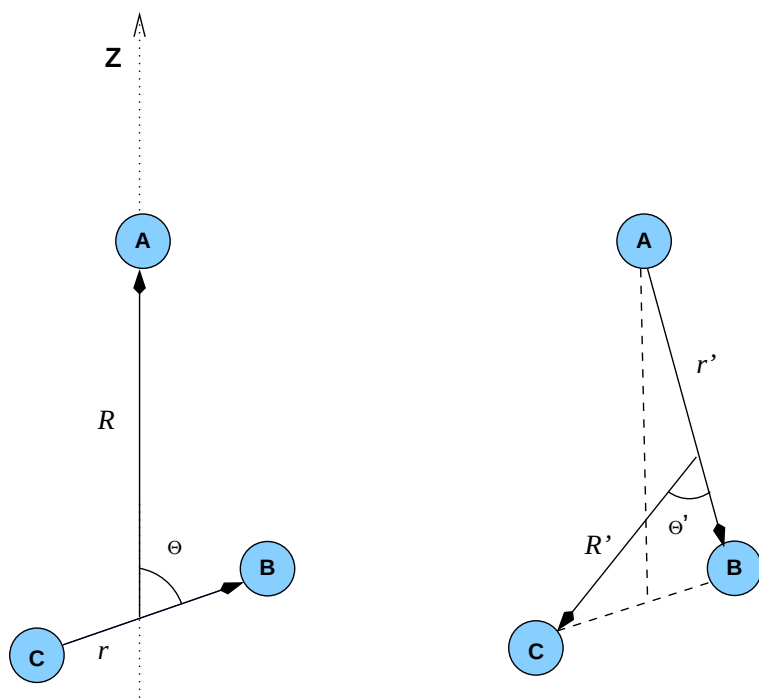


Figure 2.3: Reactant (unprimed) and product (primed) Jacobi coordinates for a triatomic system. Reactant Jacobi coordinates are shown on the product Jacobi coordinates as dashed lines.

of the wavefunction and the formulation of both initial and final conditions. In TD approaches the problem of defining a suitable continuity variable is straightly solved because the time itself is an ideal continuity variable. The delicate point is therefore the definition of both the initial and the final conditions of the wavefunction. In fact, in reactive processes the coordinate system of the reactants is often different from that of the products since most coordinate systems are arrangement dependent. In Figure 2.3 the reactant and product Jacobi coordinates for a triatomic system used in this work are displayed. Obviously, initial conditions are properly specified in the reactant coordinates, while any final state analysis, needed for instance to determine the quantum state distribution of the products, must be performed in the appropriate set of product coordinates.

The most straightforward choice is to carry out the calculations using reactant coordinates. This makes it immediate to define initial conditions. When one is interested in computing the properties of the products the wavefunction has to be mapped onto the final diatomic molecule wavefunctions and the related r' coordinate has to be used. Accordingly, the wavefunction, initially set up in reactant Jacobi coordinates R, r and Θ , is transformed into the product ones R', r' and Θ' . Note that the generic coordinates $\mathbf{R}_\lambda$ and $\mathbf{r}_\lambda$ (see Figure 2.1) used in Section 2.1 to formulate the reactive quantum treatment have been now replaced by unprimed R, r and Θ for the reactant Jacobi coordinates and primed R', r' and Θ' for the product Jacobi coordinates.

In principle, the analysis of the wavefunction in the product region requires at each step of the evolution a mapping of the wavefunction onto the product coordinates. As an alternative one can transform the entire wavepacket onto a product coordinate representation at a given appropriate time, for example when the wavepacket is concentrated in the strong interaction region. The propagation then proceeds in product coordinates which are suitable for the final state analysis. It may be also desirable, to reduce the computational effort, to perform a short propagation in the entrance channel using reactant Jacobi coordinates and then transform the wavepacket to product Jacobi coordinates [103]. Recently some interesting and efficient methods have been developed to perform the transformation from reactant to product Jacobi coordinates [104].

2.4 Initial wavepacket

The initial wavepacket $\psi^{J\Omega p}(R, r, \Theta, t = 0)$ for the atom-diatom A + BC system and a given value of J, Ω and p is formulated as (for simplicity the parity index is dropped):

$$\psi^{J\Omega}(R, r, \Theta, t = 0) = \chi^J(R) \varphi_{vj}^{\text{BC}}(r, \Theta) \quad (2.21)$$

where the function $\chi^J(R)$ represents the dependence on R of the initial wavepacket and the function $\varphi_{vj}^{\text{BC}}(r, \Theta)$ is the wavefunction of the initial rovibrational state of the molecule BC.

The function $\chi^J(R)$ is built up from a Gaussian function $e^{-\alpha(R-R_0)^2}$, where R_0 is the center of the wavepacket, multiplied by a phase factor of the form $e^{-ik_0(R-R_0)}$ which gives the initial wavepacket a relative kinetic energy, k_0 , towards the interaction region. This factor is made up of appropriate incoming Ricatti-Hankel functions, thus avoiding the problem of having to start the wavepacket propagation sufficiently far away from the centrifugal barrier. Therefore, the function $\chi^J(R)$ is formulated by:

$$\chi^J(R) = N e^{-\alpha(R-R_0)^2} e^{-ik_0(R-R_0)} h_l^1(k(R-R_0)) \quad (2.22)$$

where k_0 is the wavenumber which determines the relative kinetic energy of the collision partners and h_l^1 is the Hankel function of the first order.

The function $\varphi_{vj}^{\text{BC}}(r, \Theta)$ is set up from a vibrational function $\phi_v^{\text{BC}}(r)$ multiplied by an angular function:

$$\varphi_{vj}^{\text{BC}}(r, \Theta) = \phi_v^{\text{BC}}(r) P_j^\Omega(\Theta) \quad (2.23)$$

where $P_j^\Omega(\Theta)$ are the normalized associated Legendre polynomials.

The function of eq. 2.22 describes a Gaussian wavepacket travelling inwards with an average momentum of $k_0\hbar$. The wavepacket is localized in space. Due to Heisenberg uncertainty Principle this means that it has a spread in momentum (or kinetic energy). Since the total energy is a constant of motion, each portion of the wavepacket with a definite total energy may be considered to scatter independently of other parts of the same wavepacket which have different total energies.

In order to evaluate the reaction probability one needs to know which portion of the original wavepacket has a particular total energy. This means that, since the

internal energy is fixed, one needs to know the amplitude of the initial wavepacket having a particular momentum (or kinetic energy). This is obtained by a Fourier transform of the initial wavepacket:

$$g(k) = \frac{1}{\sqrt{2\pi}} \int_{R=0}^{\infty} \exp(-ikR) \chi^J(R) dR \quad (2.24)$$

where $\chi^J(R)$ is the gaussian wavepacket in space and $g(k)$ is the component of wavepacket with momentum $k\hbar$.

2.5 Hamiltonian

The action of the hamiltonian operator onto the wavepacket $\psi^{J\Omega}(R, r, \Theta, t)$ will allow to determine, through the TD Schrödinger equation, its temporal evolution. In an exact quantum time-dependent treatment the time differentiation of the system wavefunction is related to the application of the hamiltonian $\hat{H}$ to the wavefunction itself. Accordingly, the partial wave equations to be integrated read:

$$\hat{H}\psi^{J\Omega} = \left[\hat{T}_{R,r,\Theta,J,\Omega} + V(R, r, \Theta) \right] \psi^{J\Omega} + C_{\Omega,\Omega\pm 1}^J \psi^{J\Omega\pm 1} \quad (2.25)$$

being

$$\begin{aligned} \hat{T}_{R,r,\Theta,J,\Omega} &= \hat{T}_R + \hat{T}_r + \hat{T}_\Theta + \frac{J(J+1) - 2\Omega^2}{2\mu_R R^2} \\ \hat{T}_R &= -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} \\ \hat{T}_r &= -\frac{1}{2\mu_r} \frac{\partial^2}{\partial r^2} \\ \hat{T}_\Theta &= -\left(\frac{1}{2\mu_R R^2} + \frac{1}{2\mu_r r^2} \right) \left(\frac{1}{\sin \Theta} \frac{\partial}{\partial \Theta} \sin \Theta \frac{\partial}{\partial \Theta} - \frac{\Omega^2}{\sin^2 \Theta} \right) \\ C_{\Omega,\Omega\pm 1}^J &= \frac{[J(J+1) - \Omega(\Omega \pm 1)]^{1/2} [j(j+1) - \Omega(\Omega \pm 1)]^{1/2}}{R^2} \end{aligned}$$

where $\hat{T}_R$ and $\hat{T}_r$ are radial kinetic energy terms, $\hat{T}_\Theta$ is the angular kinetic energy term, $(J(J+1) - 2\Omega^2)/2\mu_R R^2$ is the centrifugal term, $V(R, r, \Theta)$ is the potential

energy term and the last two terms correspond to the coupling between wavepackets having different values of Ω , i.e., the non-diagonal terms of the Coriolis coupling.

In this work, two methods are used to evaluate the hamiltonian. They are the fast Fourier transform method to evaluate the radial terms and the discrete variable representation method to evaluate the angular ones.

2.5.1 Fast Fourier transform method

The introduction of the fast Fourier transform (FFT) method by Feit *et al.* [105, 106] and Kosloff [107] for computing the action of the kinetic energy part of the hamiltonian on the wavepacket function was a significant development in TD quantum calculations. To compute the second derivative of the wavefunction the FFT method performs a Fourier transform from the coordinate space to the momentum space, multiplies it by $-k^2$ (where k is the wavenumber), and transforms it back to the coordinate space by an inverse Fourier transform. These steps can be formulated as:

$$\begin{aligned}\psi(k) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(x) \exp(-ikx) dx = \text{FFT}[\psi(x)] \\ \psi(x) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(k) \exp(-ikx) dx = \text{FFT}^{-1}[\psi(k)] \\ \frac{d\psi(x)}{dx} &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(k)(ik) \exp(-ikx) dk = \text{FFT}^{-1}[(ik)\psi(k)] \\ \frac{d^2\psi(x)}{dx^2} &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \psi(k)(ik)^2 \exp(-ikx) dk = \text{FFT}^{-1}[-k^2\psi(k)]\end{aligned}\tag{2.26}$$

where $x \equiv R, r$. Since the kinetic energy operator is local in the momentum space, its action on the wavefunction is evaluated very accurately, just as in the case of the potential energy operator in the coordinate space. The method requires that the wavefunction satisfies periodic boundary conditions and is exact for band-limited functions. If the wavefunction is not band-limited and/or boundary the conditions

are not satisfied, the wavefunction would wrap around the opposite side introducing errors in the calculation (aliasing effects).

It is worthwhile to add that, in a discrete representation, operators corresponding to physical observables in the original Hilbert space are mapped onto a discrete Hilbert space. Thus operators in the discrete Hilbert space should obey all quantum mechanical commutation relations observed by corresponding physical observables in the original Hilbert space. In this case a one-to-one mapping of the operators to the discrete space is achieved. It has been shown that this is indeed the case with the Fourier discretization for a band limited function with a finite support that is, of finite extent in configuration as well as in momentum space [107]. This confirms the versatility of the Fourier transform method over that of other methods. In cases where the wavefunction is not periodic or band-limited, one has to employ a semilocal approximation for the kinetic energy operator (as is the case of the finite difference scheme or the discrete variable representation described in the following Section).

It is worth comparing the kinetic energy discrete spectrum in the Fourier discretization and in the finite difference (FD) approximation. For the wavefunction given in eq. 2.26, the former gives the exact kinetic energy spectrum [107]:

$$T_{\text{FFT}}(k) = \frac{\hbar^2}{2m} k^2 \quad (2.27)$$

while the latter yields [108]:

$$T_{\text{FD}}(k) = \frac{\hbar^2}{2m} \left[\frac{2 \sin(k\Delta x/2)}{\Delta x} \right]^2 \quad (2.28)$$

Upon inspection it becomes clear that, if the mesh size Δx is chosen to be very small, the kinetic energy discrete spectrum in the FD scheme approaches the exact one given by the FFT discretization. Thus for comparable accuracy one should employ a finer mesh in the FD scheme than for the FFT discretization.

2.5.2 Discrete variable representation

The discrete variable representation (DVR) was originally introduced in Molecular Reaction Dynamics by Light and coworkers for solving the time-dependent Schrödinger equation [109–111]. This method is a very general and powerful method and has extensively been used in the evaluation of the hamiltonian operation on the wavefunction in time-dependent calculations [112–116]. It is applied to one-dimensional problems or direct product basis functions in multidimensional problems.

The DVR method is a localized (in coordinate space) but discrete representation. For any given finite basis set $\phi_n(x)$ ($n = 1, 2, 3, \dots, N$), one can define a unique DVR by diagonalizing the matrix:

$$x_{mn} = \langle \phi_m | \hat{x} | \phi_n \rangle \quad (2.29)$$

which generates n eigenvalues x_n and eigenfunctions:

$$|X_n\rangle = \sum_m |\phi_m\rangle C_{mn} \quad (2.30)$$

such that:

$$\hat{x}|X_n\rangle = x_n|X_n\rangle \quad (2.31)$$

This equation implies that, in this N -dimensional vector space, the coordinate operator $\hat{x}$ is approximated by:

$$\hat{x} = \sum_{m=1}^N \sum_{n=1}^N |\phi_m\rangle x_{mn} \langle \phi_n| = \sum_{n=1}^N |X_n\rangle x_n \langle X_n| \quad (2.32)$$

With this prescription for the operator $\hat{x}$, $|X_n\rangle$ is also an eigenstate of any operator function $F(\hat{x})$, i.e.:

$$F(\hat{x})|X_n\rangle = F(x_n)|X_n\rangle \quad (2.33)$$

Since DVR basis set $|X_n\rangle$ is related to the finite basis set $\phi_n(x)$ through a unitary or orthogonal transformation of the eq. 2.30, it is an equivalent basis set to $\phi_n(x)$ in this N -dimensional vector space. The DVR basis functions are highly localized in coordinate space, i.e. $\langle x|X_n\rangle$ is highly peaked near $x = x_n$. Due to this particular local property of the DVR basis, the matrix element of any local operator in the DVR basis is approximately diagonal. For example, the matrix element of the potential energy operator in the DVR basis is approximated by:

$$\langle X_m|V(\hat{x})|X_n\rangle = \delta_{mn}V(x_n) \quad (2.34)$$

This result applies to any local operator which is a function of coordinates only, and should be understood in the sense that the coordinate operator is approximated by eq. 2.32 in the N -dimensional vector space. As the dimension of the vector space increases, the approximation in eq. 2.34 becomes increasingly better. Since the most potential energy operators are local in functions of coordinates, they are diagonal in the DVR representation, and the integration over the coordinates to construct the potential matrix can be eliminated.

If the basis functions used to define DVR are polynomials $P_n(x)$ that are orthogonal with the weighting function $W(x)$:

$$\langle P_m|P_n\rangle = \int_a^b W(x)P_m(x)P_n(x)dx = \delta_{mn} \quad (2.35)$$

then one can use a Gaussian quadrature to evaluate the integral:

$$\langle P_m|P_n\rangle = \sum_{k=1}^N P_m(x_k)P_n(x_k)w_k = \delta_{mn} \quad (2.36)$$

where x_k and w_k are Gaussian nodes and weights, respectively. The property of Gaussian quadrature guarantees that eq. 2.36 is exact for $m, n = 0, 1, 2, \dots, N - 1$. Thus for orthogonal polynomials, the associated DVR points are just Gaussian nodes, and the orthogonal transformation between the DVR and the polynomial basis is

simply given by the relation:

$$\langle P_n | X_k \rangle = \sqrt{w_k} P_n(x_k) \quad (2.37)$$

If one evaluates the matrix element of a local operator such a potential $V(x)$ in the basis of orthonormal polynomials by Gaussian quadrature, one has:

$$\begin{aligned} \langle P_m | V | P_n \rangle &= \sum_{k=1}^N P_m(x_k) V(x_k) P_n(x_k) w_k \\ &= \sum_{k=1}^N \langle P_m | X_k \rangle V(x_k) \langle X_k | P_n \rangle \end{aligned} \quad (2.38)$$

which is equivalent to inserting a complete DVR set $\sum_k |X_k\rangle \langle X_k|$ directly into the integral and using DVR result:

$$V | X_k \rangle = V(x_k) | X_k \rangle \quad (2.39)$$

This means that one can think of the Gaussian quadrature as a special case of DVR when the associated basis functions are orthogonal polynomials. Thus evaluating the potential matrix elements of a local operator, such as the potential operator, in an orthogonal polynomial basis by the DVR method is equivalent to using Gaussian quadrature to evaluate the matrix element. This directly relates the approximation used in the DVR evaluation of the potential matrix to that of numerical quadrature.

Computationally, the DVR method scales as N^2 compared to the $N \log N$ scaling of the FFT method. The advantage of the DVR approach is that, unlike the FFT one, the wavefunction needs not to be transformed to the momentum space forth and back every time step, avoiding, so far, a considerable overhead. Furthermore, it is possible to keep at a minimum the number of the basis functions required for the expansion if an appropriate basis is chosen according to the nature of the potential.

2.5.3 Evaluation of the hamiltonian

The evaluation of $\hat{H}\psi$ is the most important operation for each time step. Fortunately it can be nicely separated in two parts: the evaluation of $\hat{T}\psi^{J\Omega}$ and of $V\psi^{J\Omega}$, where as already mentioned, $\hat{T}$ is the kinetic energy operator and V the potential energy one. The evaluation of the potential term is a relatively simple task. In fact, this is a local operation being the potential energy operator diagonal if one uses the representation of Jacobi coordinates. Therefore, the $V\psi^{J\Omega}$ term is obtained by multiplying the wavepacket at each grid point by $V(R_i, r_j, \Theta_k)$, where R_i , r_j and Θ_k represent respectively the i th point of the R grid, the j th point in the r grid and the k th point in the Θ grid. However, the evaluation of the action of the kinetic operator on the wavepacket is a more complicated issue, since $\hat{T}\psi^{J\Omega}$ term is not local in the representation adopted.

The effect of applying the R term of the kinetic operator, $\hat{T}_R$, is expressed as:

$$\hat{T}_R\psi^{J\Omega}(R, r, \Theta, t) = -\frac{1}{2\mu_R}\frac{\partial^2}{\partial R^2}\psi^{J\Omega}(R, r, \Theta, t) \quad (2.40)$$

This operation can be performed in three steps. The first one is a first Fourier transform:

$$\begin{aligned} \psi^{J\Omega}(k_R, r, \Theta, t) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \exp(-ikR) \psi^{J\Omega}(R, r, \Theta, t) dR \\ &= \text{FFT} [\psi^{J\Omega}(R, r, \Theta, t)] \end{aligned} \quad (2.41)$$

to obtain the momentum representation of the wavepacket. The second step is the multiplication of the previous result by $k^2/2\mu_R$ (which is the representation of the kinetic operator in the momentum space) and is a local operation at each grid point of the momentum space. The third step consists in an inverse Fourier transform. Accordingly, the action of $\hat{T}_R$ on the wavepacket is accomplished by:

$$\hat{T}_R\psi^{J\Omega}(R, r, \Theta, t) = \text{FFT}^{-1} \left[\frac{k^2}{2\mu_R} \text{FFT} [\psi^{J\Omega}(R, r, \Theta, t)] \right] \quad (2.42)$$

A similar procedure can be adopted for the r term of the kinetic operator, $\hat{T}_r$.

As for the angular term of the kinetic operator, $\hat{T}_\Theta$, one can realize that:

$$\left\{ -\frac{1}{\sin \Theta} \frac{\partial}{\partial \Theta} \sin \Theta \frac{\partial}{\partial \Theta} \right\} P_j(\cos \Theta) = j(j+1) P_j(\cos \Theta) \quad (2.43)$$

and then its grid representation is:

$$T_{li} = \sum_{j=0}^{N_\theta} U_{lj} j(j+1) U_{ij}^T \quad (2.44)$$

where $\mathbf{U}$ is the matrix that transforms the Legendre polynomial basis set to the grid representation:

$$U_{ij} = P_j(\cos \Theta_i) \sqrt{w_i} \quad (2.45)$$

where w_i are the Gauss-Legendre weights $w_i = \sin \Theta_i$. Note that this equation is the application of the general DVR eq. 2.37 to the angular part of the kinetic operator.

Therefore, the action of the angular part of the kinetic energy operator at a given point l is formulated as:

$$\{\hat{T}_\Theta \psi\}_l = \left(\frac{1}{2\mu_R R^2} + \frac{1}{2\mu_r r^2} \right) \sum_i^{N_\theta} T_{li} \psi_i \quad (2.46)$$

2.6 Wavepacket propagation

The evolution in time of the wavepacket requires that the evolution operator $\exp(-i\hat{H}\tau/\hbar)$ is applied onto the wavefunction (eq. 2.19). A Taylor expansion for the evolution operator reads:

$$\exp\left(\frac{-i\hat{H}\tau}{\hbar}\right) \psi(\mathbf{R}, \mathbf{r}, t) = \left\{ 1 - \left(\frac{i\hat{H}\tau}{\hbar}\right) - \frac{1}{2!} \left(\frac{\hat{H}\tau}{\hbar}\right)^2 + \frac{i}{3!} \left(\frac{\hat{H}\tau}{\hbar}\right)^3 + \dots \right\} \psi(\mathbf{R}, \mathbf{r}, t) \quad (2.47)$$

Therefore, the propagation method requires the knowledge of the result of applying the hamiltonian operator onto the wavefunction to solve the TD Schrödinger equation. The coordinates used will strongly affect the efficiency and precision of the propagation. Several methods can be employed for the propagation of them. The most popular are the split operator [105, 117], the Lanczos recursive [118–120] and the Chebyshev [121, 122]. In the work reported here, the Chebyshev iteration has been used. In the followings we describe it in some detail.

The Chebyshev expansion for the evolution operator reads:

$$\exp\left(\frac{-i\hat{H}\tau}{\hbar}\right)\psi(\mathbf{R}, \mathbf{r}, t) = \exp\left(\frac{-i\left(\frac{\Delta E}{2} + V_{\min}\right)\tau}{\hbar}\right) \sum_{n=0}^N (2 - \delta_{n0}) J_n\left(\frac{\Delta E \tau}{2\hbar}\right) P_n(-i\hat{H}_s) \quad (2.48)$$

where P_n are the Chebyshev polynomials of complex argument (the first three Chebyshev polynomials are: $P_0(-ix) = 1$, $P_1(-ix) = -2ix$ and $P_2(-ix) = -4x^2 + 1$). They obey the recursion formula $P_{n+1} = -2i\hat{H}_s P_n + P_{n-1}$, where $\hat{H}_s$ is a normalized hamiltonian whose eigenvalues are confined into the interval -1 and $+1$. This normalization is performed by finding the range of the hamiltonian operator ($\Delta E = E_{\max} - E_{\min}$):

$$\hat{H}_s = \frac{\hat{H} - \hat{I}\left(\frac{\Delta E}{2} + V_{\min}\right)}{\frac{\Delta E}{2}} \quad (2.49)$$

Since it is essential to limit the range of the hamiltonian a potential cut off is applied to make $V = V_{\max}$ when $V > V_{\max}$.

In eq. 2.48, J_n are Bessel functions. They play a very important role in the convergence of the expansion. For n values greater than the argument $\Delta E \tau / 2\hbar$, J_n decreases exponentially in value. One can therefore predict that the number of terms needed in the expansion is approximately $N \approx \Delta E \tau / 2\hbar$. This means that the number of terms required to expand the time evolution operator is proportional to the

range of the hamiltonian operator. Or, equivalently, N is the number of operations that the hamiltonian operator must perform in order to propagate the wavepacket forward by τ .

The wavepacket is subsequently propagated using the modified TD Schrödinger equation suggested by Balint-Kurti and Gray [93]. According to this scheme, the hamiltonian $\hat{H}$ in the ordinary TD Schrödinger equation is substituted by an analytic function of itself, denoted here by $f(\hat{H})$. If this analytic function is chosen appropriately (for instance $f(\hat{H}) = -\arccos \hat{H}_s$), the subsequent propagation of the wavepacket by the Chebyshev scheme is significantly simplified. Thus, the propagation equation used is :

$$f(\hat{H})\psi = i\hbar \frac{\partial \psi}{\partial t}$$

To carry out the propagation, the wavepacket is located on a regularly spaced grid on R and r and on a grid of Gauss-Legendre quadrature points in the Jacobi angle Θ . The initial wavepacket is transformed into the Jacobi product coordinates R' , r' and Θ' of the channel of interest and the entire propagation is carried out in these coordinates. At the initial time ($t=0$) the wavepacket is placed far in the reactant channel and it is mapped into a product coordinate grid. The product coordinate grid has to be large enough to contain the initial wavepacket and to properly describe the wave packet during its evolution in time including the region where the analysis line is drawn and the interaction region. At the same time, the grid has to be fine enough to accurately describe the structure of the wavefunction. Figure 2.4 shows a typical grid domain in the reactant R and r coordinates.

As time progresses, the wavepacket moves into the interaction region. At the grid edges, an absorption region is introduced to prevent the wavepacket amplitude from reaching the edge of the grid and causing the already mentioned problem of aliasing in Fourier transform theory [123, 124]. In this absorption region the wavepacket is

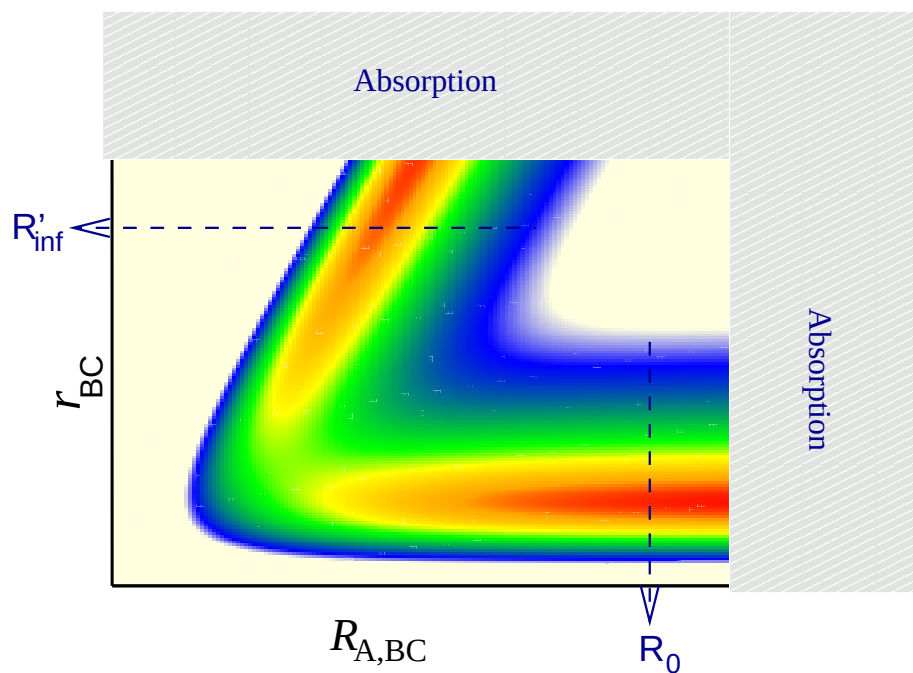


Figure 2.4: Schematic representation of the grid domain in the reactant $R \equiv R_{A,BC}$ and $r \equiv r_{BC}$ coordinates. The starting point $R = R_0$ of the propagation is placed in reactant channel and the analysis line $R' = R_{inf}$ is drawn in the product channel.

multiplied by a damping function of the form:

$$\phi(R) = \exp\left(-\frac{(R - R_a)^2}{2b^2}\right) \quad (2.50)$$

where b is a measure of the effective length of the potential and R_a is the value of R beyond which the value of the function differs from unity.

The wavepacket is then propagated in time until it has mainly been absorbed near the edge of the grid. The wavepacket is analysed at every time step along an analysis line in the asymptotic region of the product channel [93, 125] so as to accumulate the data needed for the computation of the detailed state to state $\mathbf{S}$ matrix elements $S_{vj\Omega, v'j'\Omega'}^{Jp}(E_{tr})$ at the various values of the collision energy, E_{tr} , contained within the wavepacket.

Before the propagation starts, suitable representations of the hamiltonian to be used are calculated and stored in memory. The values of the potential energy surface are calculated for all points of the grid used and are stored in the diagonal positions of an array. Also the diagonal elements of the hamiltonian which are local in the coordinate representation (and therefore can be regarded as parts of the potential energy) are calculated and stored in the diagonal positions of the same array. Then, once the propagation starts, the corresponding off-diagonal terms, both local and non-local in coordinate space are calculated and stored in the appropriate off-diagonal positions of the same array.

At each stage of the propagation, the overlap of the wavepacket with each of the open product channels is calculated and stored. Since the product wavefunction are effectively localized in the product region, this overlap is zero at early times and attains high values only for relative narrow time window for a direct reaction (as N + N₂ is). At the end of the propagation, the $\mathbf{S}$ matrix elements for all open product channels and for all energies of interest are computed using the overlap values calculated throughout the propagation by a half-Fourier transform, taking into account the

fact that $f(\hat{H})$ rather than $\hat{H}$ was used to propagate the wavepacket.

2.7 Wavepacket analysis

There are mainly two well known methods to analyse the wavepacket. One of them is called asymptotic analysis [93, 95, 126] and the other one flux method [127]. In this work, to study the $N + N_2$ reaction, the asymptotic analysis has been used. In this method by analysing the wavepacket along a cut at the product at each time step one could compute all the important properties for the scattering process. The analysis is performed by projecting a cut taken through the wavepacket at the analysis line onto the product eigenfunctions, $\phi_{v'j'}^{AB}(r')$. This yields a coefficient for each possible final quantum states of the system. which is a function of time. If one then Fourier transforms this coefficient over time, one obtains an energy dependent function which is proportional to the S matrix elements.

The time-dependent coefficients are obtained by the following integration:

$$C_{vj\Omega, v'j'\Omega'}^{Jp}(t) = \int_{r'} dr' \int_{\Theta} \sin \Theta' P_{j'}^{\Omega'}(\Theta') \phi_{v'j'}^{BC}(r') \psi^{J\Omega p}(R' = R'_{\infty}, r', \Theta') d\Theta' \quad (2.51)$$

The C coefficients are then Fourier transformed in order to obtain the elements of the energy-dependent collision matrix A :

$$A_{vj\Omega, v'j'\Omega'}^{Jp}(E) = \frac{1}{2\pi} \int_{t=0}^{\infty} \exp(iEt/\hbar) C_{vj\Omega, v'j'\Omega'}^{Jp}(t) dt \quad (2.52)$$

from which the S matrix elements are calculated using the expression:

$$S_{vj\Omega, v'j'\Omega'}^{Jp}(E) = \left(\frac{k_{vj} k_{v'j'}}{\mu \mu'} \right)^{1/2} \frac{\hbar A_{vj\Omega, v'j'\Omega'}^{Jp}(E)}{g(-k_{vj})} \exp(-ik_{v'j'} R'_{\infty}) \quad (2.53)$$

where k_{vj} and $k_{v'j'}$ are the wavenumber of the reactant and product rovibrational states, μ and μ' is the reduced mass of the reactants and products, and $g(-k_{vj})$ is the amplitude of the initial wavepacket with momentum $-\hbar k_{vj}$.

2.8 Rate coefficients

By summing the square modulus of the detailed $\mathbf{S}$ matrix elements over Ω , Ω' and p and one can evaluate state-to-state reaction probabilities:

$$P_{vj,v'j'}^J(E_{\text{tr}}) = \frac{1}{(2j+1)} \sum_{\Omega=-\Omega_{\text{max}}}^{\Omega_{\text{max}}} \sum_{\Omega'=-\Omega'_{\text{max}}}^{\Omega'_{\text{max}}} \sum_{p=0}^1 \left| S_{vj\Omega,v'j'\Omega'}^{Jp}(E_{\text{tr}}) \right|^2 \quad (2.54)$$

where E_{tr} is the relative collision energy (the total energy E minus the rovibrational energy of the initial state vj) and $\Omega_{\text{max}} = \min(j, J)$. In this equation, the $\mathbf{S}$ matrix elements are set equal to twice the value calculated for a single product arrangement channel.

The summation over v' and j' allows to obtain the initial state-specific reactive probabilities, $P_{vj}^J(E_{\text{tr}})$, expressed as:

$$P_{vj}^J(E_{\text{tr}}) = \sum_{v'} \sum_{j'} P_{vj,v'j'}^J(E_{\text{tr}}) \quad (2.55)$$

In this summation, probabilities for even j' states contributes twice because the nuclear spin of the N atom is one [138].

A more detailed dynamical property is the product vibrational distribution(PVD). It can be worked out at each initial vibrational state of the reactants by taking for each final vibrational state of the products the fraction of the total probability associated with it.

The integral reactive state-specific cross section can instead be worked out using the formula:

$$\sigma_{vj}(E_{\text{tr}}) = \sum_{J=0}^{\infty} \sigma_{vj}^J(E_{\text{tr}}) = \sum_{J=0}^{\infty} \frac{\pi}{k_{vj}^2} (2J+1) P_{vj}^J(E_{\text{tr}}) \quad (2.56)$$

where $k_{vj} = \sqrt{2\mu E_{\text{tr}}}/\hbar$ is the wavenumber of the system in the vj state.

Then the state-specific rate coefficients can be calculated averaging on the translational energy by:

$$k_{vj}(T) = \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} \frac{1}{(k_B T)^2} \int_0^\infty \sigma_{vj} \exp(-E_{tr}/k_B T) E_{tr} dE_{tr} \quad (2.57)$$

where T is the temperature (in this case, the translational temperature), μ is the reduced mass of the reactive system and k_B the Boltzmann constant.

By averaging over the vj initial states (weighed for the proper thermal distribution function) one can calculate the thermal rate coefficient $k(T)$.

2.9 Centrifugal sudden approximation

The calculation of the thermal rate coefficients implies the integration of the Schrödinger equation at all the populated vj initial states, all the total angular momentum quantum number values J contributing to reaction and all the allowed projections Ω of J . This makes the size of the single vj calculations proportional to J^2 frustrating, in practice, all the attempts to carry out a full J exact calculation. Even more, for high J values calculations become increasingly difficult. In fact, the hamiltonian of eq. 2.25 for $J=0$ becomes significantly simplified because the terms $(J(J+1) - 2\Omega^2)/2\mu_R R^2$ and $C_{\Omega, \Omega \pm 1}^J$ are zero. On the contrary, for non zero total angular momenta the non-diagonal terms of the Coriolis coupling must be considered and one may need to propagate as many as $2J+1$ wavepackets. Thus, it is necessary to find alternative simplified procedures.

To reduce the dimensionality of the problem, different approaches have been developed. Two of them are the sudden [128, 129] and the adiabatic [36, 130–133] approximations. These theories make diametrically opposite assumptions about the internal angular motion. The sudden theory assumes that motion is frozen throughout

the collision, whereas the adiabatic theory assumes it changes but with preservation of the bending quantum numbers. The sudden approximation is valid when the interaction time is short compared to the perturbed angular motion of the diatomic molecule. The adiabatic approximation applies in the opposite situation, i.e., when the interaction time is comparable or longer than that of the perturbed angular motion. In general, the angular motion of most molecules is slow compared to the interaction times for hyperthermal or even thermal collisions. However, if there is a large amount of induced angular hindering of the diatom by the atom, then simple sudden dynamics does not apply, except for high collision energies. For those reactions (which are angularly strongly constrained), the adiabatic approximation is the choice of election, even (as we shall discuss later) at hyperthermal collision energies. In the case of the N + N₂ reaction, that is a direct one, a sudden approximation is more appropriate. In particular, we shall discuss here in detail the use of the centrifugal sudden (CS) approximation [134, 135].

In practice the CS approximation implies the cancellation of the centrifugal term. Accordingly, the angular velocity of the system is slower than the collision velocity and, therefore, the collision can be considered instantaneous with respect to the orbiting and the projection of the total angular momentum along the BF Z axis be conserved during the collision. For this reason, the approximation is also called "Jz conserving" or "helicity conserving" approximation. The CS approximation can be also seen as deriving from the assumption that Ω is a good quantum number. Rigorously, only the total angular momentum J is a good quantum number whereas Ω is not since the dynamics of the system mixes up different Ω values. The different Ω values are coupled by the "centrifugal coupling" terms in the hamiltonian operator of eq. 2.25. This indicates that one has a separate wavepacket, $\psi^{J\Omega}(R, r, \Theta, t)$ for each value of Ω and that these wavepackets are coupled together (one wave packet couples with $J + 1$ wavepackets when the total parity is even and with J wave packets when is odd). The centrifugal coupling $C_{\Omega, \Omega \pm 1}^J$ makes the hamiltonian representation tridi-

agonal (while the interaction potential is diagonal). Therefore, the CS approximation consists in simply neglecting the Ω coupling in eq. 2.25. In other words, the CS approximation considers Ω as a good quantum number and Ω is conserved during the collision. Using the CS approximation, the hamiltonian representation becomes diagonal and the effort for its diagonalization not exceeding that of the $J = 0$ one. This make the CS program suitable for running on distributed computational platforms.

2.10 *J*-shift approximation

The CS approximation reduces significantly the computational effort needed to calculate cross sections and rate coefficients. However, even for moderately heavy systems (like the $N + N_2$ considered here), a huge number of (decoupled) partial wavepackets are involved. For this reason, the calculations are often further simplified by adopting the so called *J*-shift model [36, 133]. In *J*-shift approximation, the calculation of the $\mathbf{S}$ matrix is performed for a low value of J (or a certain number of J values) and this value (or this set of values) is used to estimate the probabilities for the values of J for which calculations are not performed. In the most simplified version, exact probabilities are calculated only for $J = 0$.

In the *J*-shift approximation, the state-specific probabilities for $J > 0$, $P_{vj}^J(E_{tr})$, are worked out by shifting in energy the probabilities obtained for $J = 0$, $P_{vj}^{J=0}(E_{tr})$, as follows:

$$P_{vj}^J(E_{tr}) = P_{vj}^{J=0}(E_{tr} - \Delta E^J) \quad (2.58)$$

with ΔE^J being defined as:

$$\Delta E^J = BJ(J + 1) \quad (2.59)$$

and corresponding to the rotational energy of the rigid collinear triatom geometry associated with the saddle to reaction.

When the saddle of the surface is bent, one can still fit the $\Omega = 0$ probabilities calculated at different J values using eq. 2.59 as an empirical expression. A more theoretically sound approach is the one making the probability shift depend also on Ω as follows:

$$P_{vj}^J(E_{\text{tr}}) = \frac{1}{2\Omega_{\text{max}} + 1} \sum_{\Omega=-\Omega_{\text{max}}}^{\Omega_{\text{max}}} P_{vj}^{J=0}(E_{\text{tr}} - \Delta E^{J\Omega}) \quad (2.60)$$

with $\Delta E^{J\Omega}$ being defined as:

$$\Delta E^{J\Omega} = \overline{B}J(J+1) + (A - \overline{B})\Omega^2 \quad (2.61)$$

that is the homologous of eq. 2.59 for bent transition state systems when the calculations are performed only for $\Omega=0$. This approach is built on top of the approximation that the geometry of the system at the bent saddle is a prolate symmetric top one, where $\overline{B} = (B + C)/2$ with A , B and C being the three rotational constants of the triatom at the saddle.

2.11 Potential energy surfaces

The first ⁴A'' (ground) global potential energy surface (PES) for the N+N₂ reaction was formulated in our group as a London-Eyring-Polanyi-Sato (LEPS) functional, which has a linear transition state of 1.55 eV [21].

However, later ab initio investigations by Petrongolo provided new features of the interaction of the N + N₂ system at the saddle to reaction [30, 31]. In particular, these ab initio calculations showed that the geometry of the system at the saddle to reaction is bent and that the $\widehat{\text{NNN}}$ angle has a value around 120° in contrast with the collinear geometry associated with the saddle of the LEPS surface. This finding motivated to assemble new PESs [32]. These PESs have a bent transition state and

are based on the so called largest angle generalization of the rotating bond order (LAGROBO) functional [27–29].

Recently, a new global PES (WSHDSP) was fitted to 3326 ab initio values obtained from open shell CCSD(T)/aug-cc-pVTZ calculations [35]. This PES is drastically different from the LEPS and the LAGROBO ones. It exhibits a double barrier (i.e. two saddle points connected by a shallow well), besides a transition state 0.49 eV higher than that of the LEPS.

Unfortunately, neither WSHDSP PES nor ab initio values are available for distribution. For this reason, the dynamic calculations reported in the present work were performed on the LEPS and the LAGROBO potential energy surfaces. These PESs will be briefly described below. We also propose in the present work a new LAGROBO surface based on a limited set of ab initio CCSD(T)/aug-cc-pVTZ values.

2.11.1 LEPS surface

Using a many-body expansion scheme the popular LEPS functional, V^{LEPS} , describes the interaction of atom-diatom systems using the expression [136]:

$$V^{\text{LEPS}}(r_{ij}, r_{jk}, r_{ik}) = V^{(2\text{B}-\text{LEPS})} + V^{(3\text{B}-\text{LEPS})} \quad (2.62)$$

where i , j and k label the atoms of the system. The two body terms of the functional read:

$$V^{(2\text{B}-\text{LEPS})} = \sum_l {}^1E_l(r_l) \quad (2.63)$$

with l being the sequential label for the ij , jk and ik diatomic pairs and ${}^1E_l(r_l)$ being the Morse diatomic potential defined as

$${}^1E_l(r_l) = D_l \left(e^{-2\beta_l(r_l - r_{el})} - 2e^{-\beta_l(r_l - r_{el})} \right) \quad (2.64)$$

The three body term reads:

$$V^{(3B-LEPS)} = - \sum_l J_l - \sqrt{\frac{1}{2} \sum_l \sum_{m>l} (J_l - J_m)^2} \quad (2.65)$$

with

$$2J_l = {}^1E_l(r_l) - \frac{1 - \Delta_l}{1 + \Delta_l} {}^3E_l(r_l) \quad (2.66)$$

and

$${}^3E_l(r_l) = \frac{D_l}{2} \left(e^{-2\beta_l(r_l - r_{el})} + 2e^{-\beta_l(r_l - r_{el})} \right) \quad (2.67)$$

in which ${}^3E_l(r_l)$ is the anti-Morse diatomic potential, Δ_l is the l_{th} empirical (Sato) parameter and D_l , β_l and r_{el} are, respectively, the dissociation energy, the force constant and the equilibrium distance of the diatom l .

The LEPS parameters for the triatomic system N+N₂ can be easily derived from literature data. The Morse (eq. 2.64) and anti-Morse (eq. 2.67) parameters come from the spectroscopic data of the ($X^1\Sigma_g^+$) electronic ground state of the N₂ molecule [137]. They are: internuclear equilibrium distance $r_e = 1.0977$ Å; dissociation energy $D_e = 9.905$ eV; harmonic and anarmonic vibrational constants $\omega_e = 2358.57$ cm⁻¹ (0.292 eV) and $\omega_e x_e = 14.324$ cm⁻¹ (0.00178 eV). Using these data, one can easily calculate the value of β [138], that for N₂ turns out to be $\beta = 2.689$ Å⁻¹.

Since N+N₂ reaction is homonuclear, all the Sato parameters will have the same value. To determine this value, it was assumed on the ground of measured rate coefficients that the barrier to reaction was 1.55 eV. This led to a value of -0.023 [21].

2.11.2 LAGROBO surfaces

The LAGROBO (largest angle generalization of the rotating bond order) surfaces are, instead, functionals based on exchange process terms (τ) and have the form [32]:

$$V^{\text{LAGROBO}}(r_{\tau,\tau+1}, r_{\tau+1,\tau+2}, r_{\tau+2,\tau}) = \sum_{\tau} w(\Phi_{\tau}) V_{\tau}^{\text{ROBO}}(\rho_{\tau}, \alpha_{\tau}, \Phi_{\tau}) \quad (2.68)$$

where the process index τ (cyclic of module 3) indicates the exchanged atom and V_{τ}^{ROBO} is the ROBO (rotating bond order) function which describes the exchange process τ . In eq. 2.68, $w(\Phi_{\tau})$ (being Φ_{τ} the angle formed by the two bonds having in common the atom τ) plays the role of properly weighing the contribution of the different ROBO representations. The form given to the weighing coefficients would be unimportant (provided that they always sum up to 1) if the three ROBO representations were equally appropriate for all values of the relative Φ_{τ} angle. However, this is in general not true since the ROBO variables are designed to describe only the exchange process of the intermediate atom τ . This means that they become inadequate as Φ_{τ} becomes small. In fact, when Φ_{τ} becomes very small the atom of the closest encounter differs from the exchanged one. To allow the most appropriate V_{τ}^{ROBO} to give the dominant contribution to $V^{\text{LAGROBO}}(r_{\tau,\tau+1}, r_{\tau+1,\tau+2}, r_{\tau+2,\tau})$ while the triatom distorts, w_{τ} is made dependent on Φ_{τ} and vary from one at large Φ_{τ} values to zero at small Φ_{τ} values. The weighing coefficient $w(\Phi_{\tau})$ is defined as:

$$w(\Phi_{\tau}) = \frac{g(\Phi_{\tau})}{\sum_{\tau} g(\Phi_{\tau})} \quad (2.69)$$

with $g(\Phi_{\tau})$ being a damping function of the type:

$$g(\Phi_{\tau}) = \frac{1}{2} (1 + \tanh [\gamma_{\tau}(\Phi_{\tau} - \Phi_{\tau}^{\circ})]) \quad (2.70)$$

This function is about 1 at large Φ_{τ} values, about zero at small Φ_{τ} values and 1/2 at Φ_{τ}° . The values of γ_{τ} and Φ_{τ}° determine the speed of variation of the damping functions and where they take the value 1/2. For the N+N₂ surface, proper values of γ_{τ} and Φ_{τ}° were found to be 50 and 75°.

In eq. 2.68, $V_{\tau}^{\text{ROBO}}(\rho_{\tau}, \alpha_{\tau}, \Phi_{\tau})$ is the model Rotating Bond Order (ROBO) potential [139, 140]. The ROBO model potential is formulated in terms of the polar bond order (BO) coordinates, ρ_{τ} and α_{τ} defined as:

$$\rho_{\tau} = \sqrt{n_{\tau,\tau+1}^2 + n_{\tau+1,\tau+2}^2} \quad \alpha_{\tau} = \arctan \frac{n_{\tau+2,\tau+1}}{n_{\tau,\tau+1}} \quad (2.71)$$

with the generic BO coordinate $n_{\tau,\tau+1}$ being defined as:

$$n_{\tau,\tau+1} = \exp[-\beta_{\tau,\tau+1}(r_{\tau,\tau+1} - r_{e\tau,\tau+1})] \quad (2.72)$$

The functional representation of the ROBO potential is:

$$V_{\tau}^{\text{ROBO}}(\rho_{\tau}, \alpha_{\tau}, \Phi_{\tau}) = D(\alpha_{\tau}, \Phi_{\tau}) F_{\tau}(\rho_{\tau}; \alpha_{\tau}, \Phi_{\tau}) \quad (2.73)$$

where $D(\alpha_{\tau}, \Phi_{\tau})$ is the function determining the depth of the fixed Φ_{τ} MEP of the reaction channel τ while α_{τ} varies from 0° (the reactant asymptote) to 90° (the product asymptote). In the same equation, F_{τ} is the function determining the shape of the cut of the reaction channel along ρ_{τ} at fixed values of Φ_{τ} and α_{τ} and the location of its minimum.

For the sake of simplicity, F_{τ} is formulated as a second order polynomial in ρ_{τ} as follows:

$$V_{\tau}^{\text{ROBO}}(\rho_{\tau}, \alpha_{\tau}, \Phi_{\tau}) = D_{\tau}(\alpha_{\tau}, \Phi_{\tau}) \left[\frac{\rho_{\tau}^2}{a_{\tau}^2(\alpha_{\tau}, \Phi_{\tau})} - 2 \frac{\rho_{\tau}}{a_{\tau}(\alpha_{\tau}, \Phi_{\tau})} \right] \quad (2.74)$$

so as to correspond at the asymptotes to the related diatomic Morse function. The D_{τ} and a_{τ} coefficients indicate respectively the depth and the location in ρ_{τ} of the fixed Φ_{τ} MEP of the reaction channel as α_{τ} varies from 0° to 90°. The values D_{τ} and a_{τ} at the asymptotes ($\alpha_{\tau} = 0^{\circ}$ and 90° respectively) were chosen to reproduce the dissociation energy, the equilibrium internuclear distance and the exponential factor of the N₂ Morse diatomic potential (values are given in the previous Section, page 58).

Again, in order to keep the formulation of the potential as simple as possible and to enforce the proper symmetry, D_τ and a_τ were given a linear dependence on the $\sin(\alpha_\tau)$:

$$D_\tau(\alpha_\tau, \Phi_\tau) = -D_e + b_{\tau 1}(\Phi_\tau) \sin(2\alpha_\tau) \quad (2.75)$$

$$a_\tau(\alpha_\tau, \Phi_\tau) = 1 + b_{\tau 2}(\Phi_\tau) \sin(2\alpha_\tau) \quad (2.76)$$

The variation of the $b_{\tau 1}(\Phi_\tau)$ and $b_{\tau 2}(\Phi_\tau)$ coefficients with Φ_τ was formulated as:

$$b_{\tau j} = \sum_{k=1}^{k_{\max}} c_{\tau j k} (\Phi_{\tau j}^{\text{TS}} - \Phi_\tau)^\zeta \quad (2.77)$$

where $\Phi_{\tau j}^{\text{TS}}$ is an angle of reference, usually the angle at the saddle geometry.

The flexibility of the relate functional allowed to generate several LAGROBO PESs, called L0, L1, L2 and L3. The L0 LAGROBO PES was obtained by fitting the existing LEPS. In this case, see eq. 2.77, both $\Phi_{\tau 1}^{\text{TS}}$ and $\Phi_{\tau 2}^{\text{TS}}$ are 180° , ζ is $2(k-1)$ and $k_{\max}$ is 4. To modify the height and the location of the transition state of the LAGROBO PESs, one can play with the analytic formulation of the $b_{\tau j}$ coefficients of eq. 2.77 and with the value of the related $c_{\tau j k}$ and $\Phi_{\tau j}^{\text{TS}}$ parameters. In fact, for the L1, L2 and L3 LAGROBO potentials the exponent ζ of eq. 2.77 was set equal to $k-1$ for $b_{\tau 1}$ and equal to $2(k-1)$ for $b_{\tau 2}$ (except for that of L2 for which the value $k-1$ was taken). At the same time, $\Phi_{\tau j}^{\text{TS}}$ was set equal to 120° for L1 and L2 and equal to 125° for L3. The value of $\Phi_{\tau 2}^{\text{TS}}$ was always set equal to 180° . In all cases, $k_{\max}$ was set at 4. The $c_{\tau 11}$ coefficient, which indicates the height of the saddle, was set to have the same height of the transition state as the LEPS in the L1 and L2 surfaces whereas in the L3 one was chosen so as to make the height of the transition state better agree with the indications of ab initio calculations of refs. [30, 31]. The value of the parameters for all the LAGROBO PESs are given in ref. [32].

In the present work the L0, L1 and L3 LAGROBO potential energy surfaces have been used in order to investigated the effect on the reactivity of the height and

location (linear or bent) of the potential barriers between reactants and products.

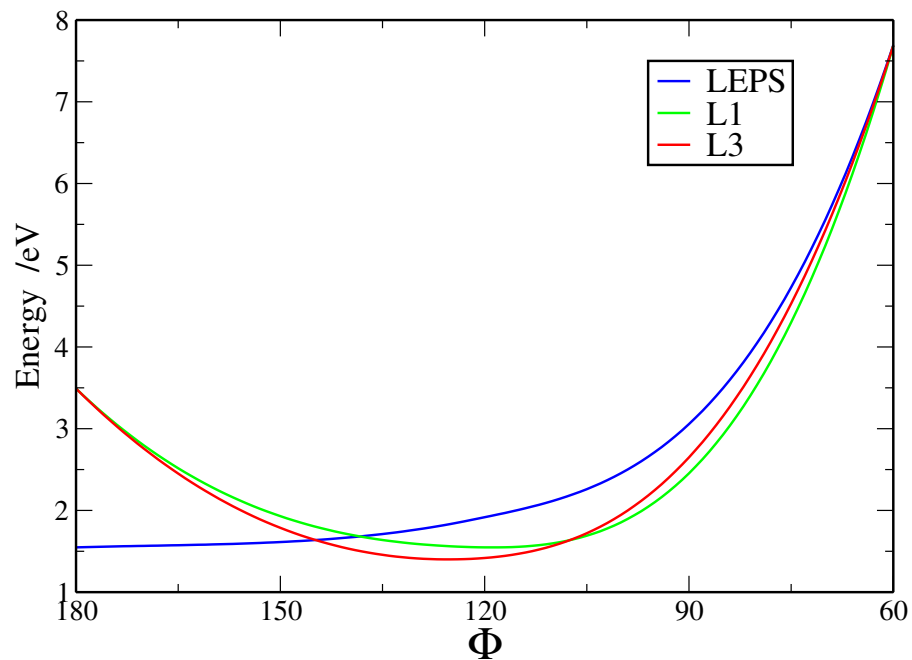
2.11.3 PES characteristics

The characteristics of the LEPS, L0, L1, and L3 potential energy surfaces are briefly summarized in this Section. The heights and bond lengths of the barriers to reaction for several internuclear angles Φ are given in Table 2.1. As clearly indicated by the Table, both the height and the geometry of L0 well reproduce those of the LEPS. The most significant difference, not apparent from the Table, is the slope of the MEP of L0, which is larger than that of the MEP of the LEPS (the MEP of L0 lies always slightly above that of the LEPS). The L1 and L3 PESs have a bent transition state. The location of the transition state is the key difference between the LEPS (L0) and the L1 surface. In fact, while the height of the transition state is the same (1.55 eV) for both surfaces, the location of the LEPS and L0 transition state is collinear while that of L1 is bent ($\Phi = 120^\circ$). At the same time, the transition state of L3 differs from that of L1 for the fact that it is high 1.40 eV and located at $\Phi = 125^\circ$. The dependence of the barrier height on the internuclear angle Φ is shown for the LEPS, L1 and L3 surfaces in Figure 2.5. (The corresponding dependence for the L0 PES is not shown because it coincides with that of the LEPS PES.) On the other hand, all PESs have almost the same dependence on the angle Φ of the N-N internuclear distance at the barriers. However, beside this agreement, the N-N distance at the transition state differs.

In order to analyse the global characteristics of the PES and find, if exists, any spurious structure, it is necessary to plot the potential energy function. Obviously a full four-dimensional plot of the PES is not possible. To reduce the dimensionality, the projection of the potential function onto a bidimensional space is needed. Generally this difficult is overtaken by resorting to the isoenergetic contour maps of the

Table 2.1: Barrier characteristics of the N+N₂ PESs

Φ	Height (in eV)				N–N distance (in Å)			
	LEPS	L0	L1	L3	LEPS	L0	L1	L3
180°	1.55	1.55	3.49	3.49	1.240	1.240	1.240	1.240
150°	1.61	1.62	1.93	1.79	1.243	1.244	1.244	1.244
125°	1.83	1.84	1.56	1.40	1.251	1.252	1.252	1.252
120°	1.92	1.91	1.55	1.42	1.254	1.254	1.254	1.254
90°	3.06	3.05	2.45	2.65	1.294	1.293	1.293	1.293
60°	7.69	7.69	7.69	7.69	1.530	1.522	1.522	1.522

Figure 2.5: Barrier heights as a function of the angle Φ for the LEPS, L1 and L3 PESs.

potential function [141]. In each plot, usually the internuclear angle Φ is fixed and the isoenergetic contours are obtained as a function of the r_1 and r_2 internuclear distances. Figure 2.6 shows these plots for the LEPS and the L3 PESs. The L0 and L1 contour plots have been omitted because they are almost equal to those of the LEPS and L3 ones, respectively.

In the plots, the entrance channel is localized in the low-right part of each panel and is extended up to ($r_1 \rightarrow \infty$) asymptotic limit where one atom is far away from the diatomic molecule and therefore the potential energy corresponds to the N₂ diatomic potential. The reactant channel moves to the left direction and arrives to the saddle point. After that, the channel moves towards the products to arrive to the product asymptotic region ($r_2 \rightarrow \infty$) located in the up-left side of each panel. Obviously, the isoenergetic maps at a given Φ angle are symmetric, since the $\text{N} + \text{N}_2 \rightarrow \text{N}_2 + \text{N}$ process is symmetric.

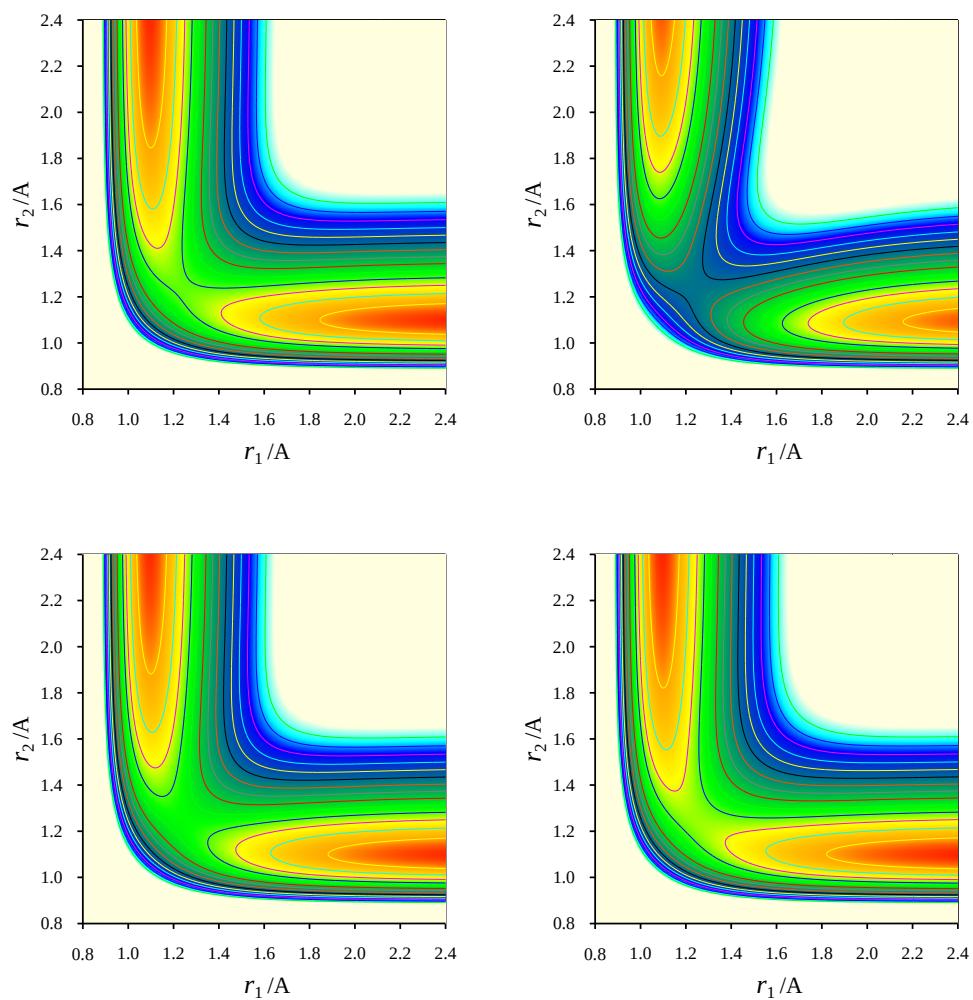


Figure 2.6: Isoenergetic contour maps for LEPS (left panels) and L3 (right panels) PESs for $\Phi = 180^\circ$ (upper panels) and $\Phi = 125^\circ$ (lower panels). The energy interval between two consecutive contours is 0.4 eV and the energy is referred to the entrance channel.

Chapter 3

The N+N₂ reaction: Calculations and results

The accurate evaluation of state-to-state cross sections and rate coefficients of atom-diatom reactions is a highly demanding computational task. It requires, in fact, full quantum calculations for several initial states and a converged sum of the fixed total angular momentum value J detailed S matrix elements. Such a tremendous computational effort is justified, however, only once the potential energy surface (PES) to be used for the calculations has already proven to be sufficiently accurate. Unfortunately, this is not the case of the LEPS PES available from the literature and used for dynamical calculations of the N + N₂ reaction [21]. In spite of that, massive quasi-classical (QCT) and quantum infinite order sudden (RIOS) computational campaigns of the cross sections and rate coefficients of this system have been quite recently carried out on the LEPS PES [22–24] because of their relevance to the modeling of nitrogen plasmas [142] and processes occurring around reentering spacecrafts [15]. More recently calculations on the same PES were extended to QCT vibrational relax-

ation and dissociation rates for the whole ladder of reactant vibrational states [25,26] and to semiclassical initial value representation thermal rate coefficient which were also compared with transition state and RIOS ones [34]. An improvement of the N + N₂ PES was the development of the (bent dominant) LAGROBO surfaces [32]. QCT and quantum RIOS calculations performed on both the LEPS and the LAGROBO PESs singled out the clearly different dynamical behaviour of the system on the different surfaces [32]. However, to found on a more robust theoretical ground both the rationalization of the reactive behaviour of the N + N₂ system and the creation of a suitable set of data for use in spacecraft reentering simulations, we carried out extended three dimensional (3D) quantum calculations on the above mentioned LEPS and LAGROBO surfaces. Unfortunately, the difficulty of reconstructing the WSHDSP PES from the information given in ref. [35] and of obtaining a copy of the related routine from the authors, did not allow us to carry out the same calculations on that surface.

3.1 Quantum detailed reactive probabilities

To carry out the actual time-dependent wavepacket calculations we made use, as already mentioned, of the RWAVEPR [33, 75, 76] program and of the input parameters given in Table 3.1. Thanks to the recent development of distributed computing platforms and technologies [77, 78, 143] it has been possible to run massive calculations of the reaction probabilities (in spite of the non light mass of the atoms involved in the process). In particular, to compare the reactive efficiency of the system on the considered PESs, exact $J=0$ state-to-state quantum reactive probabilities (excitation functions) were calculated for the ground rotational level of the first 6 vibrational states of the reactant N₂ molecule and E_{tr} ranging from threshold up to 2 eV in steps of 0.001 eV.

Table 3.1: [Input data for the RAWAVEPR calculations.](#)

Scattering coordinate (R') range (in a_0)	0-12
Number of grid points in (R')	240
Internal coordinate (r') range (in a_0)	0-12
Number of grid points in (r')	240
Grid interval (for both R' and r') (in a_0)	0.05
Number of angular grid points	120
Potential energy cut-off (in eV)	5.0
Angular kinetic energy cutoffs (in eV)	5.0,6.5
Initial center of the wavepacket (in a_0)	8.5
Width of the wavepacket	0.3
Number of Taylor terms	80
Absorbing boundary parameter (x, y) (in a_0)	11.0
Width of the absorbing potential (in a_0)	2.0
Position of the analysis line ($\mathbf{R}'_\infty$) (in a_0)	10
Number of iterations for $v \leq 1$	2000
Number of iterations for $v \geq 2$	3000

A first batch of calculations were performed on the LEPS and on the L0 PESs. Plots of the reactive probability values calculated at $J=j=0$ and v varying from 0 to 5 are given in Figure 3.1 as blue and magenta lines, respectively. The 3D quantum probabilities, although differing in absolute value from QCT and RIOS ones, confirm that, as expected, results obtained on LEPS and L0 are almost coincident. When calculations were performed also on L1 (to the end of investigating the effect of moving the barrier to reaction out of collinear geometries while preserving its height), the net result (see green lines of Figure 3.1) was at $v=0$ a clear increase of the threshold energy and an associated strong decrease of the reactive probability about the threshold region (in the temperature range of interest, this means also a substantial decrease of the thermal rate coefficient). When the calculations were extended to L3 (to the end of investigating the effect of lowering the saddle to reaction in an attempt to contrast the decrease of the reactivity due to the adoption of a bent geometry at the saddle) the net result (see red lines of Figure 3.1) was a lowering of the threshold energy back almost entirely to the LEPS and L0 values and a sharp increase of the reactive probability in the energy region immediately following the threshold. This puts on an exact quantum ground the traditional QCT finding that on collinearly dominant PESs relative collision energy is exploited better than any other mode to the end of enhancing reactivity. Such an effect is particularly strong, however, only at $v=0$ and for the just-past-the-threshold energy values. At larger v values, in fact, the picture is partially modified. The higher reactive efficiency of the collinearly dominated PESs (LEPS and L0) becomes weaker and the interplay between larger amounts of vibration and collision energy becomes so strong to efficiently enhance the reactivity also on PESs having a bent geometry at the saddle to reaction provided that the height of the barrier has been lowered as in L3. As shown by the green lines of Figure 3.1, in fact, L1 results (for which the barrier has not been lowered) remain lower than the reactive probabilities calculated on the other surfaces for a larger interval of relative collision energy even at $v=5$.

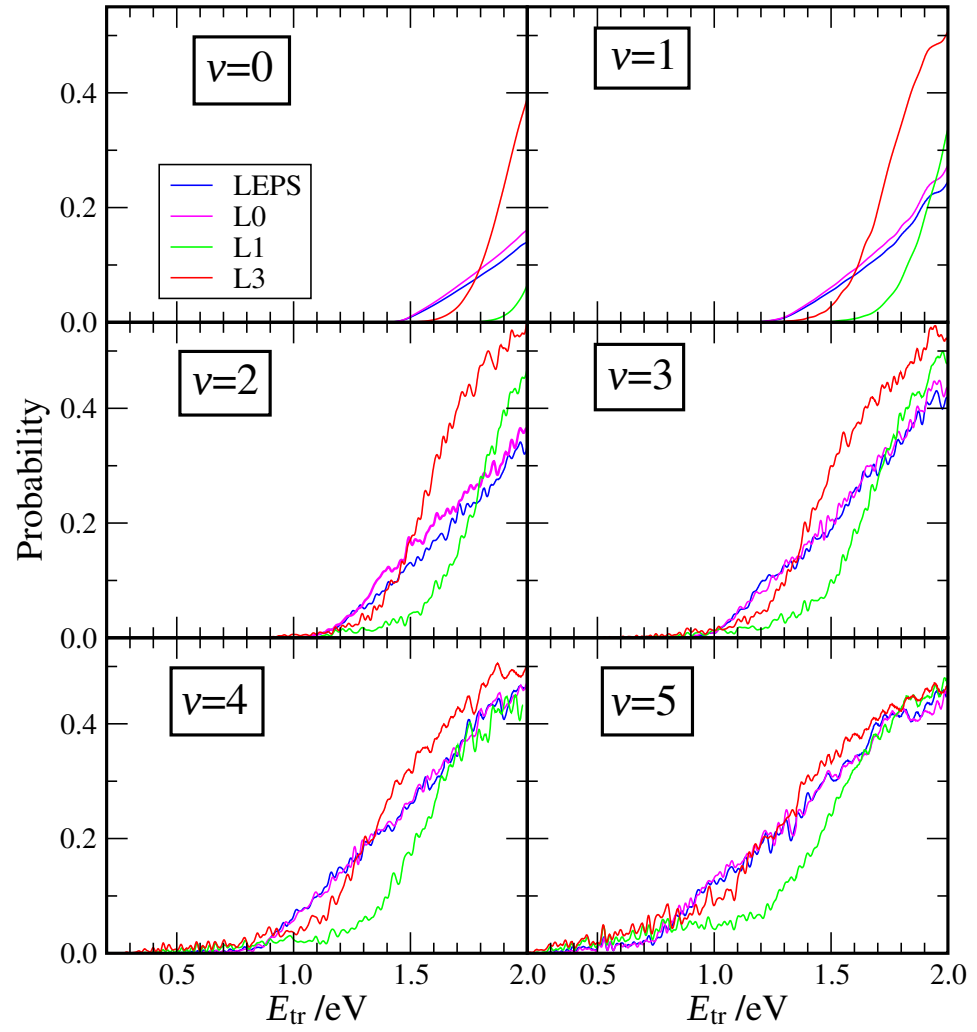


Figure 3.1: State-specific reactive probabilities, $P_{vj}^J(E_{tr})$, calculated on the LEPS (blue line), L0 (magenta line), L1 (green line) and L3 (red line) PESs for $v=0,1,2,3,4,5$ at $j=J=0$ plotted as a function of the collision energy E_{tr} .

A first consideration to make at this point is that the LAGROBO PESs which have a bent transition state geometry (such as L1 and L3) are able to emulate the reactive efficiency of the collinearly dominant PESs (such as the LEPS and L0) only when the barrier to reaction is properly lowered (in our case, as already mentioned, this amount corresponds to the zero point difference between the transition state and the asymptote).

To consider other properties of the N + N₂ reactive system, we shall focus hereafter on the comparison between LEPS and L3 results. As a first example we consider here the (normalized to the maximum) PVDs calculated at a collision energy of 1.65 eV. As apparent from Figure 3.2, the PVD calculated at $v=0$ shows the substantial vibrational adiabaticity of the related reactive process on both the LEPS and the L3 PESs. A similar feature is also shown by the PVDs calculated at $v=2$ though with a wider distribution over the product states. Vibrational adiabaticity progressively deteriorates as v increases to 3, 4 and 5 as shown by the progressive extension of the higher v' branch of the distribution. The efficiency in promoting the system to more excited vibrational states is so pronounced for the LEPS PES to generate a second peak at large v' values. On the contrary, not only L3 shows a weaker tendency to produce more vibrationally excited products but it also shows a marked deexcitation at $v=1$.

Further interesting information about the dynamical behaviour of the N + N₂ system on L3 and the LEPS are also obtained by plotting the reactive probabilities at increasing rotational excitation of the reactant molecule. For illustrative purposes state-specific reactive probabilities calculated on both surfaces are plotted at $v=0$, 1, 2 and 3 in Figures 3.3, 3.4, 3.5 and 3.6, respectively. As is apparent from the figures, while at low j values the threshold energy is definitely higher for L3 results, it gradually shifts to lower energy as j increases (while the corresponding shift down of the LEPS results is much less appreciable). The two effects become comparable only

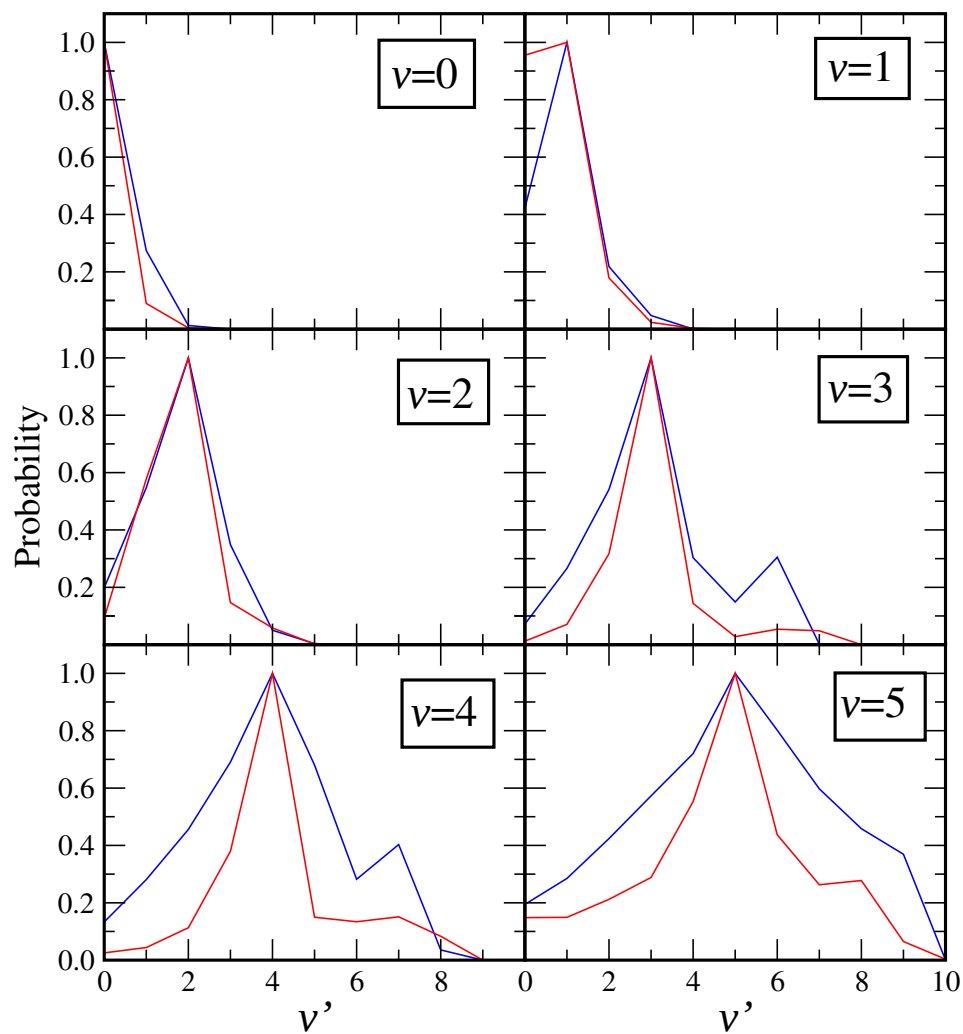


Figure 3.2: Product vibrational distributions calculated on the LEPS (blue line) and L3 (red line) PESs for $v=0,1,2,3,4,5$ at $j=J=0$ and $E_{tr} = 1.65$ eV plotted as a function of the product vibrational state v' . Distributions are normalized to their maxima.

around $j=30$. This confirms that the already commented inefficient exploitation of the relative collision energy near the threshold to enhance reactivity on L3 is largely compensated by an efficient exploitation of the other degrees of freedom (contrary to what happens on the LEPS PES). The lowering of the threshold with j is also accompanied by a simultaneous increase of the reactive probability on L3 that is significant mainly at low j values. No such an effect is found on the LEPS PES.

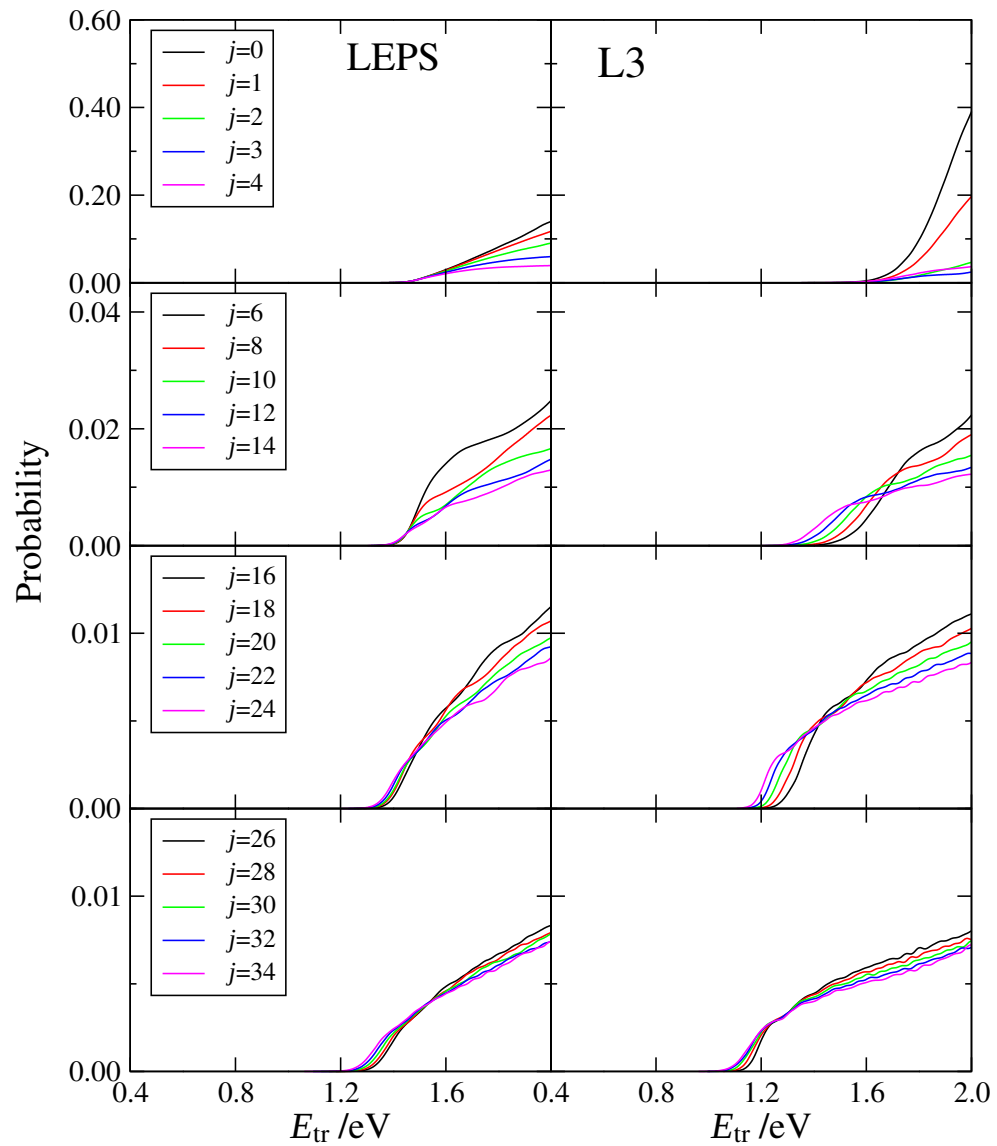


Figure 3.3: State-specific reactive probabilities, $P_{vj}^J(E_{tr})$, calculated on the LEPS (left panels) and L3 (right panels) PESs at $v=0$, $J=0$ and $j=0-4$ (upper panels), $j=6-14$ (central upper panels), $j=16-24$ (central lower panels) and $j=26-34$ (lower panels), plotted as a function of the collision energy E_{tr} . Note the different scales in the various panels.

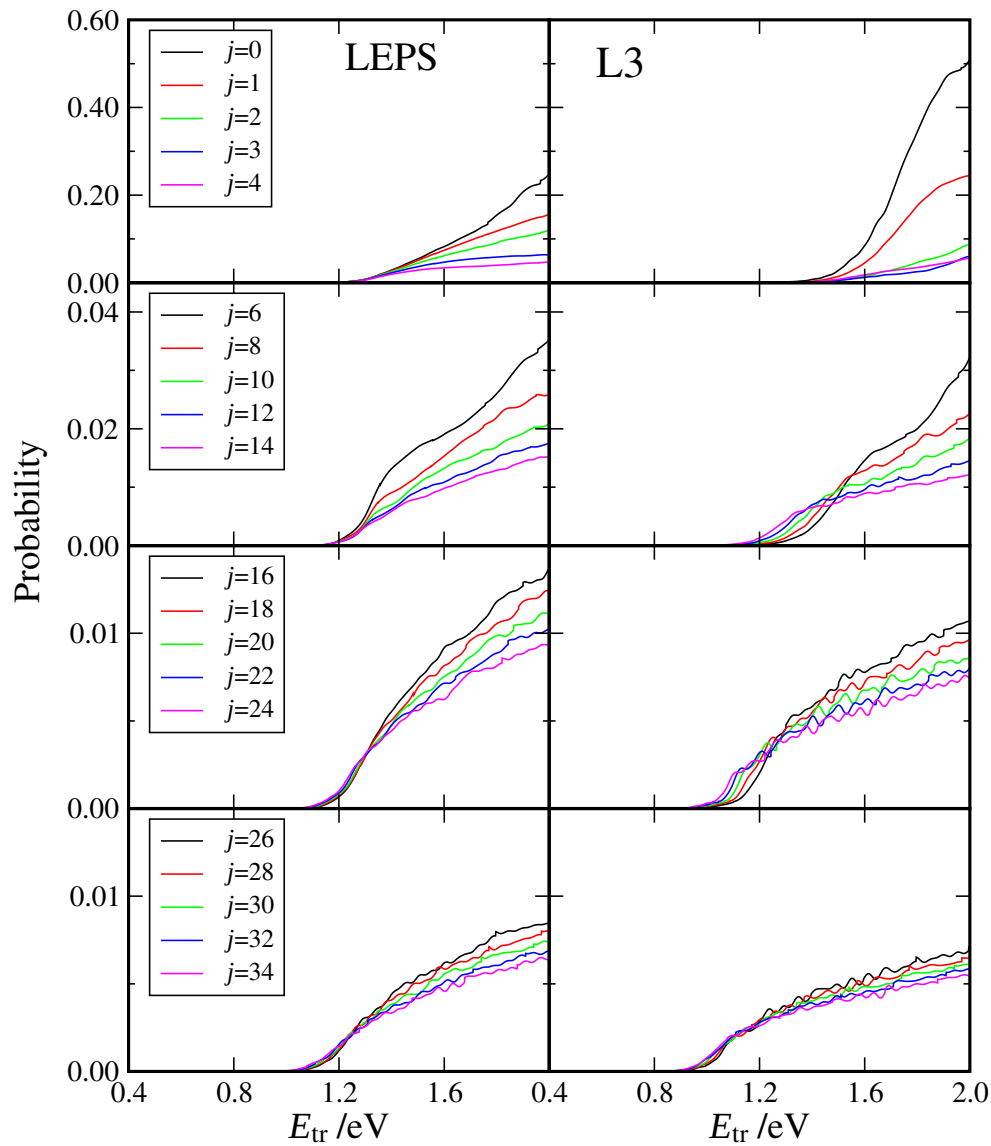


Figure 3.4: State-specific reactive probabilities, $P_{vj}^J(E_{tr})$, calculated on the LEPS (left panels) and L3 (right panels) PESs at $v=1$, $J=0$ and $j=0-4$ (upper panels), $j=6-14$ (central upper panels), $j=16-24$ (central lower panels) and $j=26-34$ (lower panels), plotted as a function of the collision energy E_{tr} . Note the different scales in the various panels.

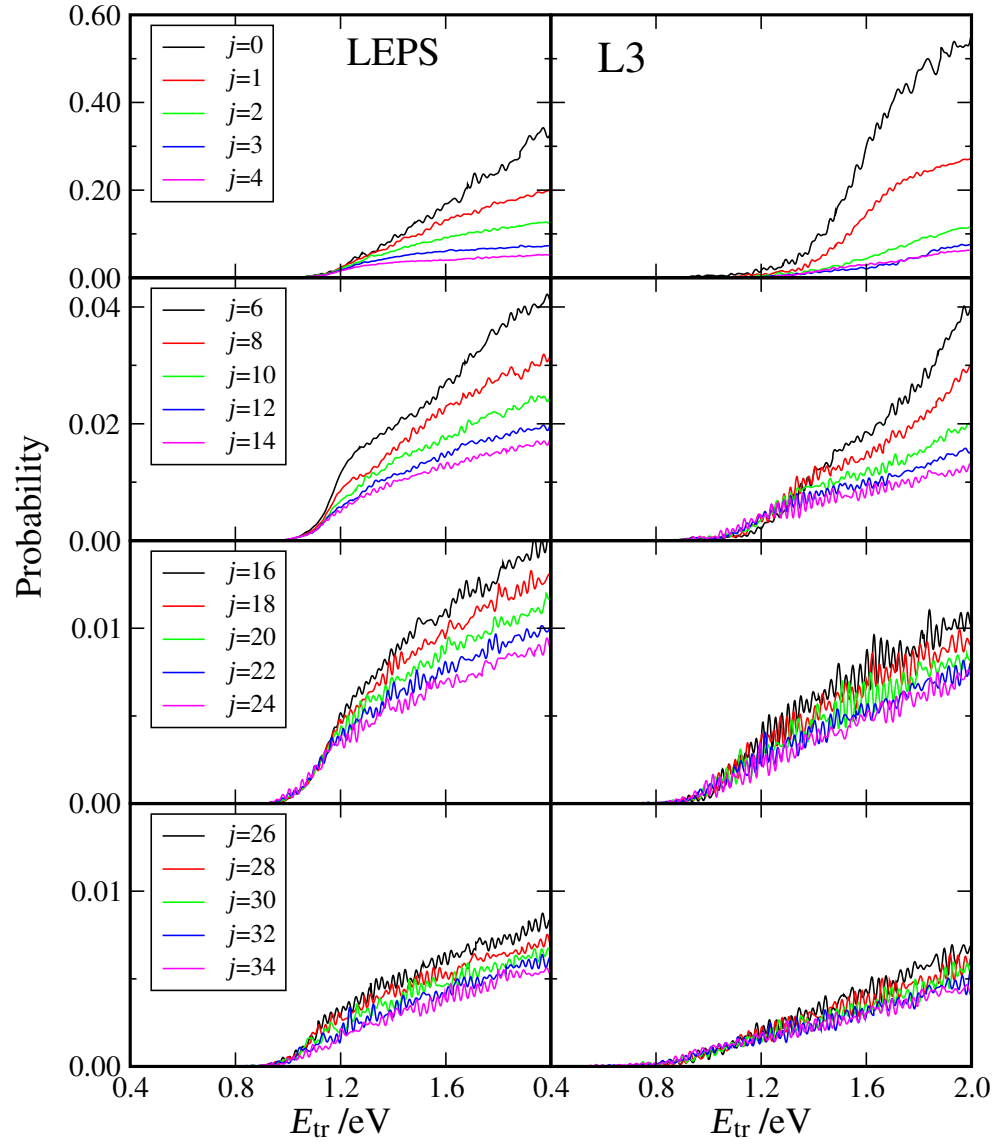


Figure 3.5: State-specific reactive probabilities, $P_{vj}^J(E_{tr})$, calculated on the LEPS (left panels) and L3 (right panels) PESs at $v=2$, $J=0$ and $j=0-4$ (upper panels), $j=6-14$ (central upper panels), $j=16-24$ (central lower panels) and $j=26-34$ (lower panels), plotted as a function of the collision energy E_{tr} . Note the different scales in the various panels.

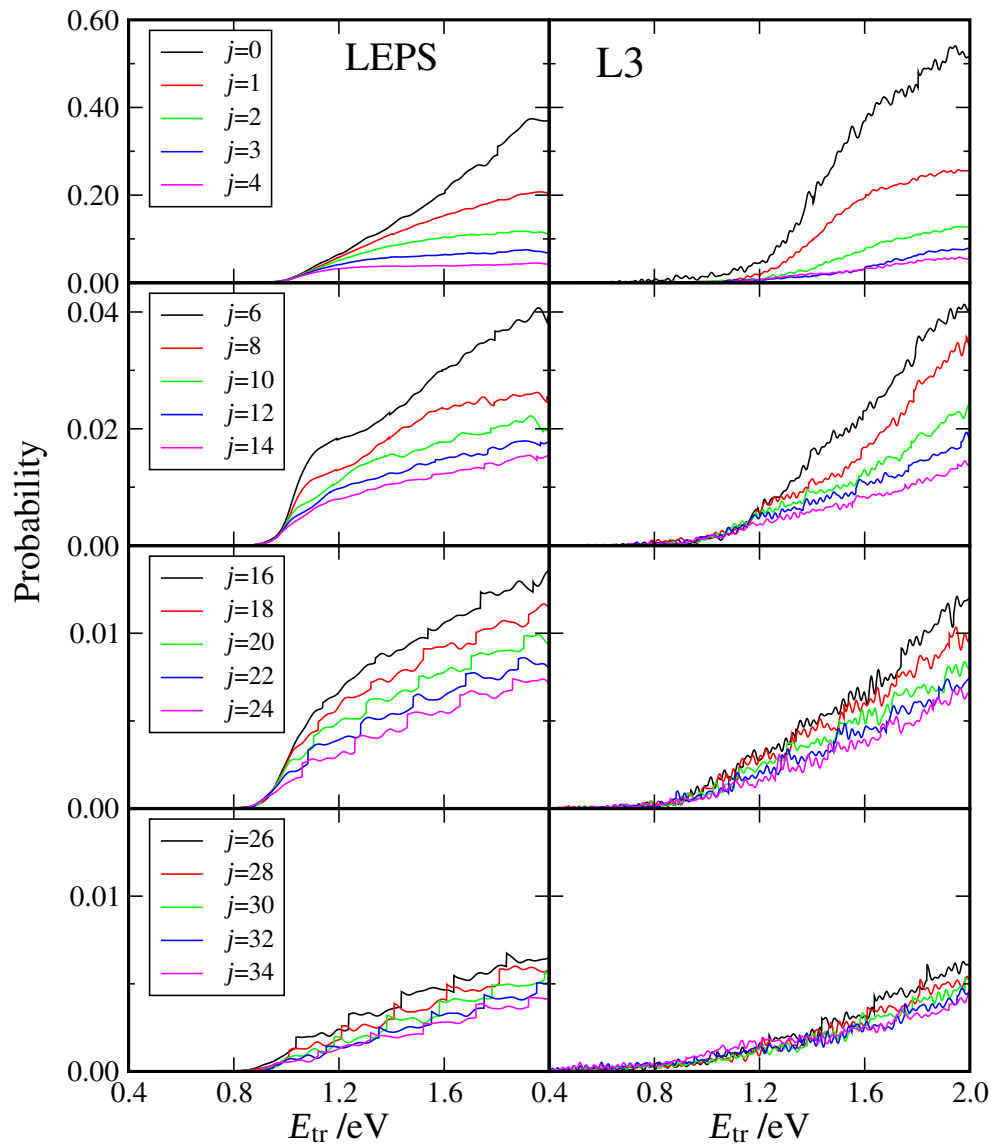


Figure 3.6: State-specific reactive probabilities, $P_{vj}^J(E_{tr})$, calculated on the LEPS (left panels) and L3 (right panels) PESs at $v=3$, $J=0$ and $j=0-4$ (upper panels), $j=6-14$ (central upper panels), $j=16-24$ (central lower panels) and $j=26-34$ (lower panels), plotted as a function of the collision energy E_{tr} . Note the different scales in the various panels.

3.2 *J*-shift rate coefficients

To calculate thermal rate coefficients and compare them with the experiment [18–20] (which is, after all, the ultimate goal of our investigation) we shall first work out of the state-specific probabilities integral reactive state-specific cross sections, $\sigma_{vj}(E_{\text{tr}})$, using equation 2.56 and then by integrating over E_{tr} and averaging (taking into account the different degeneration for even and odd rotational states) over the vj initial states one can calculate the corresponding thermal rate coefficient $k(T)$.

As already mentioned, the calculation of the thermal rate coefficients, even when using the CS approximation, requires to integrate the Schrödinger equation at all the populated vj initial states, all the total angular momentum quantum number J contributing to reaction and all the allowed values of the J projection Ω . For this reason the computational effort has to be significantly reduced. A way to reduce the computational effort is to use the *J*-shift approximation. In this approximation, for each vj initial state the Schrödinger equation has to be integrated only for the total angular momentum zero, $J=0$, and then the computed probabilities are simply shifted in energy according to the rotational levels of the system at the saddle to reaction.

To check the applicability of the *J*-shift model to the $\text{N} + \text{N}_2$ reaction we computed the CS reactive probability at $v=j=\Omega=0$ for several J values. The calculated state-specific CS probabilities are plotted in the lower panel of Figure 3.7 for the LEPS. The figure shows a clear regular spacing in both sets of curves as J increases. Moreover, when the homologous values of the reactive probabilities are plotted as a function of $J(J+1)$ they lie on a straight line (see the lower panel of Figure 3.8).

These lines, though, are slightly shifted for different probability values. For the LEPS probabilities the slopes of these lines are all close to the value of the rotational constant B (see eq. 2.59) of the collinear NNN geometry at the reaction saddle. The calculated average value of B coincides (within an error of 10%) with the theoretical

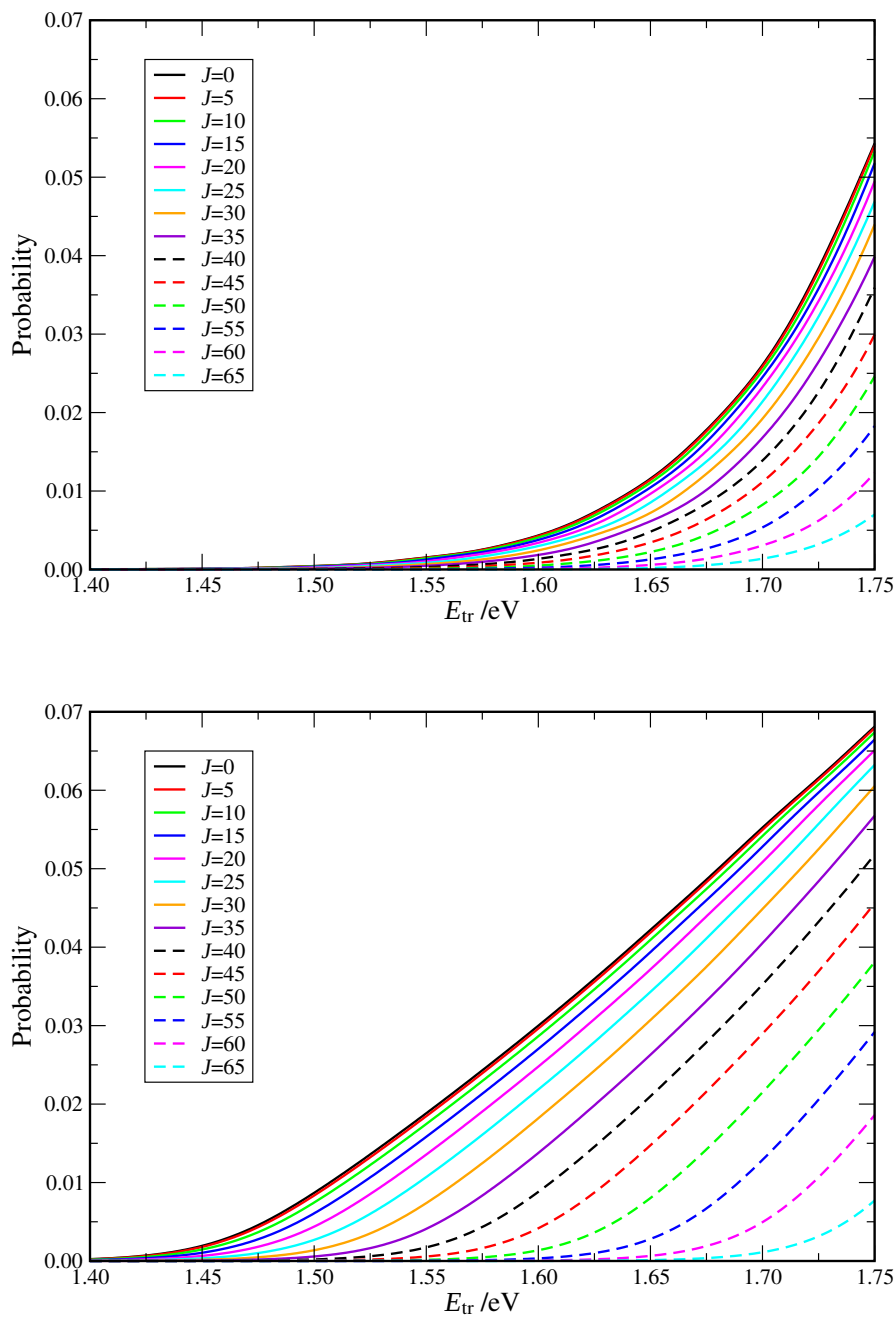


Figure 3.7: State-specific reactive probabilities, $P_{vj}^{J\Omega}(E_{tr})$, calculated on the LEPS (lower panel) and L3 (upper panel) PESs for $v=j=\Omega=0$ at various values of J plotted as a function of the collision energy E_{tr} .

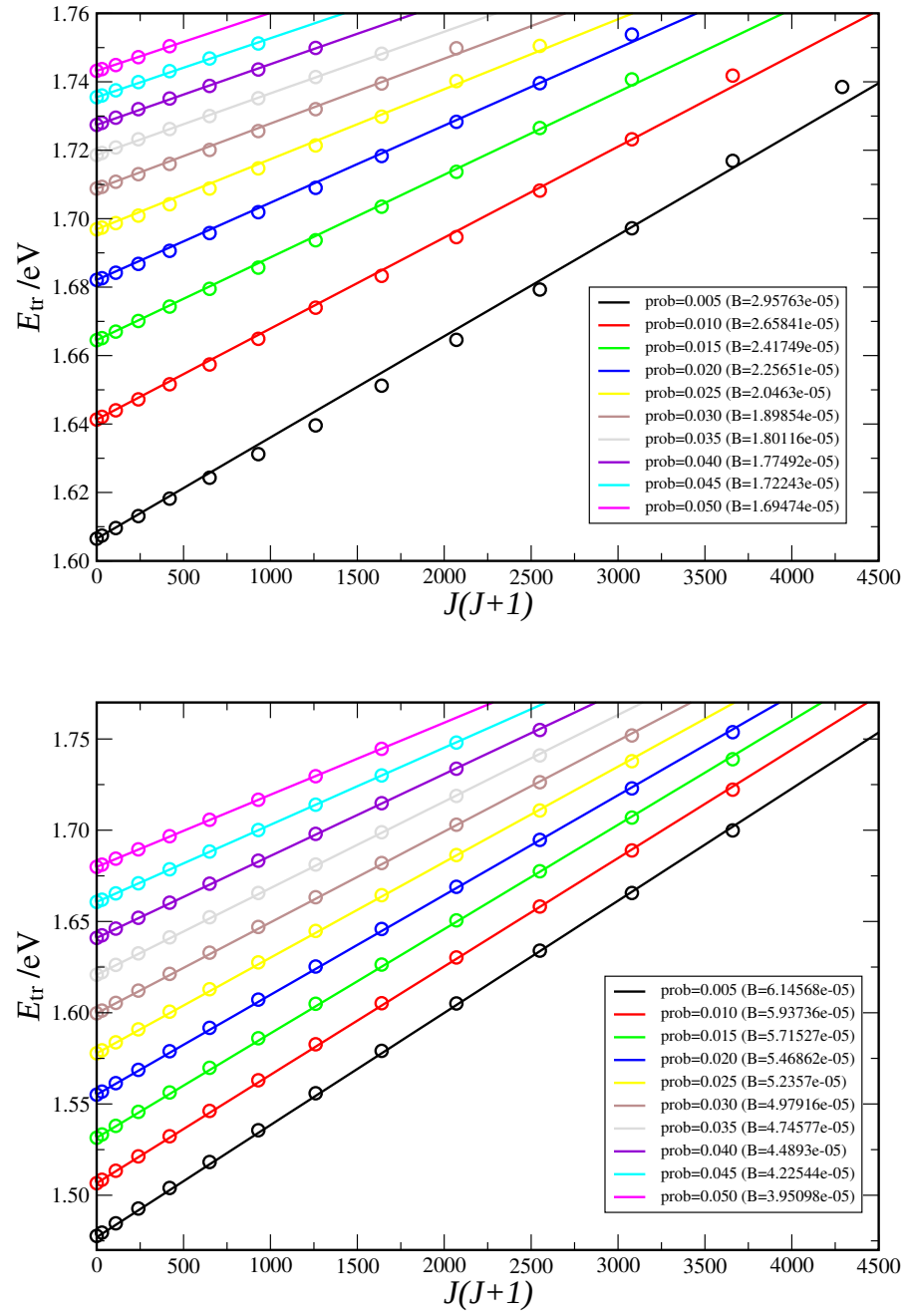


Figure 3.8: Linear fit of the state-specific reactive probabilities, $P_{vj}^{J\Omega}(E_{tr})$, calculated on the LEPS (lower panel) and L3 (upper panel) PESs for $v=j=\Omega=0$ plotted as a function of $J(J+1)$.

one (4.9×10^{-5} eV) derived from the value of the coordinates of the system geometry at the saddle.

A similar treatment was also applied to the L3 results using the probability values plotted in the upper panel of Figure 3.7. In this case, however, due to the bent geometry of the system at the saddle, eq. 2.61 was used to fit the $v=j=\Omega=0$ probabilities (see the upper panel of Figure 3.8). From this a value of $\overline{B}$ (that is equal to the average of B and C) of 2.0×10^{-5} eV was obtained. On the contrary, a calculation of the rotational constants of the system at the bent geometry of the L3 transition state gives for A , B and C values of 6.7×10^{-4} , 6.0×10^{-5} and 5.5×10^{-5} eV, respectively. This leads to a $\overline{B}$ value about 2.5 times larger than the one obtained from a fitting of the calculated probabilities (that, given the assumptions made, is a more than acceptable result).

In order to be able to use the previously described J -shift models to evaluate the thermal rate coefficients, the exact $J=0$ calculations were repeated for the reactant rovibrational states appreciably populated (only rovibrational states whose weight in the Boltzmann distribution is larger than 5% of the maximum probability were included) at the temperature range covered by the experiment (1000 - 4000 K). Figure 3.9 shows the Boltzmann distributions of the rovibrational levels at $T=1273$ K and $T=3400$ K, the two temperatures of the experiments. Using the mentioned criterion, the 242 lower rovibrational states were included; in particular, the j intervals 0–82 at $v=0$, 0–74 at $v=1$, 0–62 at $v=2$ and 0–50 at $v=3$. Moreover, as apparent from Figure 3.9, the most populated rovibrational states at the two temperatures of the experiment are $v=0$ and $j=14$ at $T=1273$ K and $v=0$ and $j=24$ at $T=3400$ K. As to the collision energy, calculations were performed up to 2.8 eV in steps of 0.001 eV. This range of collision energies covers the related Boltzmann distributions at the temperatures considered in this work. As a matter of fact, the most probable collision energies at $T=1273$ K and $T=3400$ K are 0.11 and 0.29 eV, respectively.

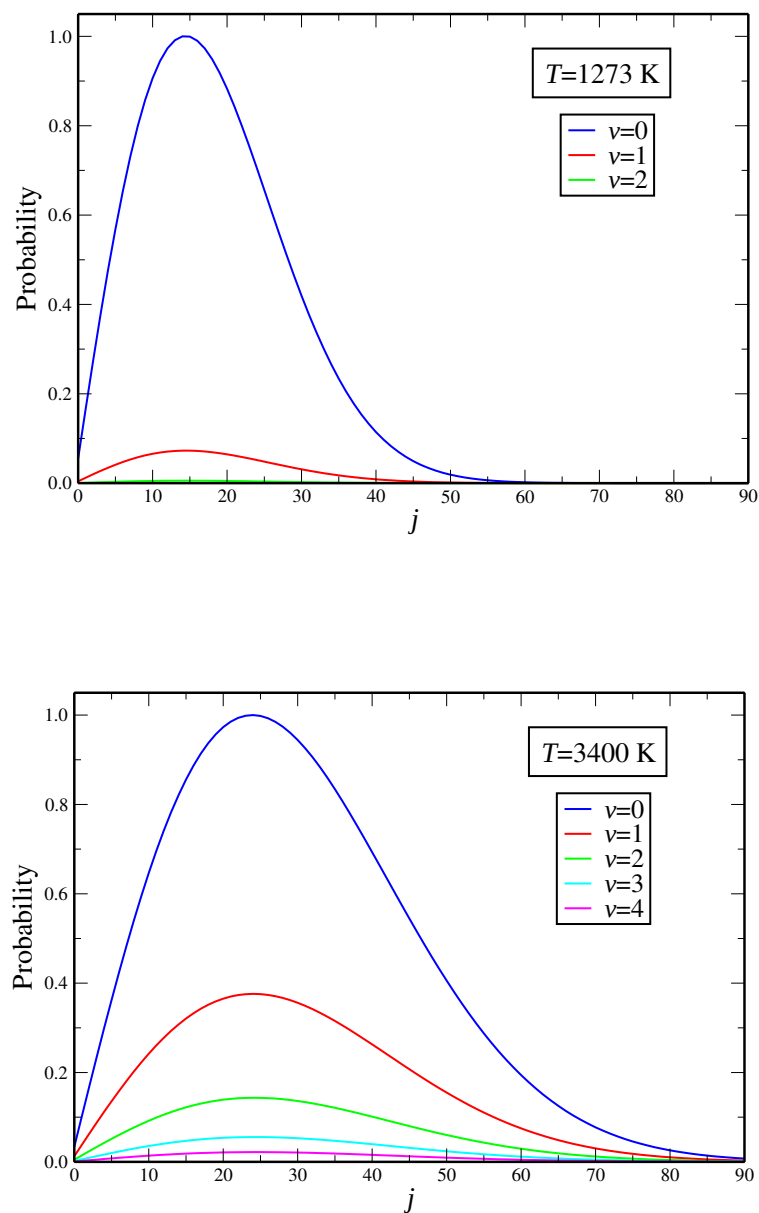


Figure 3.9: Boltzmann distribution of the rovibrational states at $T=1273$ K (upper panel) and $T=3400$ K (lower panel) plotted as a function of the rotational state j . Probabilities are normalized to their maxima. For clarity, the different degeneration for even and odd rotational states is not taken into account.

Several examples of the obtained partial state-specific reactive probabilities at $J=0$, $P_{vj}^{J=0}(E_{\text{tr}})$, have been already shown in Figures 3.3, 3.4, 3.5 and 3.6.

Once the probabilities $P_{vj}^{J=0}(E_{\text{tr}})$ at zero total angular momentum are evaluated, the probabilities at $J > 0$ are calculated by applying the J -shift approximation. In order to quantify the shift in energy of the reactive probabilities, Figure 3.10 compares the probabilities calculated at $J=0$ on the L3 PES with those obtained using the J -shift approximation (eq. 2.61) for several values of J (note that Ω satisfies the constraint $\Omega_{\text{max}} = \min(J, j)$). As clearly shown by the Figure, at $J=20$ the shift in energy is small for low values of Ω (the values corresponding to $\Omega=0$ (red lines) are often hidden by those of the next Ω values (green lines)). Only at quite larger values of Ω , the shift becomes important. As J increases, the overall shift increases but the further increase with Ω is only apparent at larger values of Ω .

By summing the J -shift $P_{vj}^{J\Omega}(E_{\text{tr}})$ contributions, the J -shift partial state-specific probabilities, $P_{vj}^J(E_{\text{tr}})$, can be calculated. Figure 3.11 shows the values of $P_{vj}^J(E_{\text{tr}})$ calculated on the LEPS and L3 PESs at $v=0$, $j=14$ and $v=0$, $j=24$ as a function of the collision energy. It is worth to recall here that the J -shift probabilities on the LEPS surface are calculated using eq. 2.59 (because the rotor is assumed to be linear due to the collinear geometry of the system at the saddle to reaction) while eq. 2.61 is used when the L3 surface is considered (because rotor is assumed to be a prolate symmetric top due to the bent geometry of the system at the saddle to reaction). Accordingly, the B factor used in eq. 2.59 was 4.9×10^{-5} eV while in eq. 2.61 the A and $\overline{B}$ factors were set to 6.7×10^{-4} eV and 5.8×10^{-5} eV, respectively. This means that the shift for the LEPS $P_{vj}^J(E_{\text{tr}})$ probabilities is directly proportional to $J(J+1)$ while the shift for the L3 surface is articulated in slightly varying shifts depending on the value of Ω . Moreover, because the B factor used in eq. 2.59 is smaller than that used in eq. 2.61 and a further term proportional to $(A - \overline{B})$ is added, the shift in energy for the LEPS probabilities is lower than that for the L3 ones. Accordingly,

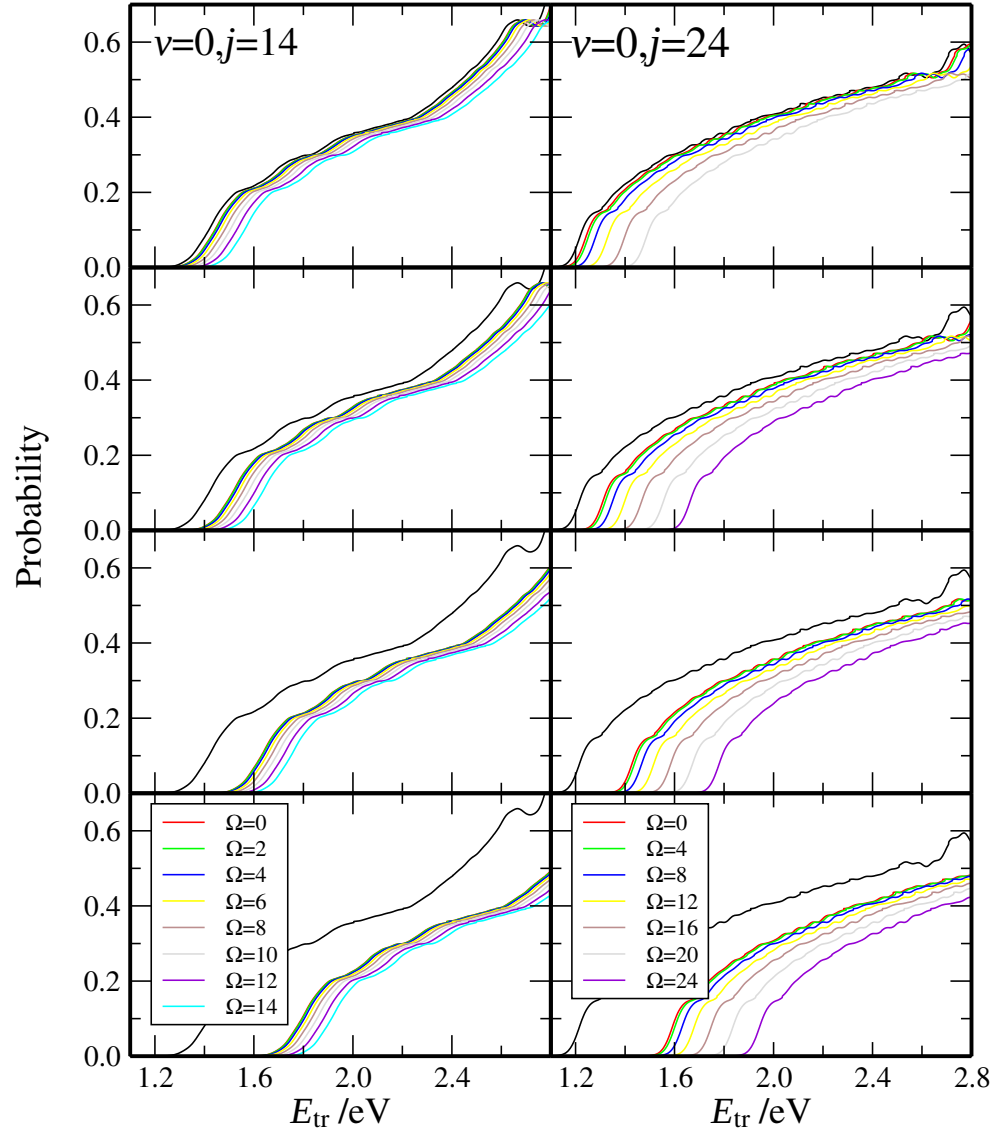


Figure 3.10: J -shift state-specific reactive probabilities, $P_{vj}^{J\Omega}(E_{tr})$, calculated on the L3 PES using eq. 2.61 at $v=0$, $j=14$ (left panels) and $v=0$, $j=24$ (right panels), for $J=20$ (upper panels), $J=40$ (central upper panels), $J=60$ (central lower panels) and $J=80$ (lower panels), plotted as a function of the collision energy E_{tr} . The black line corresponds to the probabilities calculated at $J=0$.

as J increases the partial $P_{vj}^J(E_{\text{tr}})$ probabilities for the LEPS surface tend to vanish more slowly than those for the L3 surface.

A more global vision of the effect of the J -shift approximation can be obtained by in Figure 3.12, where the J -shift partial cross section terms, $\sigma_{vj}^J(E_{\text{tr}})$, are plotted as a function of the collision energy E_{tr} and of the total angular momentum J for the same cases of Figure 3.11. These J -shift partial cross section terms were calculated by scaling the J -shift partial state-specific probabilities, $P_{vj}^J(E_{\text{tr}})$, by the factor $\pi(2J+1)/k_{vj}^2$ (see eq. 2.56). As apparent from the figure, the threshold energy for $\sigma_{vj}^J(E_{\text{tr}})$ increases as J increases similarly to what is observed for the probabilities $P_{vj}^J(E_{\text{tr}})$. On the contrary, as a consequence of the $(2J+1)$ factor, the shape of the partial cross section terms clearly differs from those of the partial probabilities. In fact, while partial probabilities show their maxima at $J=0$ and gradually decrease as J increases, the partial cross section terms show their maxima at values of J as high as 100. At the same time, Figure 3.12 clearly shows that the partial cross section terms calculated on the LEPS are significantly larger than those calculated on L3 (in spite of their slightly larger). This is due to a smaller energy shift that is a consequence of using both eq. 2.59 and a smaller value for the B factor. Another feature of Figure 3.12 that it is worth noting here is the fact that partial cross section terms begin to be negligible for values of the total angular momentum larger than $J=160$.

J -shift state-specific cross sections, $\sigma_{vj}(E_{\text{tr}})$, are calculated by simply summing the J -shift partial state-specific cross sections, $\sigma_{vj}^J(E_{\text{tr}})$. This summation includes all the total angular momentum number J contributing to reaction and, as just mentioned, partial cross section terms for J near 200 have to be considered. The obtained state-specific reactive cross sections calculated on both the LEPS and the L3 surface are plotted for several initial rotational states at $v=0, 1, 2$ and 3 in Figures 3.13, 3.14, 3.15 and 3.16, respectively. It is worth noting that the scales vary in going from bottom to top panels. The Figures show that at all the vibrational states considered

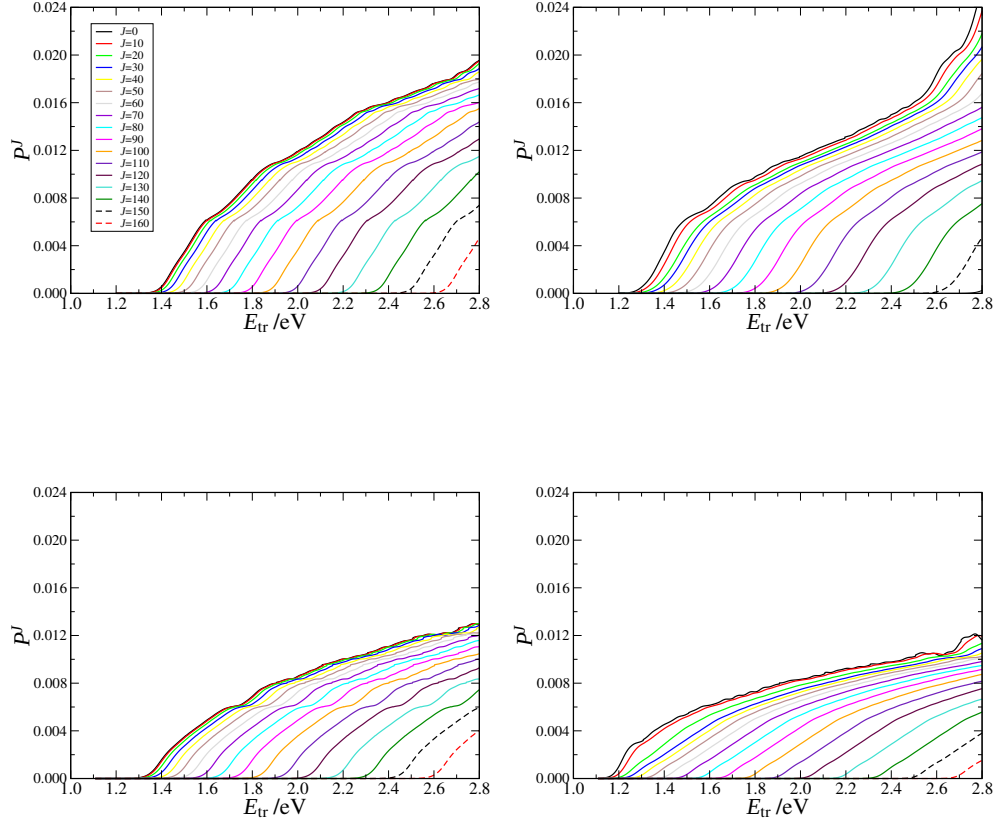


Figure 3.11: J -shift partial state-specific probabilities, $P_{vj}^J(E_{tr})$, calculated on the LEPS (left panels) and L3 (right panels) PESs at $v=0, j=14$ (upper panels) and $v=0, j=24$ (lower panels) plotted as a function of the collision energy E_{tr} .

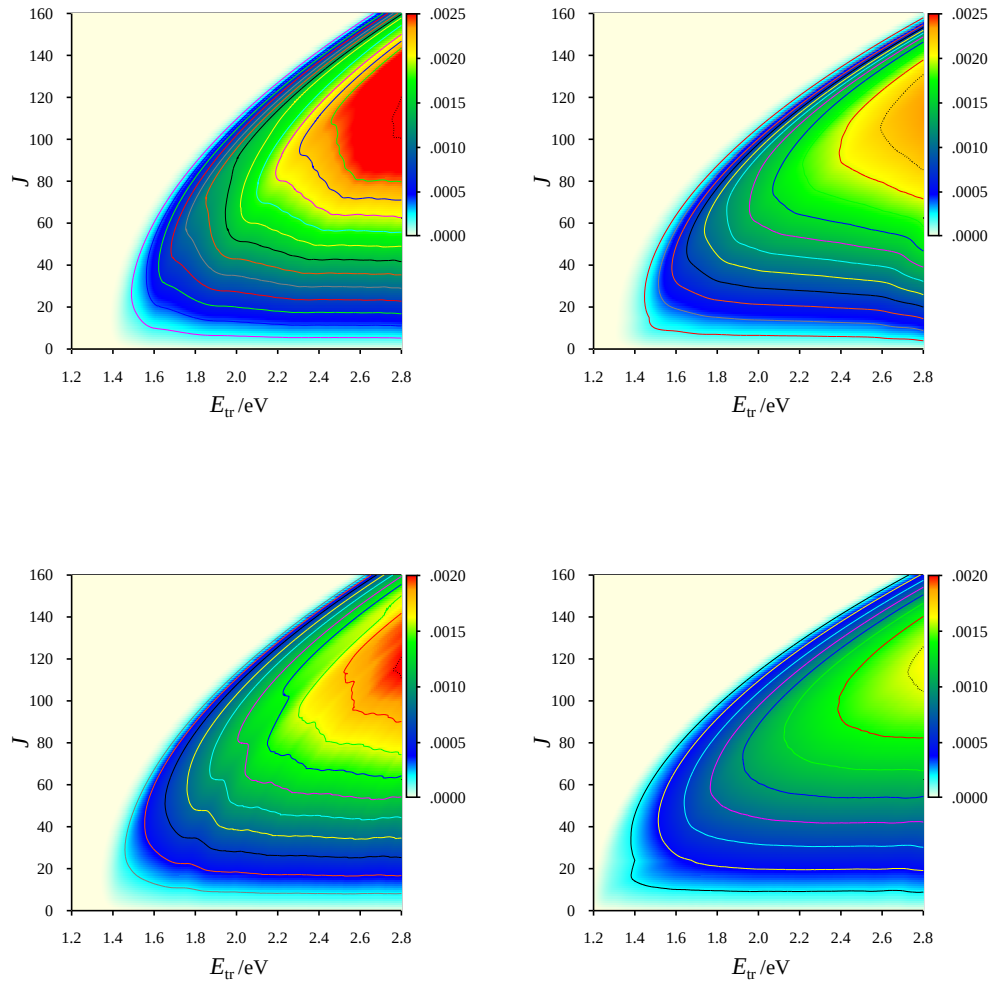


Figure 3.12: J -shift partial cross section terms, $\sigma_{vj}^J(E_{tr})$, in a_0^2 , calculated on the LEPS (left panels) and L3 (right panels) PESs at $v=0, j=14$ (upper panels) and $v=0, j=24$ (lower panels) plotted as a function of the collision energy E_{tr} and of the total angular momentum J . Contours are plotted in steps of $0.0002 a_0^2$. Note the different scale for the top panels.

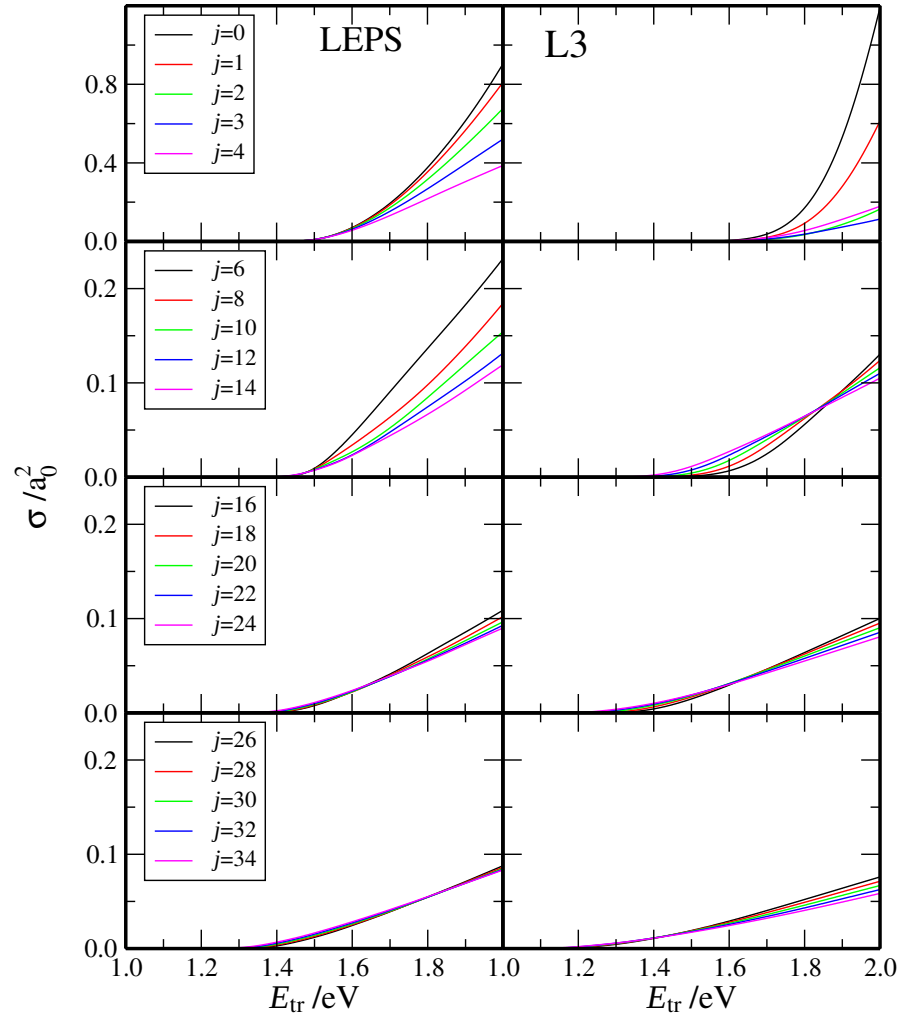


Figure 3.13: J -shift state-specific cross sections, $\sigma_{vj}(E_{\text{tr}})$, calculated on the LEPS (left panels) and L3 (right panels) PESs at $v=0$ and $j=0-4$ (upper panels), $j=6-14$ (central upper panels), $j=16-24$ (central lower panels) and $j=26-34$ (lower panels), plotted as a function of the collision energy E_{tr} . Note the different scale for the top panel.

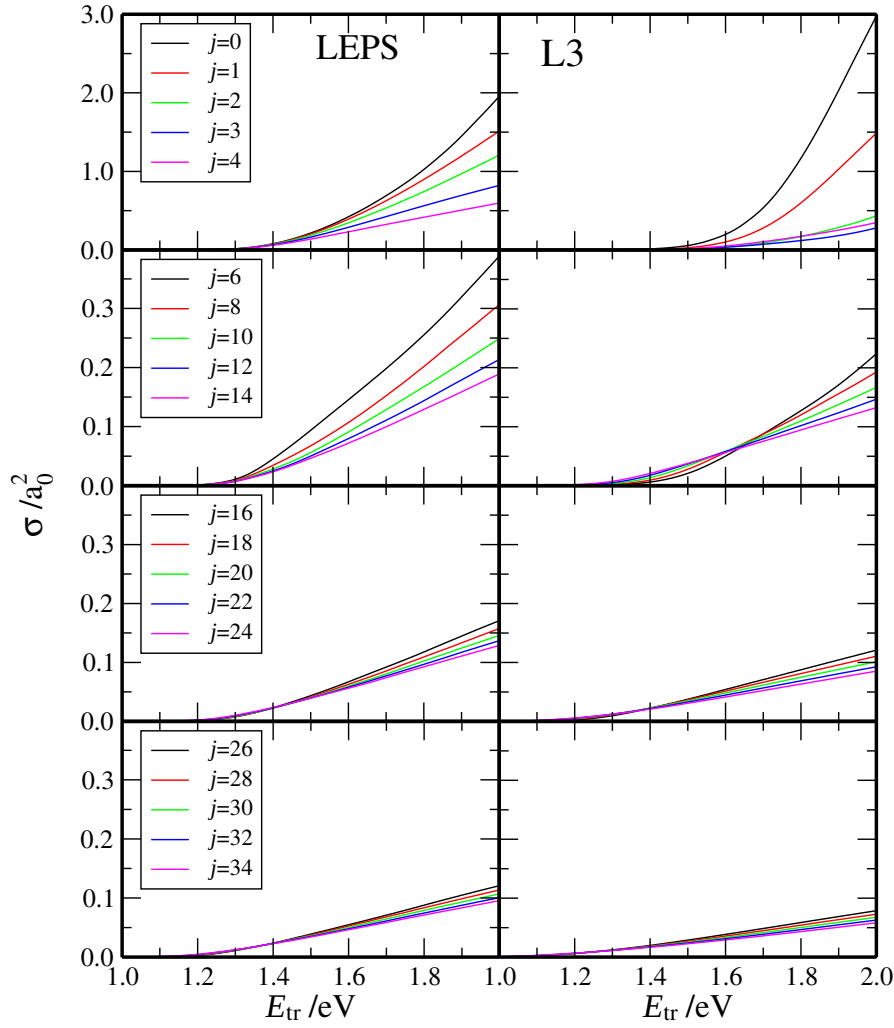


Figure 3.14: J-shift state-specific cross sections, $\sigma_{vj}(E_{tr})$, calculated on the LEPS (left panels) and L3 (right panels) PESs at $v=1$ and $j=0-4$ (upper panels), $j=6-14$ (central upper panels), $j=16-24$ (central lower panels) and $j=26-34$ (lower panels), plotted as a function of the collision energy E_{tr} . Note the different scale for the top panel.

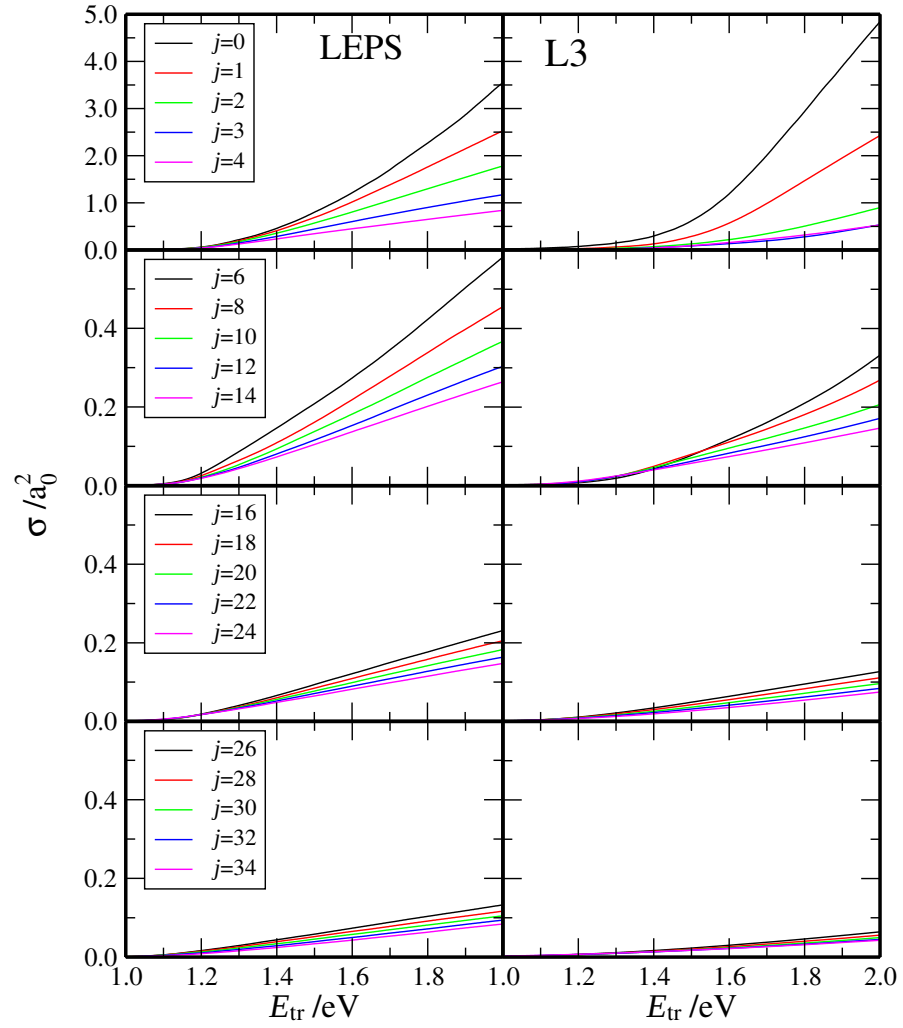


Figure 3.15: J -shift state-specific cross sections, $\sigma_{vj}(E_{\text{tr}})$, calculated on the LEPS (left panels) and L3 (right panels) PESs at $v=2$ and $j=0-4$ (upper panels), $j=6-14$ (central upper panels), $j=16-24$ (central lower panels) and $j=26-34$ (lower panels), plotted as a function of the collision energy E_{tr} . Note the different scale for the top panel.

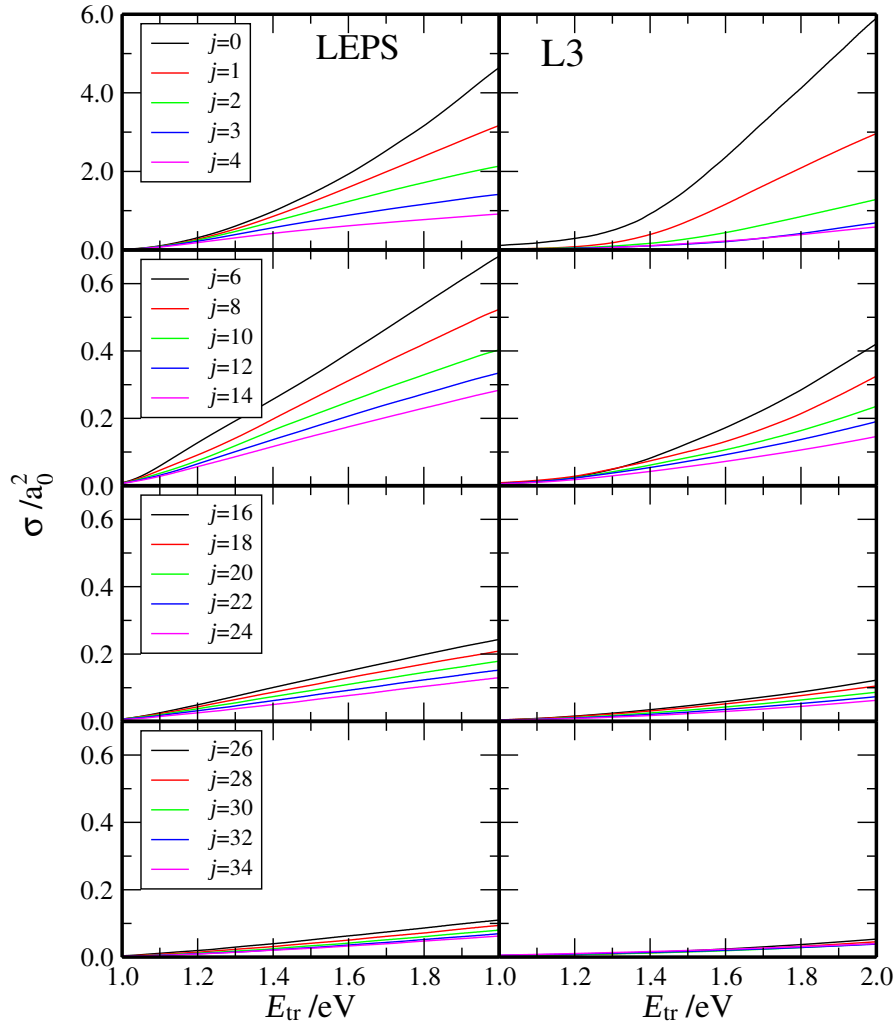


Figure 3.16: J -shift state-specific cross sections, $\sigma_{vj}(E_{tr})$, calculated on the LEPS (left panels) and L3 (right panels) PESs at $v=3$ and $j=0-4$ (upper panels), $j=6-14$ (central upper panels), $j=16-24$ (central lower panels) and $j=26-34$ (lower panels), plotted as a function of the collision energy E_{tr} . Note the different scale for the top panel.

here the largest cross section corresponds to the ground rotational state of the reactants. As the rotational quantum number j increases the cross section decreases. Such a decrease is large for low values of j and tends to vanish at high j values. This is particularly true at $v=0$ for which the cross section becomes independent of the initial rotational state. The effect of the vibrational excitation is more important. In fact, as the vibrational quantum number v increases the cross section significantly increases. As to the comparison between the LEPS and the L3 cross sections, except for the ground initial rotational state at all vibrational states, the former are clearly larger than the latter. However, this difference diminishes at high rotational states.

J-shift thermal rate coefficients, $k(T)$, are calculated from the *J*-shift cross sections by averaging over both the collision energy and the initial rovibrational energies (taking into account the different degeneration for even and odd rotational states). The usual $\log k(T)$ versus $1/T$ plot for the *J*-shift values of the rate coefficient calculated on the LEPS and L3 PESs are compared with the experimental results of refs. [18–20] in Figure 3.17. The first feature of these results that deserves to be emphasized here is the fact that the thermal rate coefficient values calculated on both L3 (using the *J*-shift model of eq. 2.61) and LEPS (using the *J*-shift model of eq. 2.59) PESs fall slightly short of the measured data at both $T=3400$ K and $T=1273$ K while sufficiently well reproducing the trend with the inverse temperature. However, at lower temperatures the LEPS rate coefficients are slightly higher than the L3 ones. This behaviour is a consequence of the fact that at low temperature the most populated initial rovibrational states are those with a relative low rotational quantum number (for instance, the most populated initial rovibrational state at $T=1273$ K is $v=0$, $j=14$) while as the temperature increases higher initial rovibrational states are gradually populated (for instance, the most populated initial rovibrational state at $T=3400$ K is $v=0$, $j=24$). At lower rovibrational states, in fact, the difference between the *J*-shift cross section calculated on the LEPS and that calculated on the L3 one is evident, as shown in Figures 3.13, 3.14, 3.15 and 3.16.

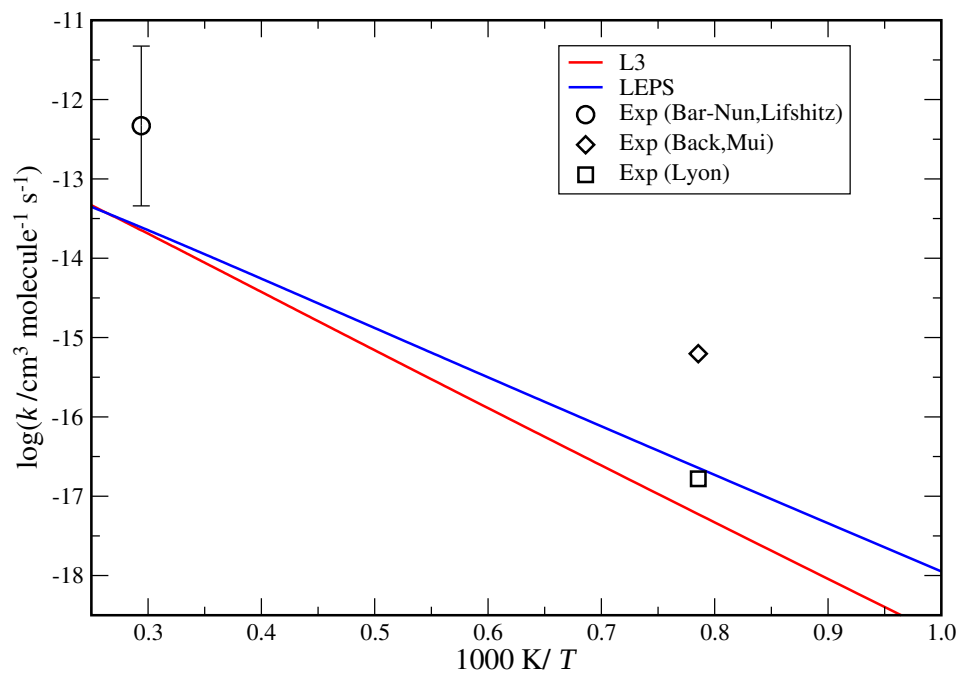


Figure 3.17: Logarithm of the J -shift thermal rate coefficient calculated on the LEPS and L3 PESs plotted as a function of the inverse temperature. Experimental data by Bar-Nun and Lifshitz (circle) [19], Back and Mui (diamond) [18] and Lyon (square) [20] are also shown for comparison. It is worth noting that experiments at $T=1273 \text{ K}$ only give upper limits for the rate coefficient.

In ref. [35], the dependence on the temperature of the *J*-shift rate coefficients calculated on the LEPS surface from time-dependent $J=0$ quantum probabilities is reported. The values of the rate coefficients there obtained are smaller than the experimental ones though falling within the experimental error bars. It is difficult to rationalize the discrepancy with the results obtained in this work because no details about the *J*-shift procedure used in ref. [35] are available.

A more quantitative comparison of the calculated thermal rate coefficient values at the temperatures of the experiment is given in Table 3.2 in which also results obtained from other approaches are shown. An apparent feature of the results given in the Table is that the thermal rate coefficient values calculated on L3 using the *J*-shift model of eq. 2.61 are always appreciably smaller than the QCT and RIOS ones (see ref. [32] for additional data). The *J*-shift values calculated on L3 are also always smaller than those calculated on the LEPS as are those calculated on the WSHDSP PES. These two sets of quantum results, however, show a clear different slope with temperature. Thermal rate coefficient values calculated on L3, in fact, are smaller than those calculated on the WSHDSP PES at $T=3400$ K while they are larger at $T=1273$ K. According to our analysis of the dependence of the reactive probability on the various internal energy modes, this may be due to the fact that at low temperature the system has an easier access to the (lower) saddle to reaction of L3 than that (higher) of the WSHDSP one. On the contrary, at 3400 K (when thanks to the larger temperature the saddle can be more easily accessed on both surfaces) the fact that the WSHDSP PES has a barrier displaced in the entrance channel (as typical of collinearly dominant reactions like the LEPS and the L0 PESs) leads to a more efficient exploitation of the collision energy to gain reactivity. These findings clearly indicate that L3 has to be improved by enforcing the reproduction of the intermediate structure shown by ab initio calculations of ref. [35]. This is not only because the reproduction of the ab initio data is always appropriate but also because it should improve the agreement with measured thermal rate coefficients. However, the above

discussed results suggest also that it might be wise, before carrying out a new fit of the ab initio data, to carry out new specifically targeted higher level ab initio calculations to obtain a more accurate evaluation of the depth and the width of the intermediate well.

Table 3.2: Logarithm of the N+N₂ rate coefficients (in cm³ molecule⁻¹ s⁻¹).

	<i>T</i> =3400 K	<i>T</i> =1273 K
Experiment from ref. [19]	-12.3 ± 1.0	
Experiment from ref. [18]		< -15.2
Experiment from ref. [20]		< -16.9
QCT on LEPS from ref. [144]	-12.2	-16.2*
QCT on L3 from ref. [32]	-11.8	—
RIOSAs on LEPS from ref. [32]	-12.3	—
RIOSAs on L3 from ref. [32]	-12.0	—
Quantum (<i>J</i> -shift) on LEPS from ref. [35]	-12.7	-15.9
Quantum (<i>J</i> -shift) on WSHDSP from ref. [35]	-13.0	-18.5
Quantum (<i>J</i> -shift using eq. 2.61) on L3	-13.6	-17.2
Quantum (<i>J</i> -shift using eq. 2.59) on LEPS	-13.6	-16.6

*extrapolated value

3.3 CS cross sections

In spite of its popularity (due mainly to its ability to lead to significant computer time savings) the J -shift model is a rather crude approximation. A more rigorous approach is the Centrifugal Sudden (CS) one. The CS method is based on the actual propagation of the wavepacket (i.e., the integration of the time-dependent Schrödinger equation) for all the necessary J , v and j quantum numbers. The approximation consists in keeping Ω decoupled during the calculation. The number of initial rovibrational states to be included to compute the rate coefficient at relatively high temperatures is of several hundreds (for instance, 242 at $T=3400$ K). The number of J values contributing to reaction though depending on the dynamical properties of the reactive system does, in general, increase with the mass of the system and for the N + N₂ reaction that has no hydrogen atoms can reach the value of one hundred. For each J value, all the possible projections Ω (with the constrain $\Omega_{\max} = \min(J, j)$) of the total angular momentum have to be considered. At the same time, for each Ω both even and odd parity p values must be considered. In conclusion, the calculation of the thermal rate coefficients at relatively high temperatures using the CS approximation has to be repeated so many times to make it still a very demanding computational task despite the fact that now each calculation has a size not larger than that of $J=0$ (24 – 30 hours of cpu time on a processor Intel Xeon 2.8 GHz). For this reason we have carried out an investigation of the accuracy of the CS approach by calculating the cross section (and its dependence on the collision energy) only on the L3 PES and only for $v=0$, $j=14$ and $v=0$, $j=24$ (the most populated states at $T=1273$ K and $T=3400$ K, the two temperatures of the experiment). The total energy values considered range from 1.4 to 2.0 eV in steps of 0.001 eV. Aim of this investigation is to single out the weak points of the J -shift method with respect to the more accurate CS one.

A first insight on the dynamics of the N + N₂ reaction afforded by the CS calcu-

lations comes indeed from the analysis of the dependence of the partial state-specific probabilities, $P_{vj}^{J\Omega p}(E_{\text{tr}})$ (hereafter the subscript vj will be dropped), on the quantum number Ω . For illustrative purpose, Figures 3.18 and 3.19 show the CS partial reactive probabilities, $P^{J\Omega p}(E_{\text{tr}})$, for all the values of Ω allowed at $v=0$, $j=14$, $J=70$, $p=0$ and at $v=0$, $j=24$, $J=70$, $p=0$, respectively. Partial J and Ω (even parity) reaction probabilities are nearly independent of Ω up to $\Omega=10$ for $j=14$ and up to $\Omega=15$ for $j=24$. Then they progressively decrease as the value of Ω increases to vanish at the highest values of Ω ($\Omega=14$ and 24 for $j=14$ and $j=24$ respectively). From this an important stereodynamics conclusion can be drawn. In fact, collisions with small values of Ω imply attacks by the atom to the molecule in which the relative velocity vector is perpendicular to the rotational angular momentum vector (the diatomic molecule rotates in a plane parallel to the velocity vector) while high values of Ω indicate that these vectors are parallel each other. Therefore, the $\text{N} + \text{N}_2$ reaction shows a clear preference for coplanar approaches with respect to perpendicular ones.

At this point it is convenient to discuss the effect of the parity on the reactive probabilities. Reactive probabilities calculated for even and odd parities are expected to be the same due to the symmetry of the system. To check numerically the effect of the parity on the value of the reactive probabilities, a few calculations for different $J\Omega$ cases were performed. The calculations confirmed the independence of the reactive probability of the $\text{N} + \text{N}_2$ system from the parity. For this reason the CS calculations have been performed only for the even parity. Therefore, to calculate the related cross sections the summation need to include a factor 2.

The next step of the investigation consisted in determining the largest total angular momentum J significantly contributing to the reaction probability. For this purpose, J was varied from 0 to 160 (as suggested by the previous J -shift calculations, see Figure 3.12), Ω and v were set equal to zero while j was chosen to be 14 and 24. The collision energy was varied from 1.2 eV to 2.0 eV, in steps of 0.001 eV. The

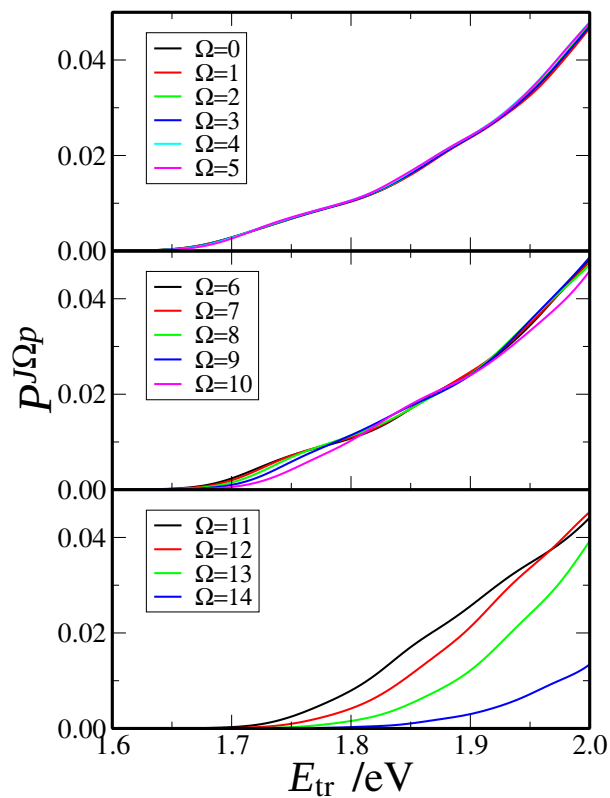


Figure 3.18: CS partial reactive probabilities, $P^{J\Omega}(E_{tr})$, calculated at $v=0$, $j=14$, $J=70$ and $p=0$ plotted as a function of the collision energy E_{tr} .

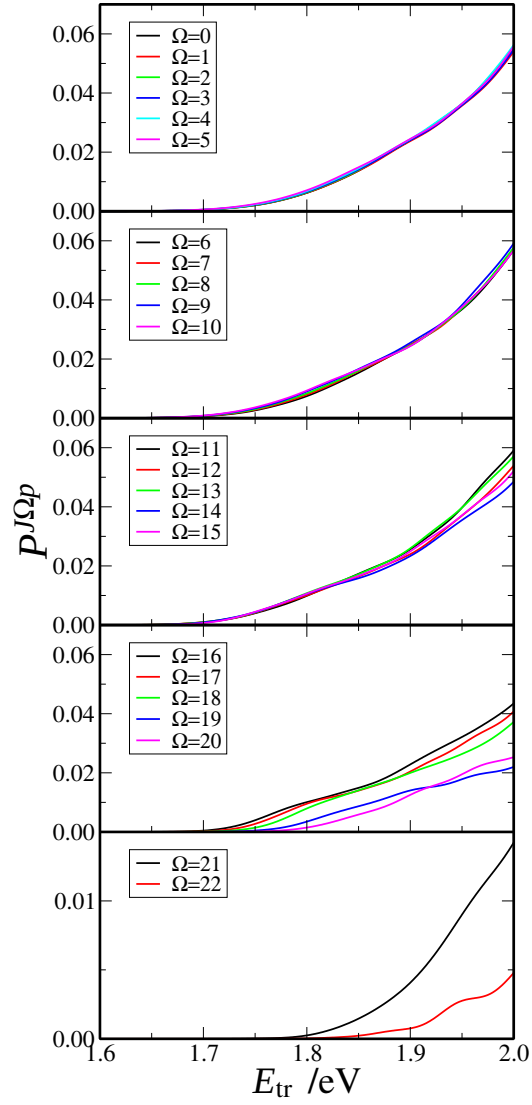


Figure 3.19: CS partial reactive probabilities, $P^{J\Omega}(E_{tr})$, calculated at $v=0$, $j=24$, $J=70$, $p=0$ plotted as a function of the collision energy E_{tr} . Note the different scale for the bottom panel.

calculated CS partial reactive probabilities, $P^{J\Omega}(E_{\text{tr}})$, vanish, at the highest collision energy considered, at $J=100$ for $v=0$, $j=14$ and at $J=90$ for $v=0$, $j=24$. These values are much smaller than those needed to reach convergence in J -shift calculations and tell us that the J -shift approach includes wrong contributions.

Once determined the maximum total angular momentum still appreciably contributing to the reactive probability, the integration of the Schrödinger equation on L3 using the CS approximation for all Ω states (and even parity) compatible with the rotational j and total J angular momenta was actually performed. In particular, values of J increasing from 0 to 100 in steps of 10 have been considered for the two initial rovibrational states and the collision energy value was varied from 1.2 eV to 2.0 eV, in steps of 0.001 eV. The integration produces the partial reactive probabilities $P^{J\Omega}(E_{\text{tr}})$. By summing each Ω (doubled for the parity) contribution the partial reactive probabilities $P^J(E_{\text{tr}})$ were calculated (see Figures 3.20 and 3.21 for $v=0$, $j=14$ and $v=0$, $j=24$, respectively, where they are plotted as a function of the total angular momentum J (upper panels) and of the collision energy (lower panels)). The Figures show a clear different dependence of the CS partial probabilities on the total angular momentum J at the lower and higher collision energies. At the lower collision energies, the probabilities decrease near linearly as J increases from $J=0$ suggesting an increasing filtering effect of J when more and more energy is allocated as overall rotation of the system. On the contrary, at higher collision energies the probabilities have their maximum at a total angular momentum value as high as 60–70. The value of the probability at the maximum is significantly larger than that for $J=0$ and it increases as the collision energy increases. On the other hand, the dependence of the partial probabilities on the collision energy varies at the lower and higher total angular momenta. Thus, at the lower values of J the probabilities show a relatively small increase with the collision energy for the energies just-past-the-threshold and then they almost reach a constant value. However, as J increases this shape significantly changes. The first feature is a clear increase of the threshold energy for the

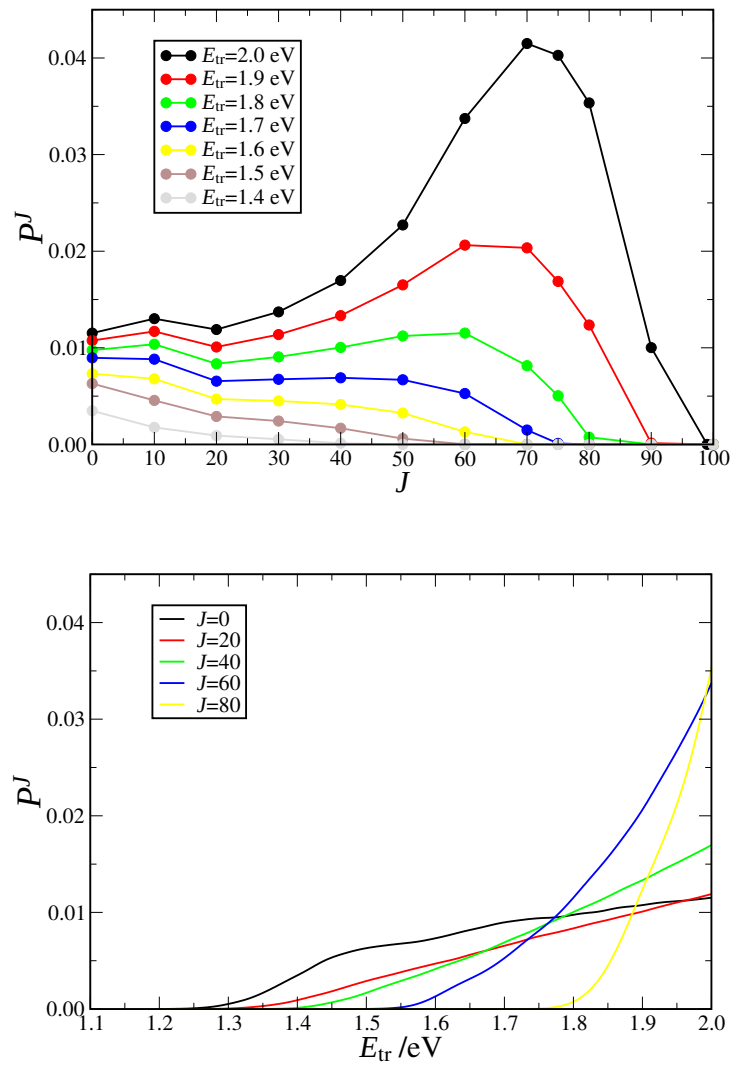


Figure 3.20: CS partial reactive probabilities $P^J(E_{tr})$ calculated at $v=0$ and $j=14$ plotted as a function of the total angular momentum J (upper panel) and of the collision energy E_{tr} (lower panel).

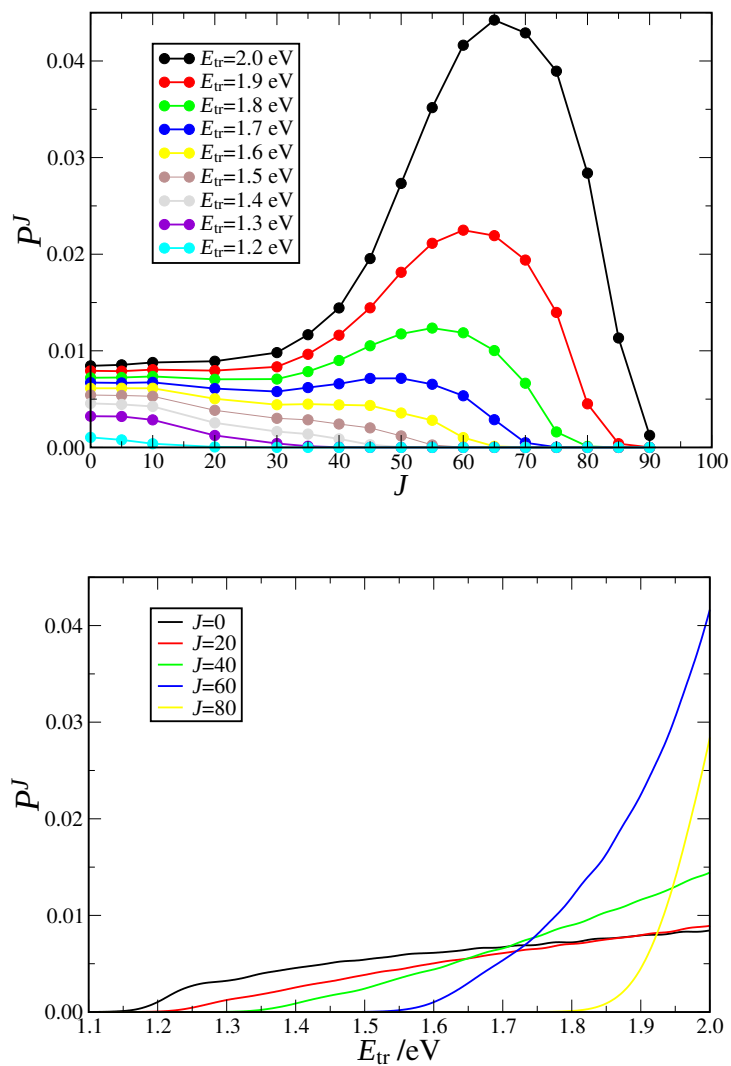


Figure 3.21: CS partial reactive probabilities $P^J(E_{tr})$ calculated at $v=0$ and $j=24$ plotted as a function of the total angular momentum J (upper panel) and of the collision energy E_{tr} (lower panel).

reaction. This feature can be explained mainly in terms of the J -shift-like mechanism that implies an increasingly larger capture of total energy fraction by the overall rotation of the system (a factor roughly proportional to $J(J+1)$) and a consequent minor availability of energy as translation. Accordingly, to obtain comparable reactive probabilities at different J values one has to move upward in the translational energy scale. Yet, there is another important change in the shape of $P^J(E_{\text{tr}})$. This is its dramatic increase at fairly large J values with the collision energy in the just-past-the-threshold region that overwhelms the decrease of the reactivity at a given E_{tr} due to the threshold shifting effect of the just mentioned J -shift-like mechanism. It suggests that, as shown in Figures 3.20 and 3.21, when the collision energy is so high to not be possibly blocked by saddle effects both the impeler of the relative velocity and the rotation of the system concertedly contribute to enhance reactivity. Only when a further increase of the velocity reduces the interaction time between the collision partners $P^J(E_{\text{tr}})$ decreases again as a function of E_{tr} .

From the CS partial probabilities the CS partial cross section terms $\sigma^J(E_{\text{tr}})$ were obtained multiplying them by the factor $\pi(2J+1)/k_{vj}^2$ (see eq. 2.56). In Figure 3.22 these values are plotted as a function of the collision energy E_{tr} and of the total angular momentum J for the two initial rovibrational states considered. The two plots are very similar though characterized by different threshold energies (smaller values for the $v=0, j=24$ state) and J location of the maximum (higher for the $v=0, j=14$ state). As previously discussed for the analogous case of the J -shift partial cross section term (plotted in Figure 3.12), the transformation from partial reactive probabilities to partial cross section term by multiplying by the factor $(2J+1)$ leads to an amplification of the higher J contributions. This feature, together with the fact that the CS partial probabilities have their maxima at high values of J , implies that the partial cross section terms have a large maximum around $J=70$ – 80 at the highest collision energy.

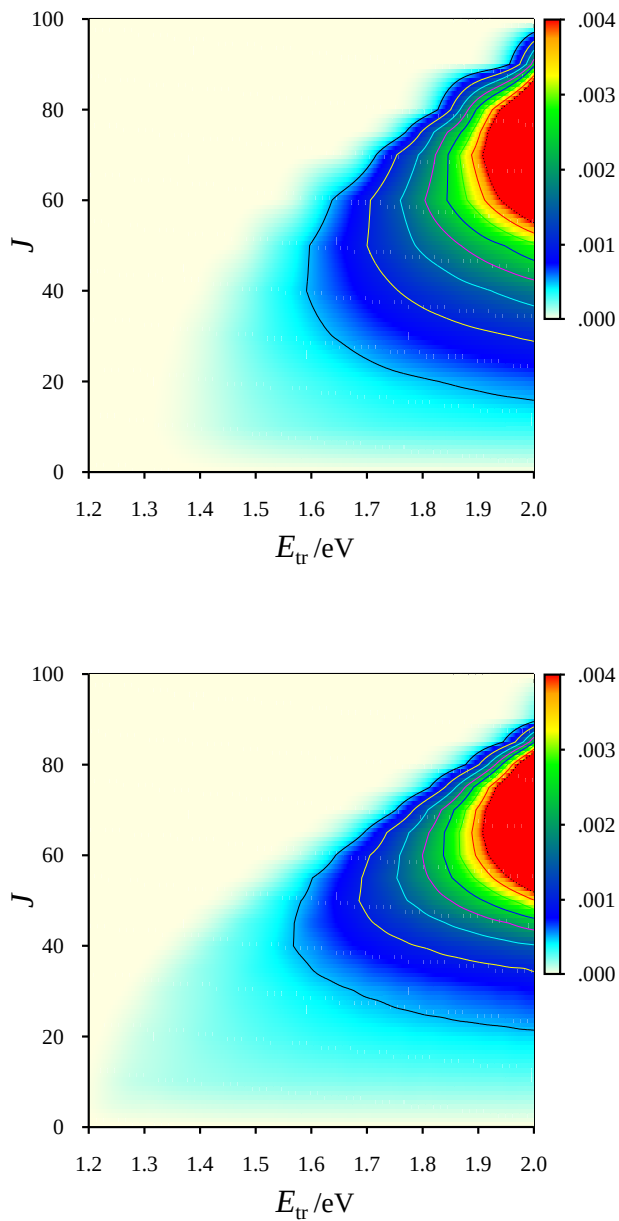


Figure 3.22: CS partial cross section terms, $\sigma^J(E_{tr})$, in a_0^2 , calculated at $v=0, j=14$ (upper panel) and $v=0, j=24$ (lower panel) plotted as a function of the collision energy E_{tr} and of the total angular momentum J . Contours are plotted in steps of $0.0004 a_0^2$.

CS state-specific cross sections, $\sigma(E_{\text{tr}})$, are calculated by simply summing the CS partial state-specific cross section terms, $\sigma^J(E_{\text{tr}})$. The reactive cross section calculated on the L3 surface at $v=0, j=14$ and $v=0, j=24$ are plotted in Figure 3.23. The dependence of the cross sections on the collision energy is very similar for the two rovibrational states. Again, however, the threshold energy for the $v=0, j=24$ state is smaller than that for the $v=0, j=14$ state. This fact can be understood in terms of the larger internal energy associated with $j=24$ and the efficient use of this internal degree of freedom by the L3 surface to promote reaction (this feature has been largely discussed in Section 3.1). The second difference is the larger cross sections calculated at the higher collision energies for the $v=0, j=14$ state that is a consequence of the fact that for this state the maximum value of the partial probabilities corresponds to higher values of J and the number of partial J contributions is larger.

A comparison of the partial cross section terms, $\sigma^J(E_{\text{tr}})$, obtained from both approaches is made in Figures 3.24 (for the $v=0, j=14$ state) and 3.25 (for the $v=0, j=24$ state) at several values of the total angular momentum. As apparent from the figures, when the values of J are lower than 20–30 the J -shift and the CS partial cross section terms agree fairly well. However, for $J > 20 - 30$ appreciable differences show up in the partial cross section terms especially when J increases. In fact, for the higher values of J , the J -shift terms show a dependence on the collision energy similar to that obtained for the lower values of J (as built-in into the J -shift idea) while the dependence of the CS terms is different in two respects. First, there is a more pronounced shift of the threshold energy for the CS cross section terms than for the J -shifted ones. Second, there is a more pronounced increase of the CS cross section terms at the just-pass-the-threshold collision energies than for the J -shift ones.

The comparison between the resulting CS and J -shift cross sections, $\sigma(E_{\text{tr}})$, is shown in Figure 3.26, where those calculated at $v=0, j=14$ and $v=0, j=24$ are plotted together. The main discrepancy occurs at the higher collision energies for

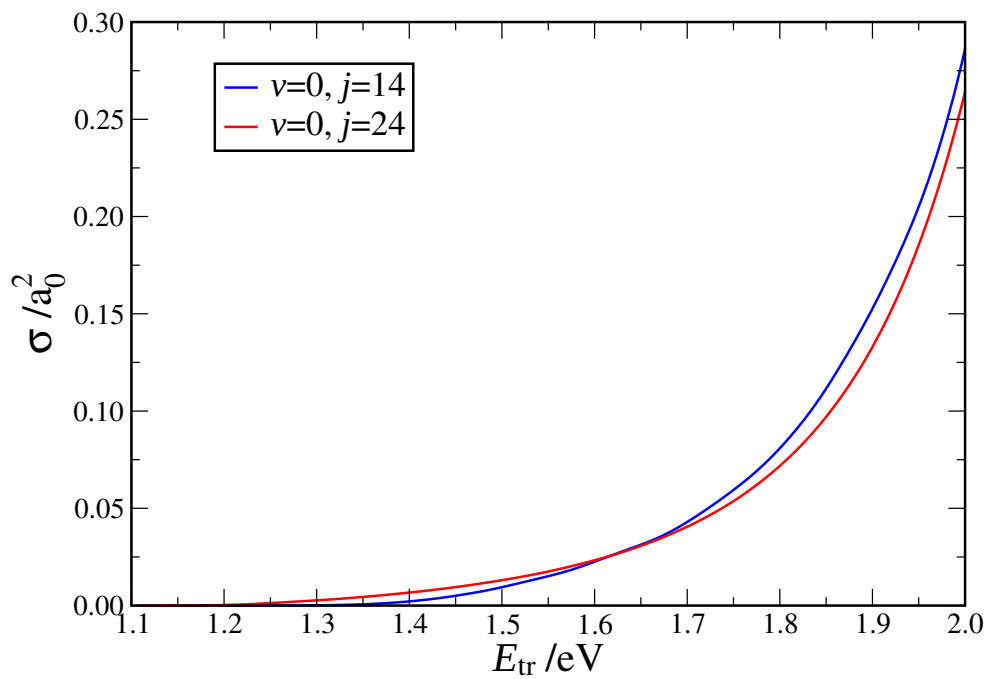


Figure 3.23: CS cross sections, $\sigma(E_{tr})$, calculated at $v=0, j=14$ and $v=0, j=24$ plotted as a function of the collision energy E_{tr} .

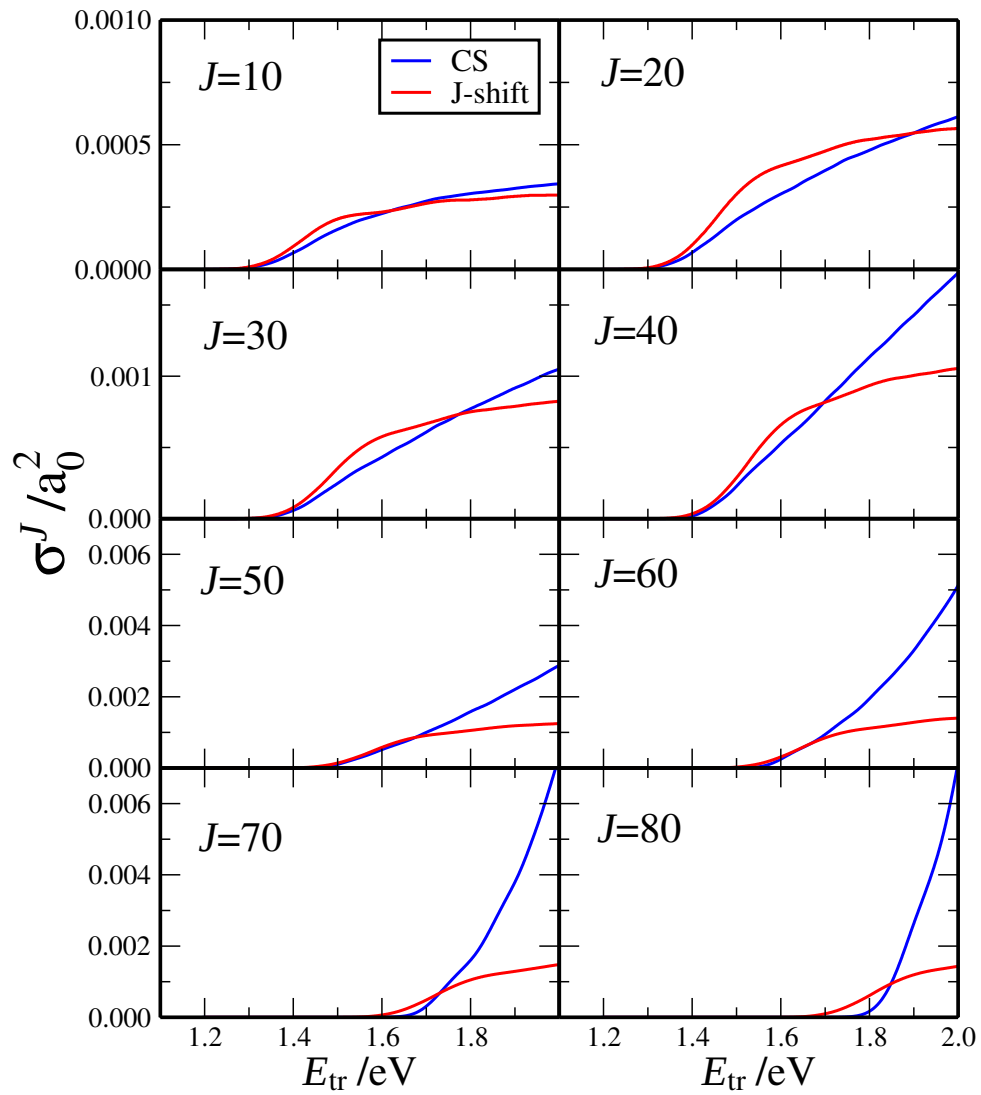


Figure 3.24: CS and J -shift partial cross section terms, $\sigma^J(E_{tr})$ calculated at $v=0$, $j=14$ plotted as a function of the collision energy E_{tr} . Note the use of different scales in the various panels.

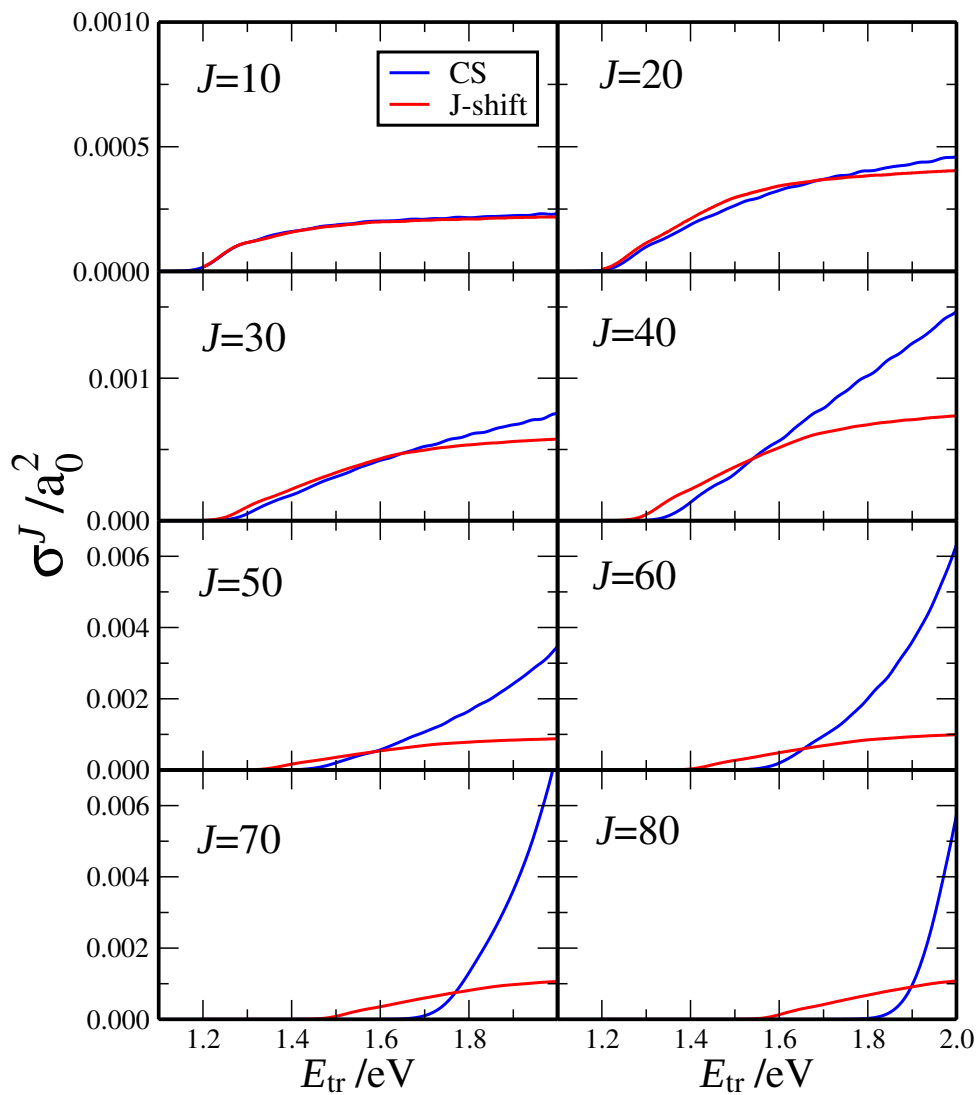


Figure 3.25: CS and J -shift partial cross section terms, $\sigma^J(E_{tr})$ calculated at $v=0, j=24$ plotted as a function of the collision energy E_{tr} . Note the use of different scales in the various panels.

which the CS cross section is twice the J -shift ones. On the contrary, at the lower collision energies the J -shift cross sections are larger than the CS ones because the related threshold energies are almost coincident. This feature can be explained as a consequence are lower and probabilities are higher. Moreover, the differences are further enhanced by the already mentioned different number of partial cross section components contributing to the J -shift and the CS value (roughly, 200 versus 100).

As mentioned at the beginning of this Section, we cannot draw any definite conclusion on the effect of carrying out the calculation of thermal rate coefficients using the CS approximation since our comparison is quite limited. However, by extrapolating the results of the considered cases ($j=14$ and $j=24$ which are the two most populated rovibrational states at the temperatures of the experiment) it is reasonable to expect that the CS estimates of the thermal rate coefficients are significantly higher than those obtained using the J -shift approximation and this is expected to improve the agreement between theory and experiment.

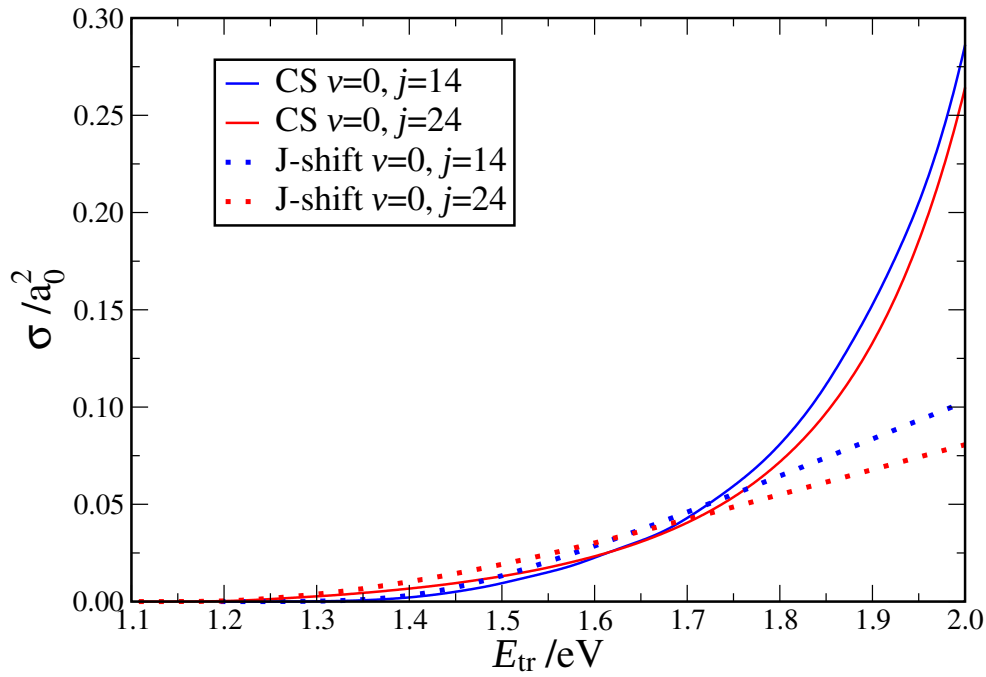


Figure 3.26: CS and J -shift cross sections, $\sigma(E_{tr})$, calculated at $v=0, j=14$ and $v=0, j=24$ plotted as a function of the collision energy E_{tr} .

3.4 Ω coupling

As already discussed in Chapter 2, in the CS approximation the coupling between the states with different Ω values is neglected and the calculation of the reactive probabilities for each single Ω state is carried out independently. In order to estimate the contribution of the Ω coupling, we have performed a limited number of calculations including the coupling between the Ω states. As a case study, the initial rovibrational state with $v=0$ and $j=24$ has been considered because it is the most populated rovibrational state at $T=3400$ K. The range of total energy values considered coincides with the one used in the CS calculations (from 1.4 to 2.0 eV in steps of 0.001 eV). Calculations have been performed on only the L3 PES.

Two types of calculations to evaluate the Ω coupling have been carried out (details are shown in the Tables 3.3 and 3.4).

Aim of the first type of calculations is to evaluate the coupling between an Ω state and the $\Omega \pm 1$ states (hereafter called $\Omega \pm 1$ coupling) and $\Omega \pm 2$ states (called $\Omega \pm 2$ coupling). This implies taking into account the coupling between three and five Ω states respectively. In Table 3.3 the total angular momentum $J=60$ (for which the CS reactive probability is very high as one can see in Figure 3.19) is considered. It is worth noting that the number of open rovibrational channels for the products depends on the Ω state in two ways. Thus the "number of surfaces" (denoted in the Table by "ns"), one for each Ω state involved, is different. On the other hand, each Ω "surface" has a different initial energy due to the different contribution to the energy of the related centrifugal term.

The second type of calculations are devoted to evaluate all Ω couplings, or in other words, to perform an "exact" calculation. As shown by the Table 3.4, only the case of total angular momentum $J=5$ has been considered. Out of the six allowed

Table 3.3: Details of the calculations for the coupling between the Ω states.

$\Omega \pm 1$ coupling						
J	Ω	p	ns	channels	memory	cpu time*
60	4	0	3	1524	1.9 GB	14.5
60	8	0	3	1428	1.8 GB	16.3
60	12	0	3	1332	1.7 GB	13.4
60	16	0	3	1236	1.5 GB	13.3
60	20	0	3	1140	1.4 GB	12.8
$\Omega \pm 2$ coupling						
J	Ω	p	ns	channels	memory	cpu time*
60	4	0	5	2540	3.7 GB	38.5
60	8	0	5	2380	3.4 GB	32.7
60	12	0	5	2220	3.1 GB	39.9
60	16	0	5	2060	2.8 GB	41.3
60	20	0	5	1900	2.5 GB	39.1

* in days on a OpteronD 2.4 GHz processor

Table 3.4: Details of the calculations for the "exact" probabilities at $J=5$.

J	Ω	p	ns	channels	memory	cpu time*
5	0	0	6	3120	4.7 GB	52.8
5	1	0	6	3120	4.7 GB	51.7
5	2	0	6	3120	4.7 GB	55.4
5	3	0	6	3120	4.7 GB	58.6
5	4	0	6	3120	4.7 GB	53.4
5	5	0	6	3120	4.7 GB	48.4
5	1	1	5	2580	3.7 GB	38.9
5	2	1	5	2580	3.7 GB	37.1
5	3	1	5	2580	3.7 GB	40.6
5	4	1	5	2580	3.7 GB	40.2
5	5	1	5	2580	3.7 GB	39.3

* in days on a OpteronD 2.4 GHz processor

projections $\Omega=0,1,2,3,4,5$, six ($\Omega=0-5$) are considered for the even parity and five ($\Omega=1-5$) for the odd parity. As a consequence, 3120 rovibrational channels are open for the even parity and 2580 for the odd parity.

As shown by the Tables 3.3 and 3.4, the calculations carried out have been computationally very expensive and memory needed sums up to 4.7 GB. As a consequence, these calculations had to be performed on a 64 bits machine in order to be able to address more than 2 GB. Also the cpu time needed (please notice that the cpu time is quoted in days) is very high. As a matter of fact, the calculations for the $\Omega \pm 1$ coupling took about two weeks, the calculations for the $\Omega \pm 2$ coupling and the "exact" calculations for $p=1$ more than one month, while the "exact" calculations for $p=0$ almost two months. Both memory and cpu time requests represent a true obstacle to "exact" single J calculations. In fact, the machines must work without interruptions during a long period of time. For instance, several runs were cancelled due to shut-downs of the machines both programmed and incidental (power cut, problems with air conditioners, disk crashes, ...).

In the followings, we first investigate the $\Omega \pm 1$ and $\Omega \pm 2$ coupling results. In particular, both the dependence of the reactive probability on Ω and the effect of increasing the number of states involved in the coupling have been analysed.

Figure 3.27 shows the state-specific partial probabilities, $P^{J\Omega p}(E_{tr})$, calculated considering the $\Omega \pm 1$ and $\Omega \pm 2$ couplings. As apparent from the Figure, for the $\Omega \pm 1$ coupling the reactive probability does not differ at $\Omega=4,8,12$. However, at $\Omega=16$ and (mainly) at high collision energies, there is a clear decrease of the reactive probability. This effect is much more evident at $\Omega=20$. In fact, the probability decreases by a factor of two or more at high collision energy and also the threshold energy shifts up significantly. As to the $\Omega \pm 2$ coupling calculations, the dependence of the reactive probabilities on Ω differs slightly from the $\Omega \pm 1$ one. The main difference is the

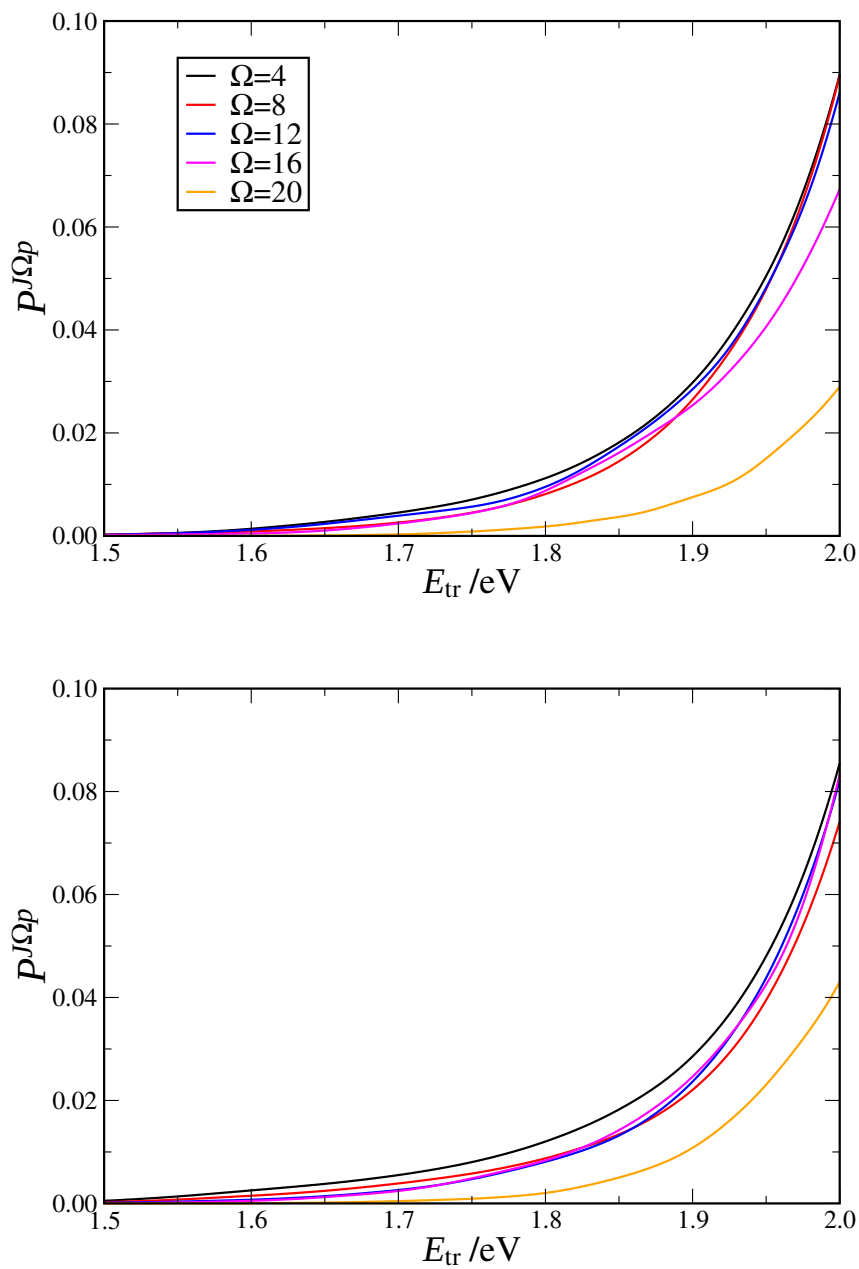


Figure 3.27: State-specific partial probabilities, $P^{J\Omega p}(E_{tr})$, calculated at $v=0$, $j=24$, $J=60$, $p=0$ by considering the $\Omega \pm 1$ (upper panel) and the $\Omega \pm 2$ (lower panel) couplings, plotted as a function of the collision energy E_{tr} .

agreement of the probabilities calculated at $\Omega=16$ with those calculated at $\Omega=4,8,12$ with respect to the $\Omega \pm 1$ disagreement. At the same time, the decrease at $\Omega=20$ for $\Omega \pm 2$ is smaller than that for $\Omega \pm 1$.

The effect of raising the level of coupling of the calculation on the reactive probability is shown in Figure 3.28, where the state-specific partial probabilities calculated considering the CS approximation (no coupling) and the $\Omega \pm 1$ and $\Omega \pm 2$ couplings are plotted. As apparent from the Figure, small differences exist at $\Omega=4,8,12,16$ between the reactive probabilities calculated considering the $\Omega \pm 1$ and $\Omega \pm 2$ couplings. On the contrary, at $\Omega=20$ the reactive probabilities calculated considering the coupling among five Ω states are clearly higher than those calculated considering the coupling among three Ω states. It seems therefore that the coupling is more effective at high values of Ω . This means that the coupling is more effective on the reactive probability when the relative atom-diatom velocity vector is parallel to the axis of rotation of the diatomic molecule.

On the other hand, both $\Omega \pm 1$ and $\Omega \pm 2$ reactive probabilities exhibit significant differences with respect to the CS reactive probabilities. In fact, the CS values overestimate at low collision energy and underestimate at high collision energy the values calculated considering the $\Omega \pm 1$ and $\Omega \pm 2$ couplings. Moreover, the underestimation at high collision energy increases as Ω increases. This fact confirms that the coupling plays an important role at high values of Ω .

Further work has been devoted to the analysis of the "exact" reactive probabilities, with "exact" meaning that the coupling among all allowed Ω states is taken into account. As previously mentioned, the limitation of computational resources has determined considering the total angular momentum $J=5$, where six Ω states are allowed for the even parity and five for the odd parity. The effect of the reactive probability on both the parity and the value of Ω has been analysed. Moreover, a

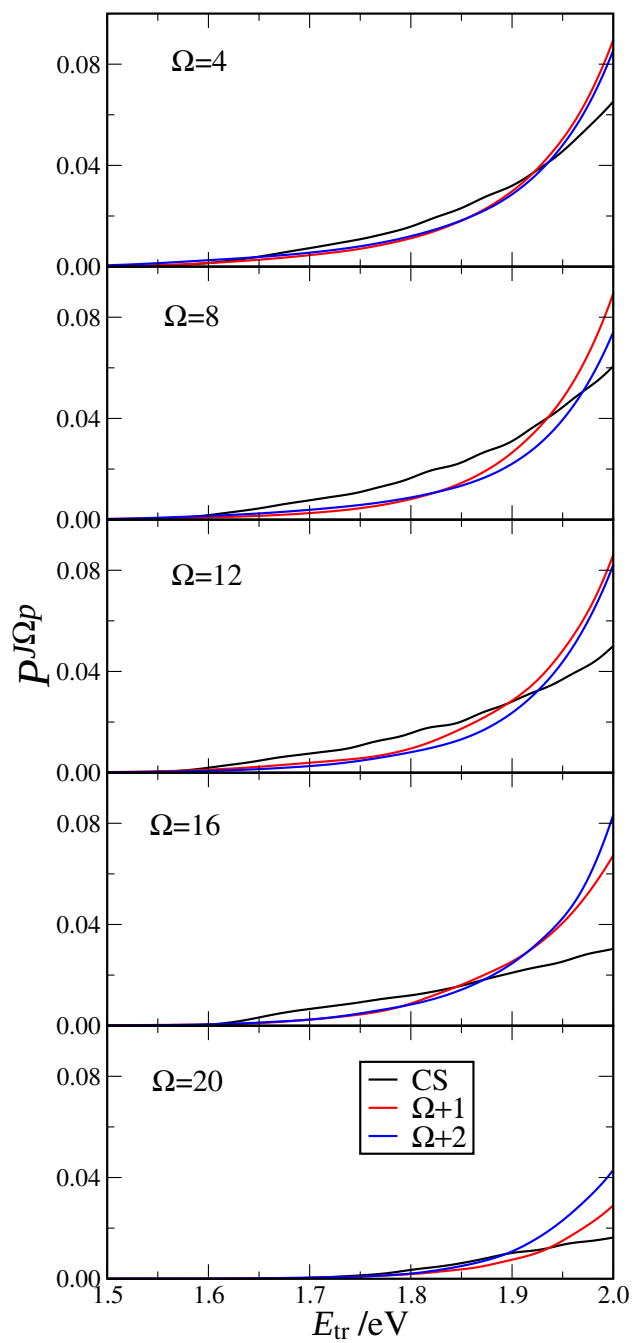


Figure 3.28: State-specific partial probabilities, $P^{J\Omega p}(E_{tr})$, calculated at $v=0$, $j=24$, $J=60$, $p=0$ with different levels of Ω coupling, plotted as a function of the collision energy E_{tr} .

comparison with the CS probabilities has also been performed.

Figure 3.29 shows the dependence of the "exact" state-specific partial probability on the parity for $\Omega=1,2,3,4,5$. As apparent from the Figure, there are differences between the probabilities calculated at even and odd parity. This feature contrasts with that found in the CS and in the $\Omega \pm 1$ and $\Omega \pm 2$ couplings where the probabilities calculated for the even and the odd parity were equal.

The dependence of the "exact" reactive probability on Ω is shown in Figure 3.30. No differences between the results obtained at the different values of Ω are observed. It is worth noting that the Ω states considered here are very small and, as illustrated previously with the partial couplings (see Figure 3.27), the probabilities calculated at the low values of Ω coincide. This feature confirms that the coupling seems to be less effective when the relative atom-diatom velocity vector is perpendicular to the rotation axis of the diatom molecule.

A comparison of the "exact" and CS partial probabilities, $P^{J\Omega p}(E_{tr})$, (that is, full Ω coupling versus no coupling) allows to estimate the contribution to the reactive probability associated with the coupling of the Ω states and to an evaluation of the error made in CS calculations. Figure 3.31 shows such a comparison for the six Ω states (only for the even parity) associated with the total angular momentum $J=5$. As apparent from the Figure, there is a clear difference between the "exact" and the CS probabilities. In fact, the "exact" probabilities are higher than the CS ones and the difference increases as the collision energy increases. In other words, it looks like if that the coupling among the various Ω projections further enhances the exploitation of coupling collision energy to promote the reactivity of the system.

By summing the $P^{J\Omega p}(E_{tr})$ probabilities for all the allowed Ω states and for both parities, the probabilities for the J state, $P^J(E_{tr})$, are calculated. The values obtained from the "exact" and the CS calculations are compared in Figure 3.32 (in

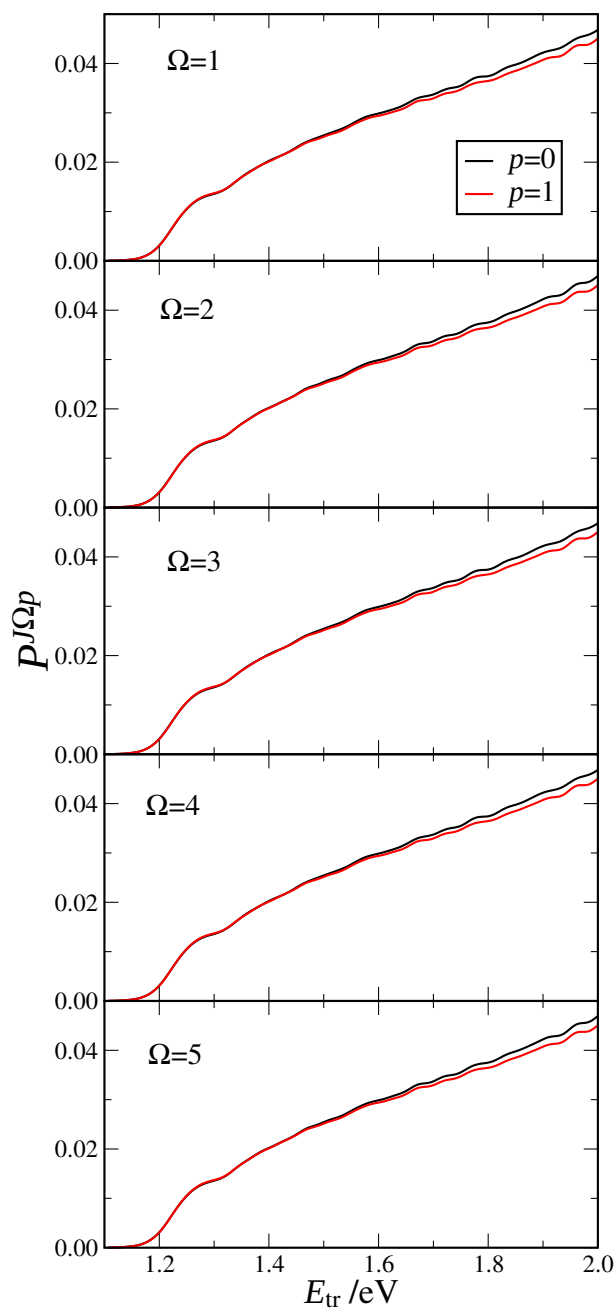


Figure 3.29: "Exact" state-specific partial probabilities, $P^{J\Omega p}(E_{tr})$, calculated at $v=0$, $j=24$, $J=5$ and either even ($p=0$) or odd ($p=1$) parity plotted as a function of the collision energy E_{tr} .

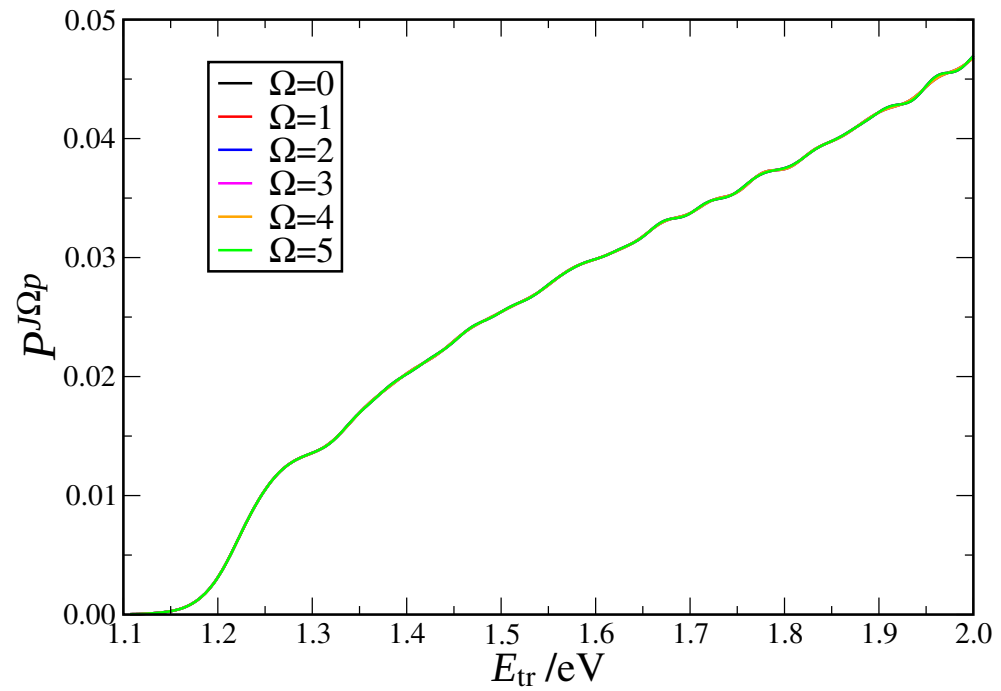


Figure 3.30: "Exact" state-specific partial probabilities, $P^{J\Omega p}(E_{tr})$, calculated at $v=0$, $j=24$, $J=5$, $p=0$ and $\Omega = 0, 1, 2, 3, 4, 5$ plotted as a function of the collision energy E_{tr} .

this Figure the factor $1/(2j + 1)$ has been applied unlike in the previous Figures). As apparent from the Figure, the "exact" probabilities are underestimated by the CS ones and the underestimation increases as the collision energy increases. Thus, at the highest collision energy considered the error sums up to about 17%.

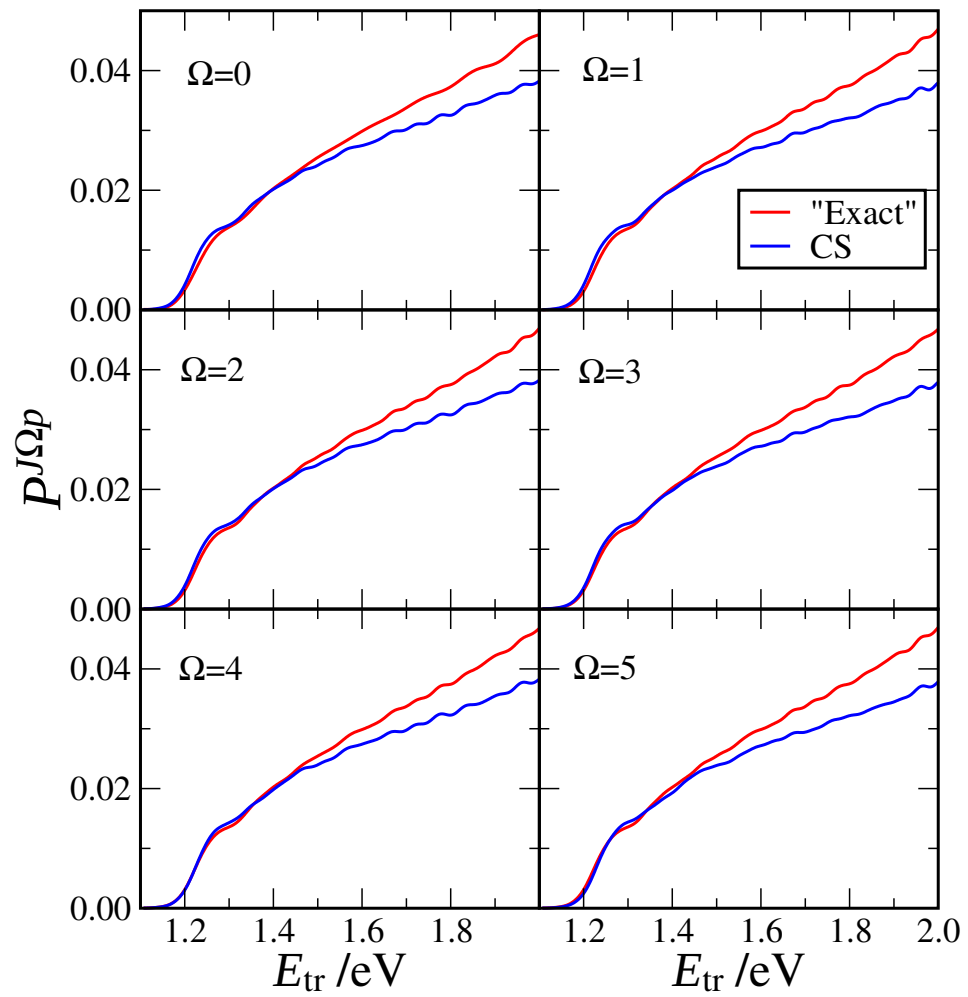


Figure 3.31: "Exact" and CS state-specific partial probabilities, $P^{J\Omega p}(E_{tr})$, calculated at $v=0$, $j=24$, $J=5$, $p=0$ plotted as a function of the collision energy E_{tr} .

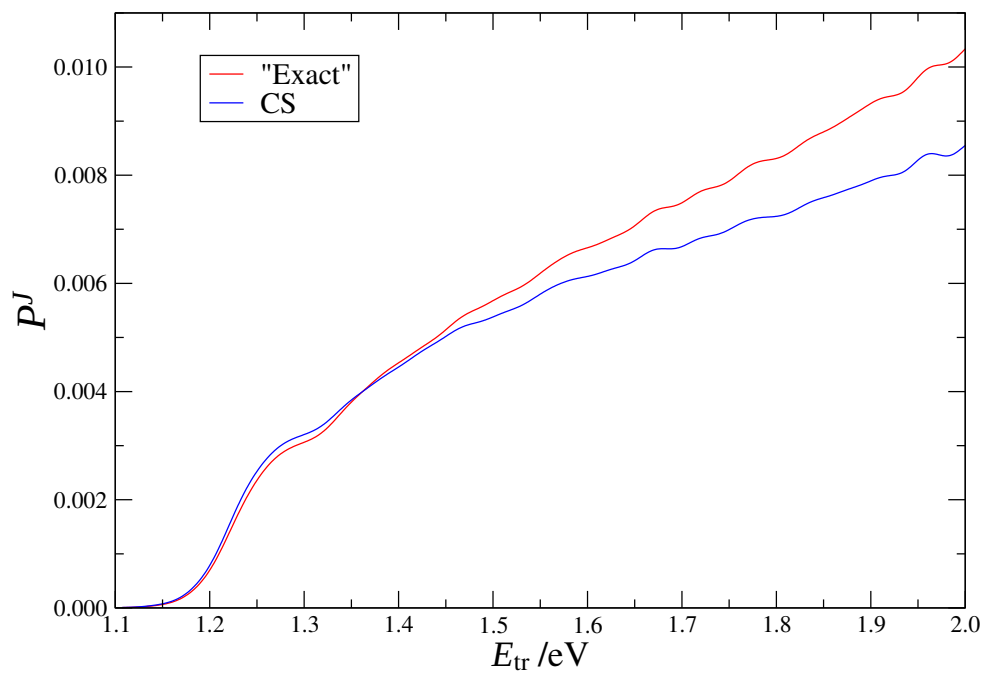


Figure 3.32: "Exact" and CS state-specific partial probabilities, $P^J(E_{tr})$, calculated at $v=0$, $j=24$, $J=5$, plotted as a function of the collision energy E_{tr} .

3.5 New LAGROBO PES

Recently accurate ab initio calculations for the $\text{N} + \text{N}_2$ exchange reaction were published [35]. By fitting the ab initio energies, an analytical global PES (WSHDSP) was obtained. This PES is formulated using a many body expansion [145]. The two body terms are formulated using extended Rydberg potentials [146]. The three body term is constructed from an expansion of the form:

$$V_3(R, r, \Theta) = \exp(-\alpha r^2 - \beta R^2) \sum_{lmn} A_{lmn} r^l R^m P_{2n}(\cos \Theta) \quad (3.1)$$

where R , r and Θ are the Jacobi coordinates and $P_{2n}(\cos \Theta)$ is a Legendre polynomial. The coefficients A_{lmn} are chosen to conform to the symmetry of the system. The values of A_{lmn} , α and β parameters are determined from the ab initio data using a nonlinear least-squares fitting. A total of 68 parameters were needed to assemble the WSHDSP PES.

The WSHDSP PES is dramatically different from the LEPS and the LAGROBO ones not only because its transition state is quite higher in energy but also because it exhibits along the minimum energy path a double barrier sandwiching a small well. Unfortunately, the WSHDSP PES is not available for distribution (neither are the ab initio data to which it was fitted). For this reason, we could not check it neither statically (by singling out all the features of the potential along and away from the minimum energy path including additional wells and barriers or the slope in the various directions) nor dynamically (by calculating the reactive probabilities using the various quantum, classical and semiclassical techniques including the reduced dimensionality ones). To investigate the effect of the key features on the reactivity we carried out afresh ab initio calculations (using the same computer code and the same level of accuracy as those of ref. [35]). Then, by exploiting the flexibility of the LAGROBO functional, a new surface was generated and its dynamical properties were calculated using a time-dependent quantum method.

3.5.1 Ab initio calculations

As in ref. [35], ab initio calculations for N + N₂ exchange reaction have been carried out using the open shell CCSD(T)/aug-cc-pVTZ method as implemented in the MOLPRO code [147]. Three sets of calculations have been performed.

The first set of calculations have been carried out to obtain a good description of the transition state. Unconstrained geometry optimization and harmonic frequency analysis have been performed to confirm the existence of a double barrier connected by a shallow well. Geometries (two bond distances, r_1 and r_2 , and the bond angle between them, Φ) and energies obtained for both the transition state and the shallow well are shown in Table 3.5. The obtained values agree with the ones obtained in ref. [35].

Aim of the second type of ab initio calculations is the description of the dependence on the bond angle Φ of both the geometry and the energy of the well placed between the double barrier structure. In the calculations the bond angle Φ has been fixed and then a geometry optimization (with $r_1=r_2$) has been carried out. The explored range of angles varied from 180° to 85°. Figures 3.33 and 3.34 show the dependence on Φ of the energy and of the location on ρ (ρ is the BO coordinate defined in eq. 2.71 as $\rho = \sqrt{n_1^2 + n_2^2}$ where $n_i = \exp[-\beta(r_i - r_{ei})]$ while the other polar BO coordinate is defined as $\alpha = \arctan(n_2/n_1)$) of the well obtained in the ab initio calculations. The minimum of the energy is located at $\Phi=118.6^\circ$. The harmonic

Table 3.5: Geometry and energy (relative to reactants) for the well and the two transition states.

	$r_1 / \text{\AA}$	$r_2 / \text{\AA}$	Φ	$\Delta E / \text{eV}$
Well	1.268	1.268	118.6°	1.93
Transition state A	1.174	1.505	116.5°	2.04
Transition state B	1.505	1.174	116.5°	2.04

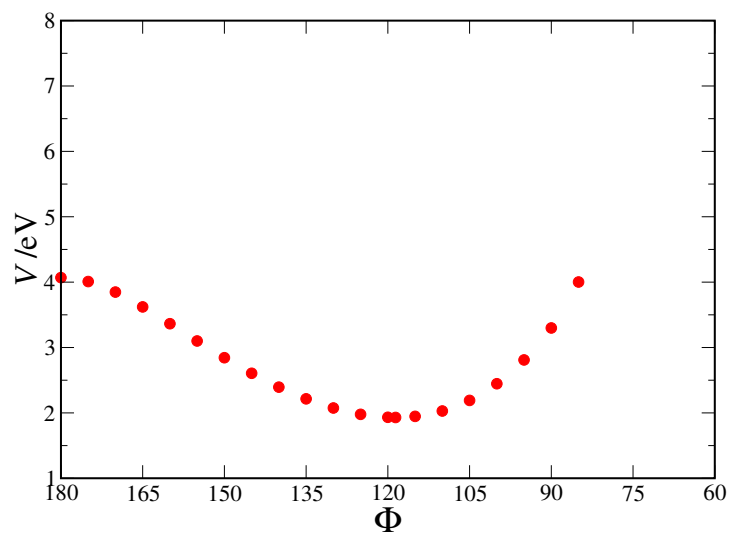


Figure 3.33: Ab initio optimized energy (relative to reactants) at the system geometry $r_1=r_2$ plotted as a function of the bond angle Φ .

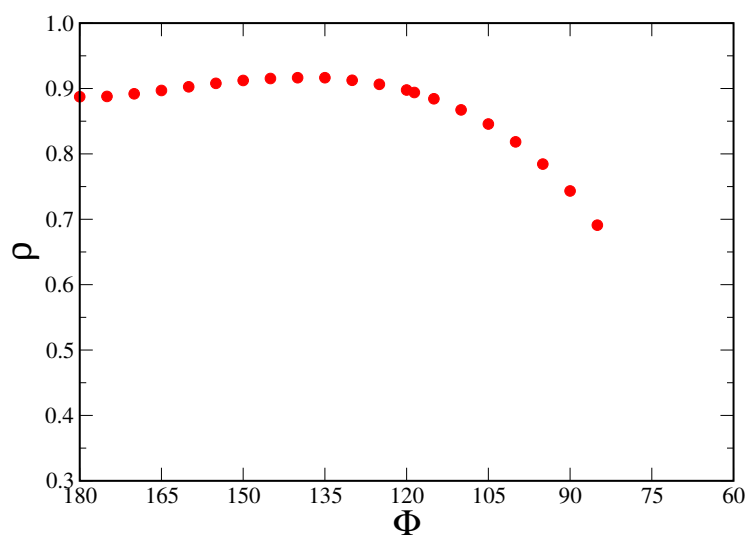


Figure 3.34: Value of ρ at the ab initio optimized system geometry $r_1=r_2$ plotted as a function of the bond angle Φ .

frequency analysis confirms that the optimized geometry is a well (a minimum) for Φ ranging from 150° to 90° . Outside this range the optimized configuration corresponds to a saddle and, therefore, there is a single barrier between reactants and products.

Aim of the third set of ab initio calculations is the characterization of the MEPs at several bond angles Φ . In the calculations, the angle Φ and one of the internuclear distances have been fixed and then an optimization of the other internuclear distance has been carried out in order to minimize the energy. Figure 3.35 shows the energy profile of the fixed Φ MEPs as a function of the BO polar angular coordinate α (defined in eq. 2.71) from the reactants ($\alpha=0^\circ$) to products ($\alpha=90^\circ$). Note that the values at $\alpha=45^\circ$, where the two BO coordinates are equal, $n_1=n_2$ (or equivalently to $r_1=r_2$), are those plotted in Figure 3.33. As shown by the Figure, the double barrier structure (and the associated well) disappear at $\Phi=180^\circ$. On the other hand, Figure 3.36 shows the location on ρ of the fixed Φ MEPs as a function of α . In this case, a double peak also appears for several angles Φ .

3.5.2 L4 potential energy surface

Using the above mentioned ab initio potential energy values and exploiting the flexibility of the LAGROBO functional, a new PES has been generated for the N + N₂ reaction. This PES will be called L4.

As shown in eq. 2.68, the LAGROBO functionals are formulated as a weighted sum of the functions describing the three possible exchange processes. The weight function privileges the contribution of the process with larger process angle. The function to describe each exchange process is a ROBO potential, formulated as:

$$V^{\text{ROBO}}(\rho, \alpha, \Phi) = a_1(\alpha, \Phi) \left[2 \frac{\rho}{a_2(\alpha, \Phi)} - \frac{\rho^2}{a_2^2(\alpha, \Phi)} \right] \quad (3.2)$$

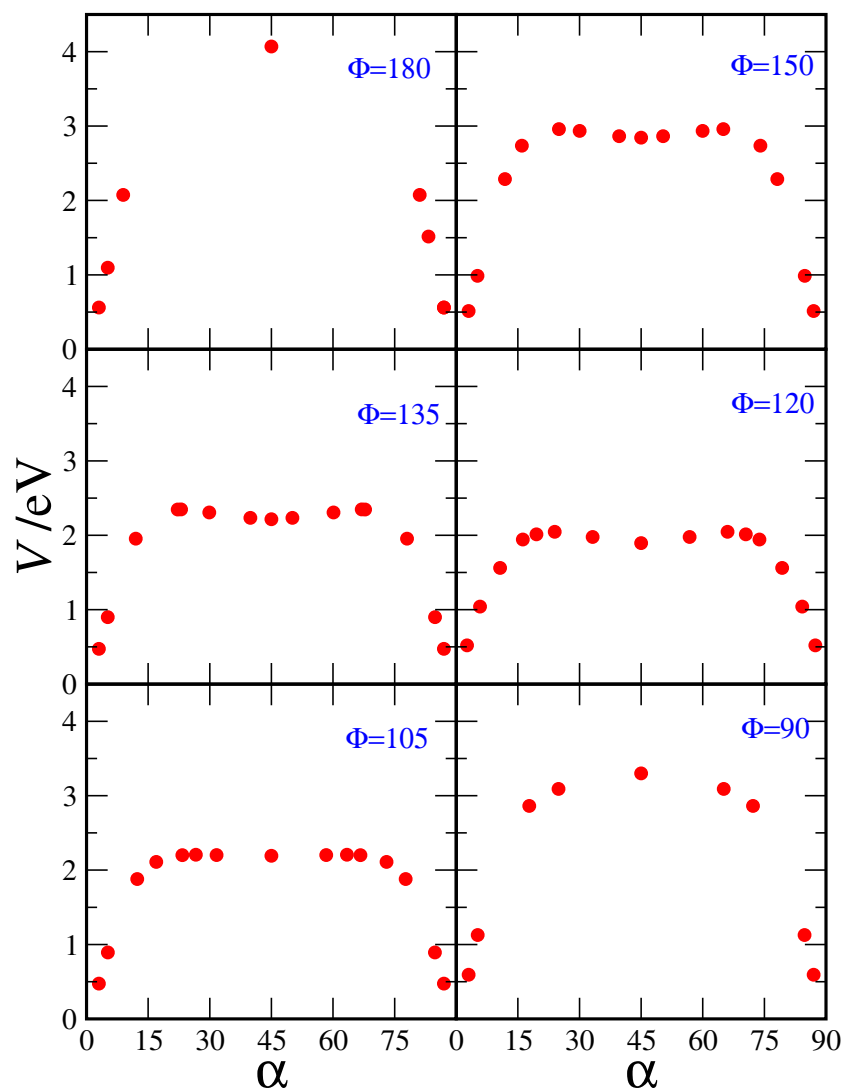


Figure 3.35: Ab initio energy (relative to reactants) of the fixed Φ MEPs plotted as a function of the BO polar coordinate α .

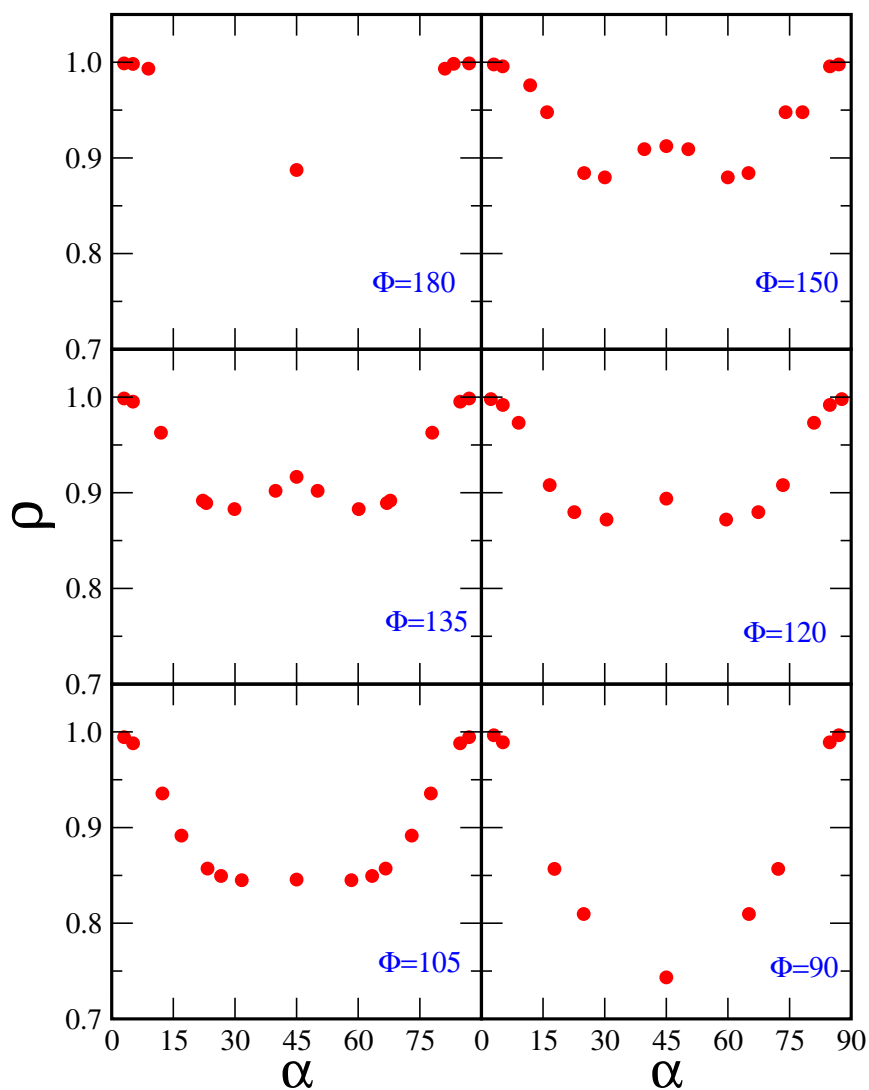


Figure 3.36: Ab initio location on ρ of the fixed Φ MEPs plotted as a function of the BO polar coordinate α .

where ρ and α are the already mentioned BO polar coordinates of eq. 2.71 and Φ is the angle formed by the two (broken and formed) bonds involved in the exchange process. Note that in eq. 3.2, the functions $a_1(\alpha, \Phi)$ and $a_2(\alpha, \Phi)$ have respectively replaced the functions $-D(\alpha, \Phi)$ and $a_\tau(\alpha, \Phi)$ of eq. 2.74. Moreover, the subscript τ is also dropped because all the three channels of the $N + N_2$ reaction are identical.

The main difference between the new LAGROBO potential energy surface and the older L0, L1, L2 and L3 ones is the formulation of the dependence of the functions $a_1(\alpha, \Phi)$ and $a_2(\alpha, \Phi)$ on α and Φ . In fact, the ab initio calculations have shown that the topology of the $N + N_2$ PES having a double barrier sandwiching a shallow well is more structured than that of the LEPS and the older LAGROBO PESs. Accordingly, the function $a_1(\alpha, \Phi)$ that describes the dependence of the well depth of the fixed Φ MEP of the exchange process on α is taken to be a quartic polynomial without odd terms. This guarantees the symmetry on α of the function. Therefore, the dependence on α of the function $a_1(\alpha, \Phi)$ reads:

$$a_1(\alpha, \Phi) = -D_{N_2} + b_{10}(\Phi) + b_{12}(\Phi)(\alpha - 45^\circ)^2 + b_{14}(\Phi)(\alpha - 45^\circ)^4 \quad (3.3)$$

where D_{N_2} is the dissociation energy of N_2 and the negative sign implies that the zero energy corresponds to the total dissociation of the three N atoms. Note that the second subscript of the b coefficients indicates the order of the α binomials.

In order to guarantee also the correct asymptotic behaviour, a relationship between the coefficients $b_{10}(\Phi)$, $b_{12}(\Phi)$ and $b_{14}(\Phi)$ has been enforced. In fact, at both the reactant and product asymptotes, $\alpha=0^\circ$ and $\alpha=90^\circ$ respectively, the function $a_1(\alpha, \Phi)$ must take the value $-D_{N_2}$. This implies that the following equation:

$$0 = b_{10}(\Phi) + b_{12}(\Phi) (45^\circ)^2 + b_{14}(\Phi) (45^\circ)^4 \quad (3.4)$$

holds and that the coefficient $b_{14}(\Phi)$ is linked to $b_{10}(\Phi)$ and $b_{12}(\Phi)$ as follows:

$$b_{14}(\Phi) = \frac{-b_{10}(\Phi) - b_{12}(\Phi) (45^\circ)^2}{(45^\circ)^4} \quad (3.5)$$

Using this relationship, the dependence on α of the function $a_1(\alpha, \Phi)$ reads:

$$a_1(\alpha, \Phi) = -D_{N_2} + b_{10}(\Phi) + b_{12}(\Phi)(\alpha - 45^\circ)^2 + \left(\frac{-b_{10}(\Phi) - b_{12}(\Phi)(45^\circ)^2}{(45^\circ)^4} \right) (\alpha - 45^\circ)^4 \quad (3.6)$$

This means that the dependence of the function $a_1(\alpha, \Phi)$ on α is parametrized only in terms of $b_{10}(\Phi)$ and $b_{12}(\Phi)$. It is worth noting here that when $b_{12}(\Phi)$ is positive the fixed Φ MEP shows an intermediate well and two transition states (barriers) while a negative value of $b_{12}(\Phi)$ leads to a single barrier with no intermediate well.

The function $b_{10}(\Phi)$ describes the dependence on Φ of the energy when $\alpha=45^\circ$, i.e. $r_1=r_2$. In other words, it describes the height of the well or of the transition state between reactants and products. This dependence has been explicitly determined by carrying out the related ab initio calculations shown in Figure 3.33.

The dependence on Φ of the coefficient $b_{10}(\Phi)$ has been instead formulated as a cubic polynomial centered at $\alpha=118.6^\circ$, where the shallow well has its minimum height. To enforce the first derivative to be zero at $\Phi=118.6^\circ$, the linear term in Φ has been omitted. Therefore, the dependence on Φ of the coefficient $b_{10}(\Phi)$ reads:

$$b_{10}(\Phi) = c_{100} + c_{102}(\Phi - 118.6^\circ)^2 + c_{103}(\Phi - 118.6^\circ)^3 \quad (3.7)$$

The parameter c_{100} represents the energy when $\Phi=118.6^\circ$, that is, at the minimum of the well. The value of the parameter c_{100} (1.93 eV) has been obtained from the ab initio calculations.

Figure 3.37 compares the fit given by eq. 3.7 (solid line) with the calculated ab initio energies (solid circles) for the dependence on Φ of the height of either the bottom of the well or of top of the transition state. The Figure confirms the accuracy of the fit.

Once the dependence on Φ of the function $b_{10}(\Phi)$ has been formulated, the defi-

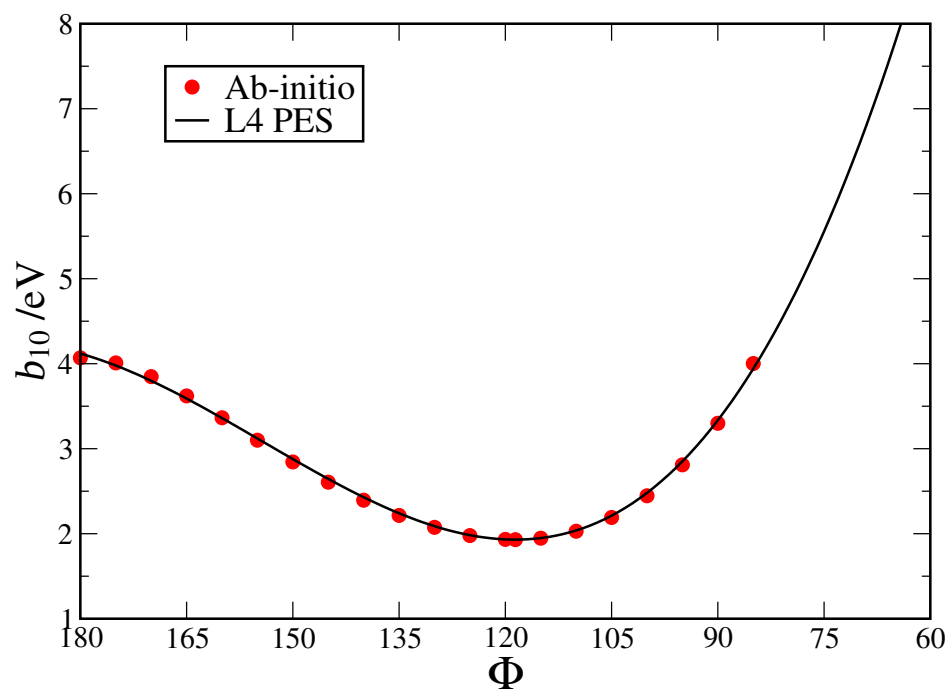


Figure 3.37: Ab initio optimized energy (solid circles), relative to reactants, at the system geometry $r_1=r_2$ plotted as a function of the bond angle Φ . The values indicate the bottom of the intermediate well or the top of the barrier. The line is the curve obtained from the L4 PES.

inition of the function $a_1(\alpha, \Phi)$ requires to express the dependence on Φ of the function $b_{12}(\Phi)$. To express this dependence, we first calculated the coefficient $b_{12}(\Phi)$ at each value of Φ by fitting the related ab initio MEPs (Figure 3.35). In particular, both the location on α and the height of the stationary points were determined. Then the dependence on Φ of the values obtained for $b_{12}(\Phi)$ was formulated as a cubic polynomial on Φ :

$$b_{12}(\Phi) = c_{120} + c_{121}\Phi + c_{122}\Phi^2 + c_{123}\Phi^3 \quad (3.8)$$

Figure 3.38 shows the ab initio energies (solid circles) for the fixed Φ MEPs (in other words, the values of the function $a_1(\alpha, \Phi)$) and the fitted values by the L4 PES (solid lines). As clearly shown by the Figure, the fit is very good. However, a slight difference between the ab initio data and the L4 curves is worth noting. In fact, at $\Phi=180^\circ$ the fitted curve shows a double barrier while the ab initio calculations predict a single one. On the contrary, at $\Phi=90^\circ$ the ab initio data suggest a double barrier while the fitted curve exhibits only one.

The function $a_2(\alpha, \Phi)$ describes the location on ρ of the minimum of the fixed Φ MEP of the exchange process. The dependence of $a_2(\alpha, \Phi)$ on α has been formulated by a sixth order polynomial without odd terms in order to guarantee the symmetry on α of the function. Thus, the chosen formulation is:

$$a_2(\alpha, \Phi) = b_{20}(\Phi) + b_{22}(\Phi)(\alpha - 45^\circ)^2 + b_{24}(\Phi)(\alpha - 45^\circ)^4 + b_{26}(\Phi)(\alpha - 45^\circ)^6 \quad (3.9)$$

The four coefficients $b_{20}(\Phi)$, $b_{22}(\Phi)$, $b_{24}(\Phi)$ and $b_{26}(\Phi)$ have been chosen not to be independent each other by imposing the following restrictions:

- The value of the function $a_2(\alpha, \Phi)$ at both the reactant and product asymptotes ($\alpha=0^\circ$ and $\alpha=90^\circ$, respectively) is 1, in order to correspond to the equilibrium internuclear distance of the reactant and product N₂ molecule.

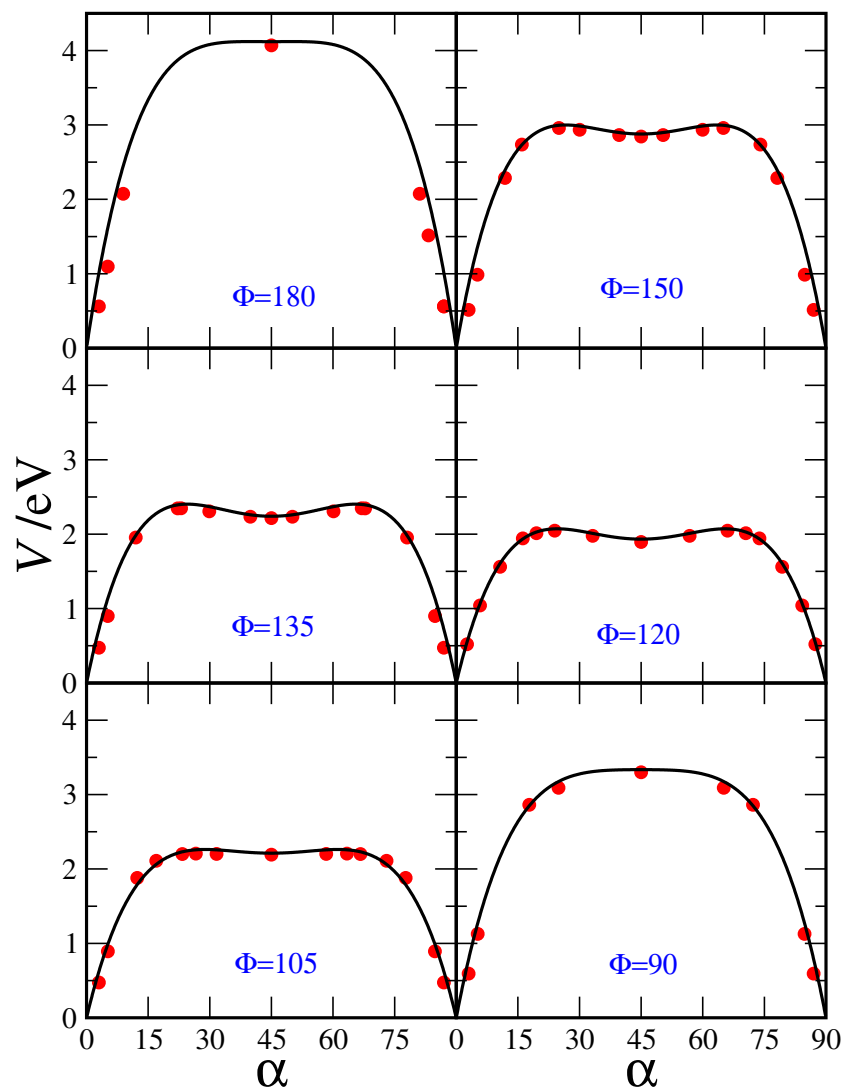


Figure 3.38: Energy of fixed Φ MEPs plotted as a function of the BO polar coordinate α . Solid circles are the ab initio values and the solid line is the curve obtained from the L4 PES.

- The value of the derivative of the function $a_2(\alpha, \Phi)$ at $\alpha=0^\circ$ and $\alpha=90^\circ$ is 0, in order the MEP to be flat at the asymptotes.

Using these two restrictions, the coefficients $b_{24}(\Phi)$ and $b_{26}(\Phi)$ can be formulated in terms of $b_{20}(\Phi)$ and $b_{22}(\Phi)$ as follows:

$$b_{24}(\Phi) = \frac{3 - 3 b_{20}(\Phi) - 2 b_{22}(\Phi) (45^\circ)^2}{(45^\circ)^4} \quad (3.10)$$

$$b_{26}(\Phi) = \frac{-2 + 2 b_{20}(\Phi) + b_{22}(\Phi) (45^\circ)^2}{(45^\circ)^6} \quad (3.11)$$

so that the dependence on α of $a_2(\alpha, \Phi)$ reads:

$$\begin{aligned} a_2(\alpha, \Phi) = & + b_{20}(\Phi) + b_{22}(\Phi)(\alpha - 45^\circ)^2 \\ & + \left(\frac{3 - 3 b_{20}(\Phi) - 2 b_{22}(\Phi) (45^\circ)^2}{(45^\circ)^4} \right) (\alpha - 45^\circ)^4 \\ & + \left(\frac{-2 + 2 b_{20}(\Phi) + b_{22}(\Phi) (45^\circ)^2}{(45^\circ)^6} \right) (\alpha - 45^\circ)^6 \end{aligned} \quad (3.12)$$

Again only two parameters, $b_{20}(\Phi)$ and $b_{22}(\Phi)$ allow to describe the dependence of the function $a_2(\alpha, \Phi)$ on α .

The function $b_{20}(\Phi)$ describes the dependence on Φ of the location on ρ when $\alpha=45^\circ$, i.e. $r_1=r_2$. This dependence has been explicitly obtained in the ab initio calculations (see Figure 3.34) and in the L4 PES has been expressed as a cubic polynomial in Φ as follows:

$$b_{20}(\Phi) = c_{200} + c_{201}\Phi + c_{202}\Phi^2 + c_{203}\Phi^3 \quad (3.13)$$

Contrary the formulation of $b_{20}(\Phi)$ in eq. 3.7, here the cubic polynomial expressing $b_{20}(\Phi)$ as a function of Φ is not centered on $\Phi=118.6^\circ$ and a linear term has been included. The location on ρ of the minimum of the reaction channel does not exhibit in fact an extreme at $\Phi=118.6^\circ$ (see Figure 3.34) as is instead the case of $b_{10}(\Phi)$.

Figure 3.39 compares the calculated ab initio values for the dependence on Φ of the location on ρ of the well or of the transition state between reactants and products with values fitted using eq. 3.13. The Figure shows again that the fit is excellent.

To formulate the dependence of $b_{22}(\Phi)$ on Φ we first fitted the location on ρ of the ab initio MEPs calculated at fixed Φ (see Figure 3.36) from which the values of $b_{22}(\Phi)$ were derived. Then, the dependence on Φ of the values of $b_{22}(\Phi)$ obtained in this way has been formulated as a cubic polynomial on Φ :

$$b_{22}(\Phi) = c_{220} + c_{221}\Phi + c_{222}\Phi^2 + c_{223}\Phi^3 \quad (3.14)$$

Figure 3.40 shows the ab initio location on ρ for the fixed Φ MEPs, that is, the values of the function $a_2(\alpha, \Phi)$, and the values fitted by the L4 PES. As clearly shown by the Figure, the fit is quite good. It is worth noting that the BO polar coordinate α (defined in eq. 2.71) is an exponential function of the internuclear distances and therefore the differences are not linear. For this reason the function $a_2(\alpha, \Phi)$ has been plotted also as a function of the internuclear distances (see Figure 3.41). In this Figure the ab initio data and the fit from the L4 PES appears to agree better.

Table 3.6 shows the value of the all parameters of the function describing the L4 surface. A total of 17 parameters (plus the parameters D_e , r_e and β needed to define the Morse curve for the N_2 molecule) are needed for the L4 PES.

The characteristics of the L4 potential energy surface are briefly summarized in Table 3.7 and in Figure 3.42. In the Table, the heights and bond lengths for both the barriers (L4B) and the shallow well (L4W) are shown for several bond (approach) angles Φ (missed values for L4B indicate only a single barrier and the related values are given under L4W). In the Figure, the dependence of the barrier height on the bond angle Φ is shown. In both the Table and the Figure, the comparison with the LEPS, L0, L1, and L3 surfaces is presented.

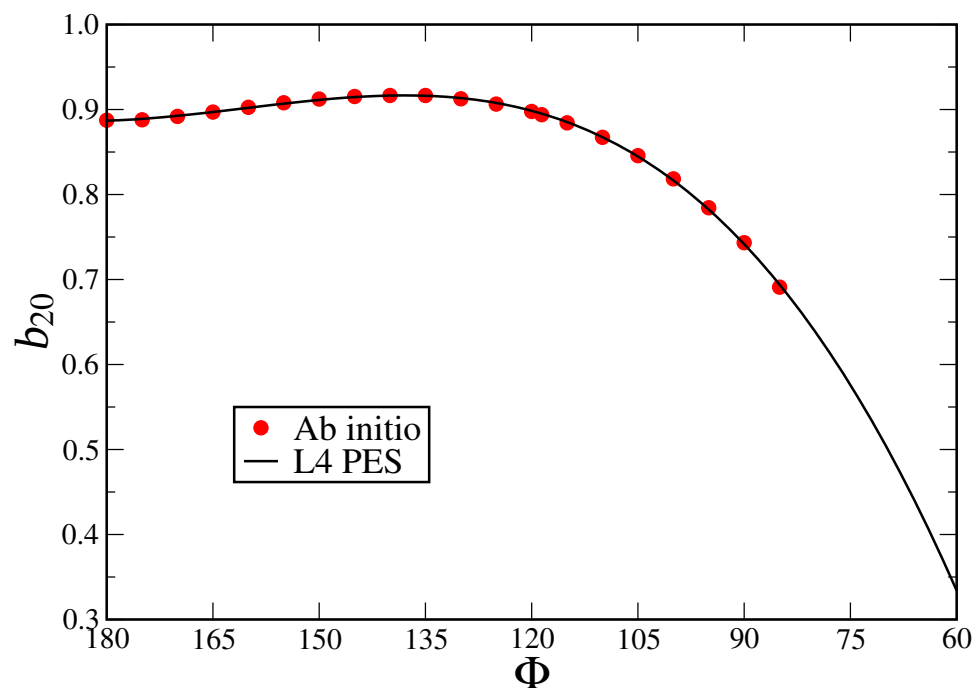


Figure 3.39: Location on ρ at the system geometry $r_1=r_2$ plotted as a function of the bond angle Φ . Solid circles are the ab initio values and the solid line is the curve obtained from the L4 PES.

Table 3.6: Parameters* for the L4 PES

c_{100}	44.517	c_{200}	-1.6614
c_{102}	0.0313099	c_{201}	0.049931
c_{103}	-0.000291921	c_{202}	-3.1748E-4
		c_{203}	6.5962E-7
c_{120}	-0.13347	c_{220}	1.50982E-3
c_{121}	0.0018589	c_{221}	-1.22426E-5
c_{122}	-1.43E-6	c_{222}	-9.23419E-8
c_{123}	-3.1007E-8	c_{223}	6.75926E-10
γ	50.0	Φ°	75°

*Energies in kcal mol⁻¹, angles in degrees.

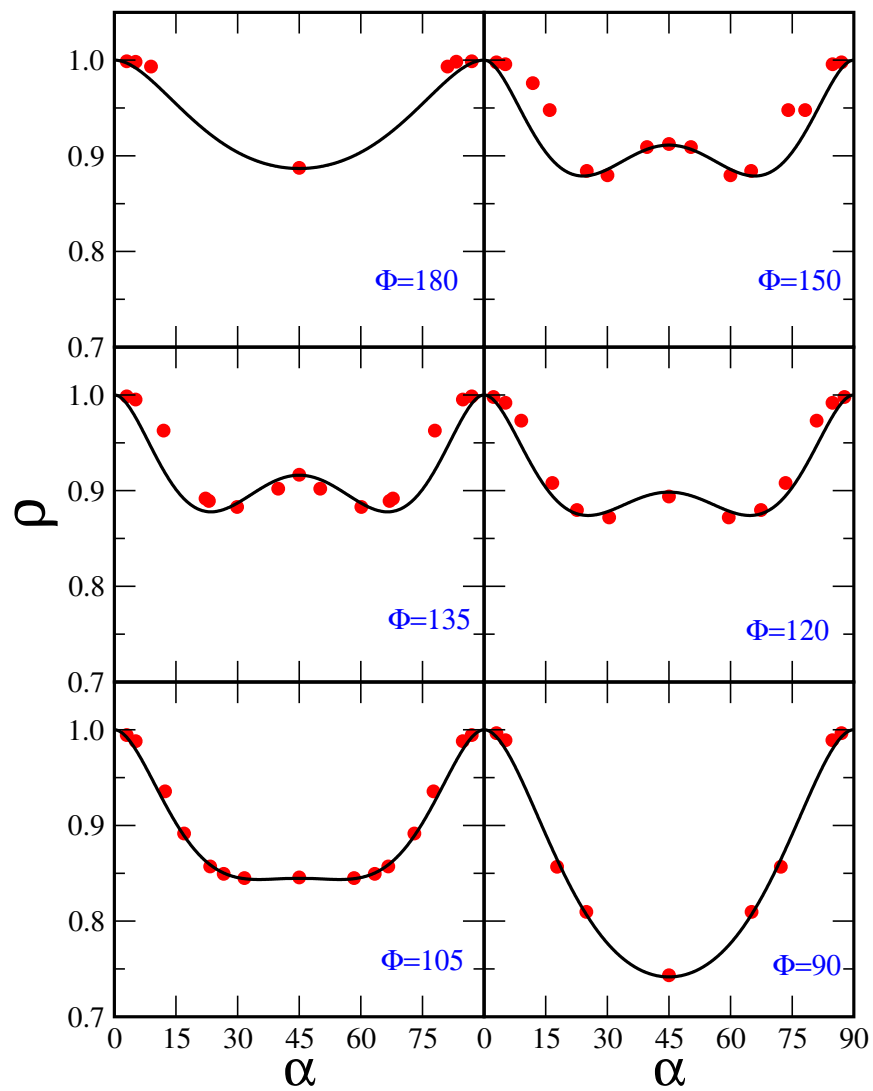


Figure 3.40: Location on ρ of the fixed Φ MEPs plotted as a function of the BO polar coordinate α . Solid circles are the ab initio values and the solid line is the curve obtained from the L4 PES.

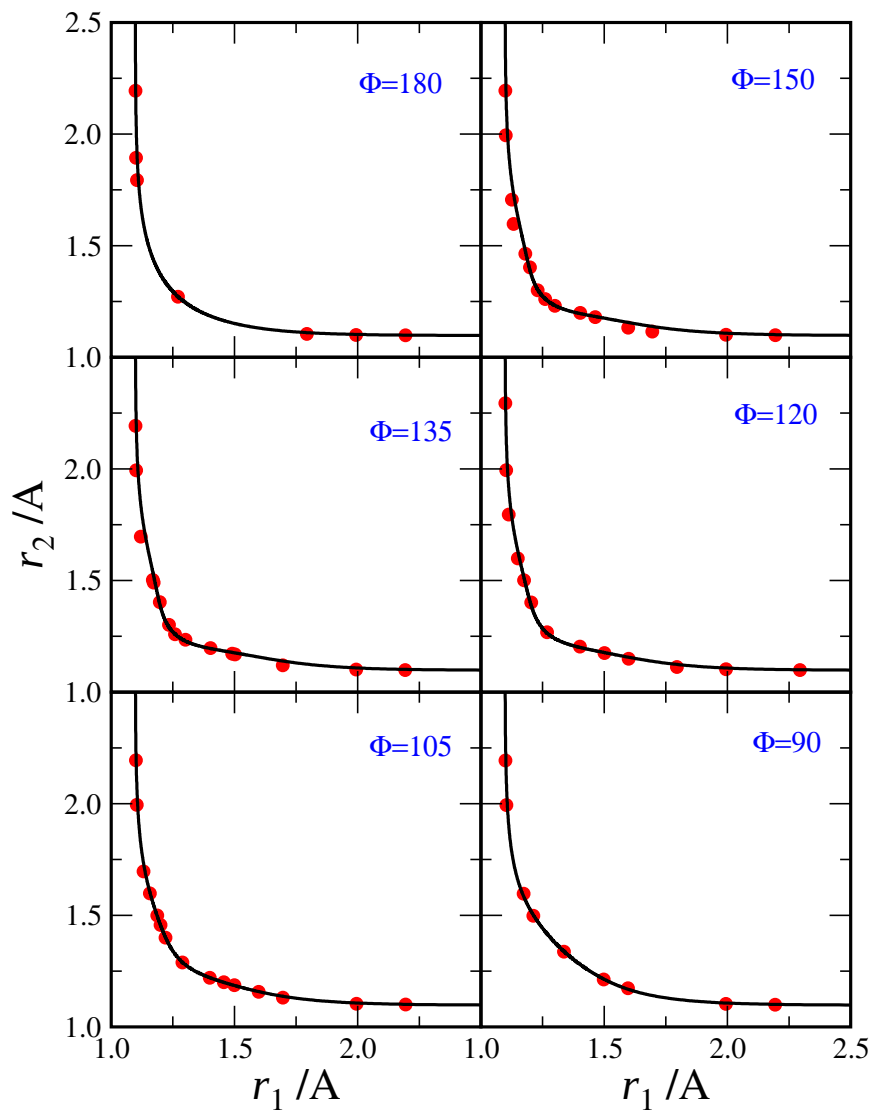
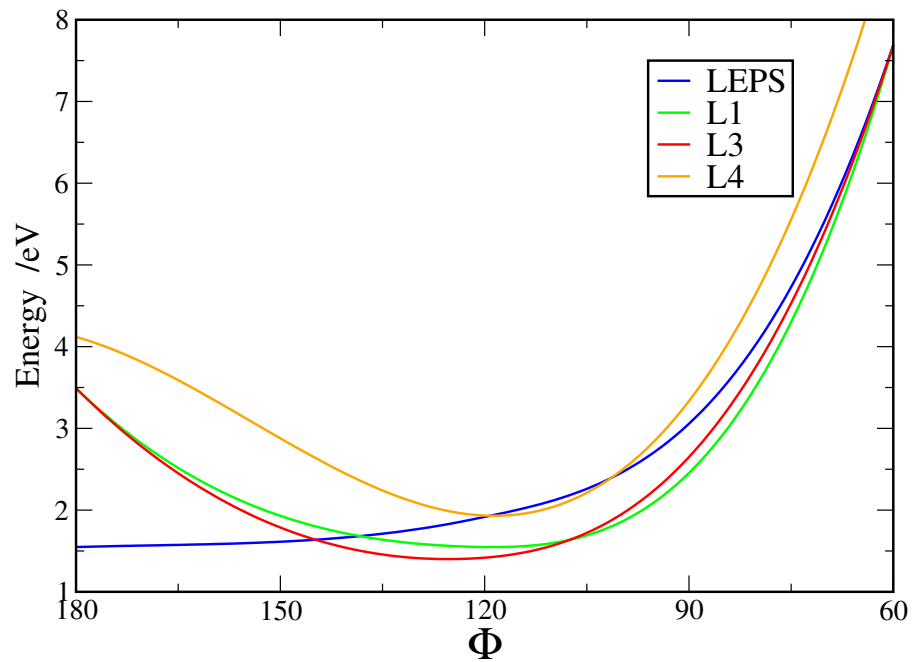


Figure 3.41: Location of the fixed Φ MEPs on the plane of the internuclear distances. Solid circles are the ab initio values and the solid line is the curve obtained from the L4 PES.

Table 3.7: Barrier characteristics of the L4 PES

Φ	Height /eV					
	LEPS	L0	L1	L3	L4W	L4B
180°	1.55	1.55	3.49	3.49	4.12	4.12
150°	1.61	1.62	1.93	1.79	2.88	3.00
120°	1.92	1.91	1.55	1.42	1.93	2.07
90°	3.06	3.05	2.45	2.65	3.34	
60°	7.69	7.69	7.69	7.69	9.62	

Φ	N–N distance /Å						
	LEPS	L0	L1	L3	L4W	L4B* r_1	L4B* r_2
180°	1.240	1.240	1.240	1.240	1.271	1.310	1.238
150°	1.243	1.244	1.244	1.244	1.261	1.445	1.187
120°	1.254	1.254	1.254	1.254	1.267	1.476	1.183
90°	1.294	1.293	1.293	1.293	1.338		
60°	1.530	1.522	1.522	1.522	1.417		

*For the other barrier interchange r_1 and r_2 .Figure 3.42: Barrier heights for the L4, LEPS, L1 and L3 PESs as a function of the angle Φ .

As apparent from Table 3.7, the reactants and products in the L4 PES are separated by a double barrier connected by a shallow well at $\Phi > 90^\circ$ (in particular, at $\Phi \geq 95^\circ$). The difference in energy between the barriers and the shallow well has its maximum (0.14 eV) at $\Phi=120^\circ$ to almost vanish at $\Phi=180^\circ$ (0.001 eV). At $\Phi=90^\circ$ the L4 PES shows a single barrier while the ab initio calculations still indicate a double one though with a hardly appreciable intermediate shallow well. At the same time, the height of the barrier of the L4 PES corresponding to a bent geometry at the saddle to reaction increases significantly as the geometry is distorted from that of the saddle. In other words, the L4 PES has a fairly small cone of acceptance to reaction. This feature can be better observed in Figure 3.42, where the barrier heights for the L4 PES is plotted as a function of the angle Φ .

As to the N–N internuclear distances at the shallow well, one can observe that the minimum values correspond to $\Phi=150^\circ$ (1.261 Å). The bond length at the well increases slightly as Φ increases. A more pronounced increase occurs when the geometry of the system becomes more bent. On the other hand, the internuclear distances at the well distort at the barriers. The maximum distortion corresponds to $\Phi=120^\circ$ where one distance increases in 0.21 Å and the other decreases in 0.08 Å.

The main difference between the L4 PES and the L3 PES is the height of the saddle. In fact, the height of the saddle of the L4 PES is 0.73 eV higher than that of the L3 PES. This difference reduces to 0.62 eV when the L1 PES is considered. However, the main difference between the L4 PES and both the LEPS and L0 PESs is the bent geometry at the saddle ($\Phi=120^\circ$) of the L4 PES that differs from the collinear geometry of the saddle on the LEPS and L1 PESs. Also the internuclear distances at the saddle of the L4 PES are slightly larger than those of the other PESs. For instance, at $\Phi=120^\circ$ this difference is 0.001 Å. However, as Φ decreases the internuclear distance at the saddle increases for the L4 PES while it increases for the previous PESs. A different trend is also observed as Φ decreases. In fact, the increase

of the N–N distance is more significant for all the previous PESs than for the L4 PES.

A global picture of the L4 PES is given in Figure 3.43, where the isoenergetic contour maps at $\Phi=120^\circ$ are plotted as a function of the bond order coordinates n_1 and n_2 . Also the region near to the minimum energy path is evidenced by the graduation of colour tones. In this Figure, the asymptote of the entrance channel is located at $n_2=0$ with the minimum at $n_1=1$ while the exit channel asymptote is located at $n_1=0$ with the minimum at $n_2=1$. The complete dissociation of the three atoms corresponds to $n_1=n_2=0$. The reaction channel connects the two asymptotes bending almost like an arc having the center at the coordinate origin. As the angle α (defined in eq. 2.71) increases from zero the energy of the bottom of the channel increases to reach a maximum at the barrier and then slightly decreases down to a minimum forming a well (at $\alpha = 45^\circ$). A further increase of the α angle leads to an increase of the energy up to the second twin barrier after which, the energy decreases again towards the product asymptote ($\alpha=90^\circ$). As apparent from the Figure, the isoenergetic contours are symmetric with respect the line at $\alpha=45^\circ$ since $\text{N} + \text{N}_2$ is symmetric with $\text{N}_2 + \text{N}$.

3.5.3 *J*-shift cross sections

In this Section, a dynamical study on the new L4 potential energy surface is presented. In particular, state-specific cross sections using the *J*-shift approximation from the exact $J=0$ state-specific quantum reactive probabilities have been calculated for $v=0$, $j=14$ and $v=0$, $j=24$, (the most populated rovibrational states at the two temperatures of the experiment) in the interval of total energy values ranging from 2.0 to 3.2 eV in steps of 0.001 eV.

Due to the fact that the L4 PES differs significantly from the LEPS and the other

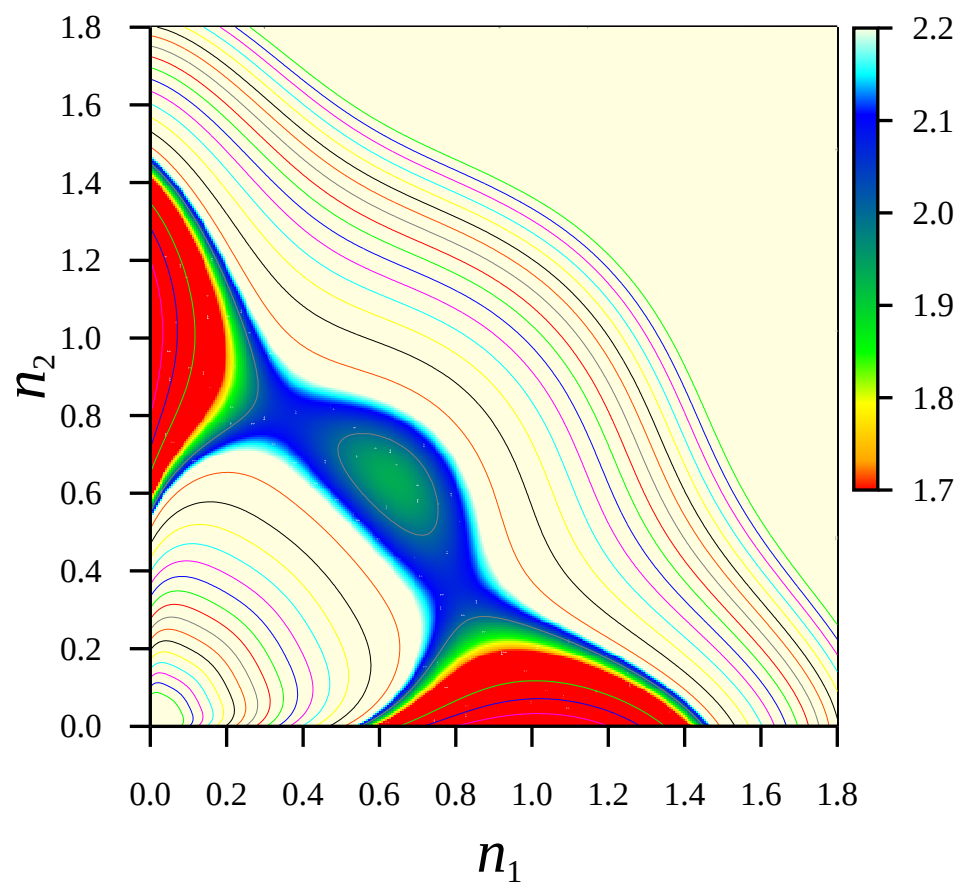


Figure 3.43: Isoenergetic contour maps for L4 PES calculated at $\Phi=120^\circ$ and plotted as a function of the bond order coordinates. The energy interval between two consecutive contours is 0.4 eV and the energy is referred to the entrance channel.

LAGROBO surfaces, an optimization of the input parameters for the RWAVEPR code has been carried out. In particular, the effect of modifying both the grid definition for the radial coordinates and the number of iterations has been considered. All the other parameter values have been taken from Table 3.1.

The effect of modifying the grid definition for the radial coordinates when solving the Schrödinger equation have been checked by considering a set of 240×240 points (as for the calculations on the previous PESs) and a set of 400×400 points. An obvious consequence of the increase of the grid points is a significant increase in the memory needed for the calculations (1.7 GB as opposed to the previous 0.7 GB). The state-specific reactive probabilities obtained in the two calculations are shown in Figure 3.44. As apparent from the Figure, the two results do not differ appreciably allowing us to carry out the calculations using the 240×240 points grid.

The effect of modifying the number of iterations to solve the Schrödinger equation have been checked by considering the flux at the analysis line. In Figure 3.45 the flux at the analysis line (normalized to its maximum) calculated on the L4 PES using 5000 iterations is plotted as a function of the number of iterations. Another calculation was carried out using 12000 iterations (this calculation took more than 157 hours) and the obtained flux confirmed that a number of 5000 iterations (this calculation took more than 66 hours) is sufficient to accurately describe the reactive event while leading to a significant saving of computational resources. As apparent from the Figure, a collision time equivalent to more than 1000 iterations is needed to the wavepacket to reach the product region. The flux exhibits a maximum at the iterations 1368 and 1293 for, respectively, $v=0, j=14$ and $v=0, j=24$. This means that the maximum flux in the product region occurs 33 and 31 fs after the begin of the collision. After the maximum, a sudden decrease of the flux is observed. However, at a collision time equivalent to 1600–1700 iterations an increase of the flux at the analysis line occurs again. This shoulder much more pronounced than for the other

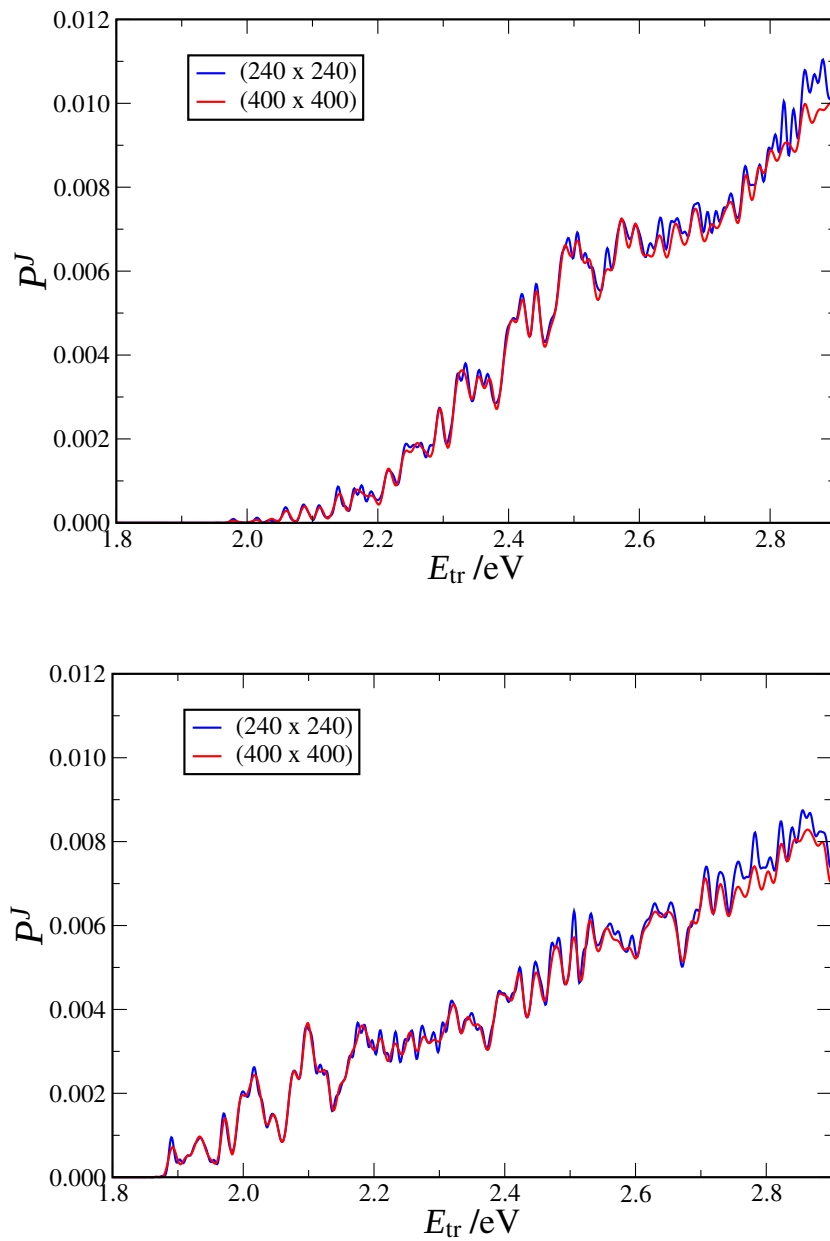


Figure 3.44: State-specific reactive probabilities, $P^J(E_{tr})$, calculated at $J=0$, $v=0$ and $j=14$ (upper panel) and at $J=0$, $v=0$ and $j=24$ (lower panel) using 240×240 and 400×400 points grid for the radial coordinates plotted as a function of the collision energy E_{tr} .

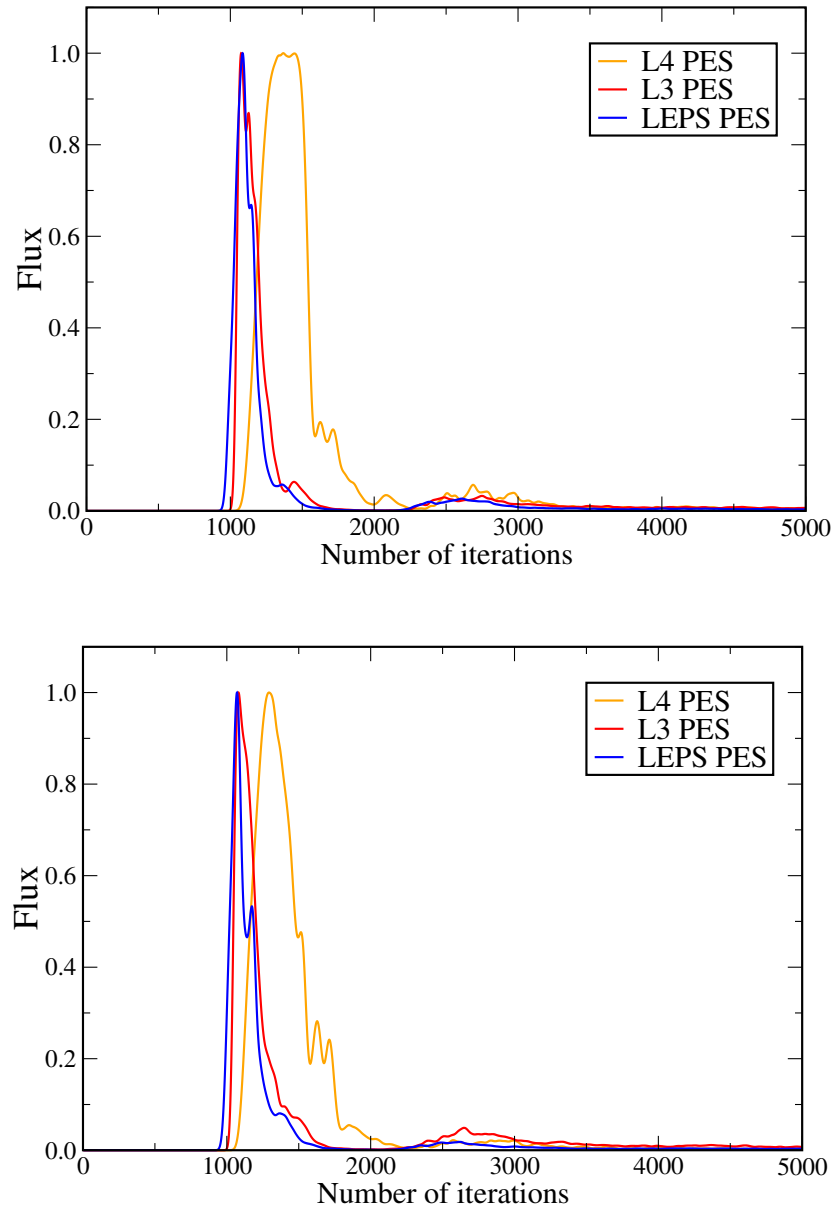


Figure 3.45: Flux (normalized to its maximum) at the analysis line plotted as a function of the number of iterations for $J=0$, $v=0$ and $j=14$ (upper panel) and at $J=0$, $v=0$ and $j=24$ (lower panel) on the L4, LEPS and L3 PESs.

PESs (also reported in the Figure) can be attributed to the larger interaction of part of the wavepacket in the more structured transition state region. As apparent from the Figure, on both the LEPS and L3 PESs the wavepacket begins to arrive to the product region in a shorter time (the maximum flux occurs at the iterations 1080 for both $v=0, j=14$ and $v=0, j=24$ cases) than on the L4 PES and in a shorter time (equivalent to 950–1350 iterations) arrives also the largest part of the wavepacket. This means that on both the LEPS and L3 PESs the reaction is more direct than on the L4 PES on which a non negligible flux continues to arrive to the product region after 2000 iterations.

Another feature of the flux at the analysis line, common to all the surfaces, is the arising of a bump around 2500–3000 iterations. This structure accounts for less than 4% of the maximum flux and it can be attributed to an incomplete absorption of the wavepacket at the analysis line when it arrives there the first time. This feature can be used as an estimate of the error of our time-dependent calculation.

Once the input parameters for the RWAVEPR code have been optimized, the exact $J=0$ reactive probabilities have been computed and from those values one can apply the J -shift procedure. To this end, use was made of eq. 2.61 because the L4 PES has a bent geometry at the saddle. In particular, the rotational constants calculated at the saddle are $A = 5.3 \times 10^{-4}$, $B = 6.3 \times 10^{-5}$ and $C = 5.6 \times 10^{-5}$ eV and, assuming a prolate symmetric rotor behaviour, a value of $\overline{B}$ (that is equal to the average of B and C) of 5.9×10^{-5} eV is obtained. The comparison with the rotational constants obtained for the L3 PES ($A = 6.7 \times 10^{-4}$ and $\overline{B} = 5.8 \times 10^{-5}$ eV) indicates that for the L4 PES the A rotational constant is smaller than that for the L3 PES while the $\overline{B}$ rotational constant is slightly higher. This means a smaller shift in energy of the partial probability J -shift curves as J increases for the L4 PES. As a consequence, higher cross sections and rate coefficient should result from the calculations.

The J -shift state-specific cross sections, $\sigma_{vj}(E_{\text{tr}})$, calculated in this way are shown in Figure 3.46. The excitation function for the two rovibrational initial states considered is very similar. In fact, both excitation functions exhibit a threshold energy and a moderate increase as the collision energy increases. There are however two significant differences. The first one is concerned with the threshold energy that is 2.2 and 2.0 eV for $v=0, j=14$ and $v=0, j=24$, respectively. The second difference is a higher rising slope as the collision energy increases for the $v=0, j=14$ rovibrational state. These differences were also found when using L3. In fact, as apparent from Figure 3.46 where the L3 J -shift cross sections are shown, both the threshold energy and the slope for the increase are higher for the $v=0, j=24$ state. However, the most important issue related to the comparison of the J -shift cross sections calculated on L4 and L3 PESs is concerned with the fact that the difference in the two threshold energies roughly coincides with the difference between the heights of the related saddles (0.7 eV, see Table 3.7). This means that the double barrier structure of the L4 PES does not introduce appreciable dynamical effects with respect to the energy needed to overtake the barrier to reaction. This apparently surprising result may be rationalized in terms of the fact that the saddles have a geometry closer to collinearity than that of the intermediate well and therefore more suited to exploit collision energy for allowing the system overtake them.

3.5.4 CS cross sections

The dynamical test of the L4 potential energy surface was also carried out using the CS approximation. In this case, cross sections have been calculated for $v=0, j=24$ (the most populated rovibrational state at $T=3400$ K) and an interval of collision energy ranging from 2.0 to 3.2 eV, in steps of 0.001 eV. Total angular momenta up to $J=120$ in steps of 10 have been considered.

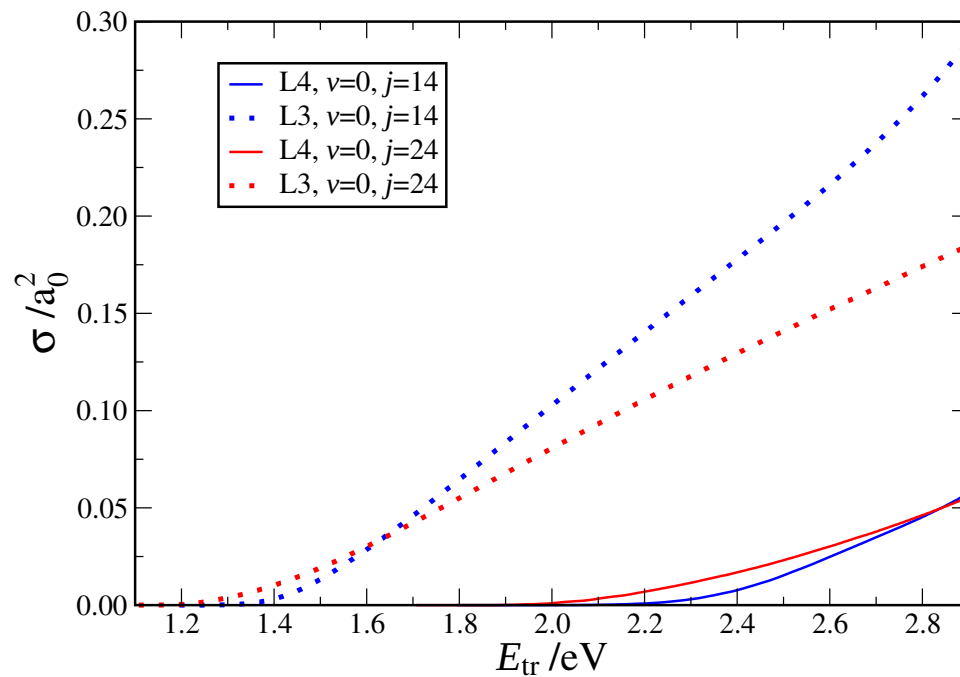


Figure 3.46: J -shift cross sections, $\sigma(E_{tr})$, calculated at $v=0, j=14$ and $v=0, j=24$ calculated on the L4 PES plotted as a function of the collision energy E_{tr} . J -shift cross sections calculated on the L3 PES are also shown.

We first analyse here the dependence of the partial state-specific probabilities, $P^{J\Omega}(E_{\text{tr}})$, on the quantum number Ω . Figure 3.47 shows the plot of the CS $P^{J\Omega}(E_{\text{tr}})$ probabilities calculated at $j=24$ for all the values of Ω allowed at $J=80$ (and $p=0$). As apparent from the Figure, partial J and Ω (with even parity) reaction probabilities are nearly independent on Ω up to $\Omega=15$. For larger values of Ω , they progressively decrease to practically vanish at $\Omega=24$. This behaviour does not differ from that found for the L3 PES (see Figure 3.19) except for the obvious shift in the collision energy.

By summing the Ω contributions of the CS $P^{J\Omega}(E_{\text{tr}})$ probabilities, the CS partial reactive probabilities $P^J(E_{\text{tr}})$ have been calculated. The calculated values are plotted in Figure 3.48 as a function of the total angular momentum J (upper panel) and of the collision energy (lower panel). As apparent from the Figure, the CS partial probabilities exhibit a different behaviour at low and high collision energy. In fact, at low collision energy they decrease with J near linearly from their value at $J=0$. On the contrary, at high collision energy the partial reactive probabilities first increase to a maximum located at about $J = 70 - 80$ and then decrease quite sharply. The height of the maximum increases as the collision energy increases. The behaviour of the $P^J(E_{\text{tr}})$ probabilities calculated on the L4 PES does not differ qualitatively from that of the L3 PES (see Figure 3.21). As expected, the main difference is the higher collision energies needed by the L4 PES to promote reaction.

We have also analysed the CS partial cross section terms $\sigma^J(E_{\text{tr}})$ obtained by multiplying the CS partial probabilities by the factor $\pi(2J + 1)/k_{vj}^2$ (see eq. 2.56). Figure 3.49 shows the plot of the CS $\sigma^J(E_{\text{tr}})$ values as a function of the collision energy E_{tr} and of the total angular momentum J . The CS partial cross section terms are small at both low total angular momentum and low collision energy and increase significantly as E_{tr} increases. On the contrary, they first increase to reach a maximum and subsequently decrease when plotted as a function of J . This means that the CS partial cross section terms have the same qualitative behaviour as the CS partial

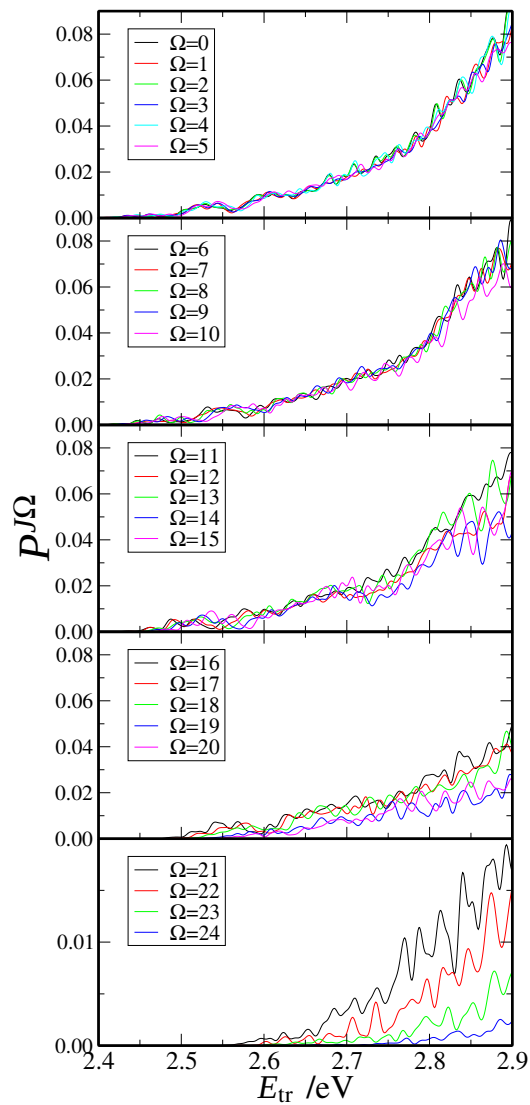


Figure 3.47: CS partial reactive probabilities $P^{J\Omega}(E_{tr})$ calculated at $v=0$, $j=24$, $J=80$ and $p=0$ calculated on the L4 PES plotted as a function of the collision energy E_{tr} . Note the different scale for the lower panel.

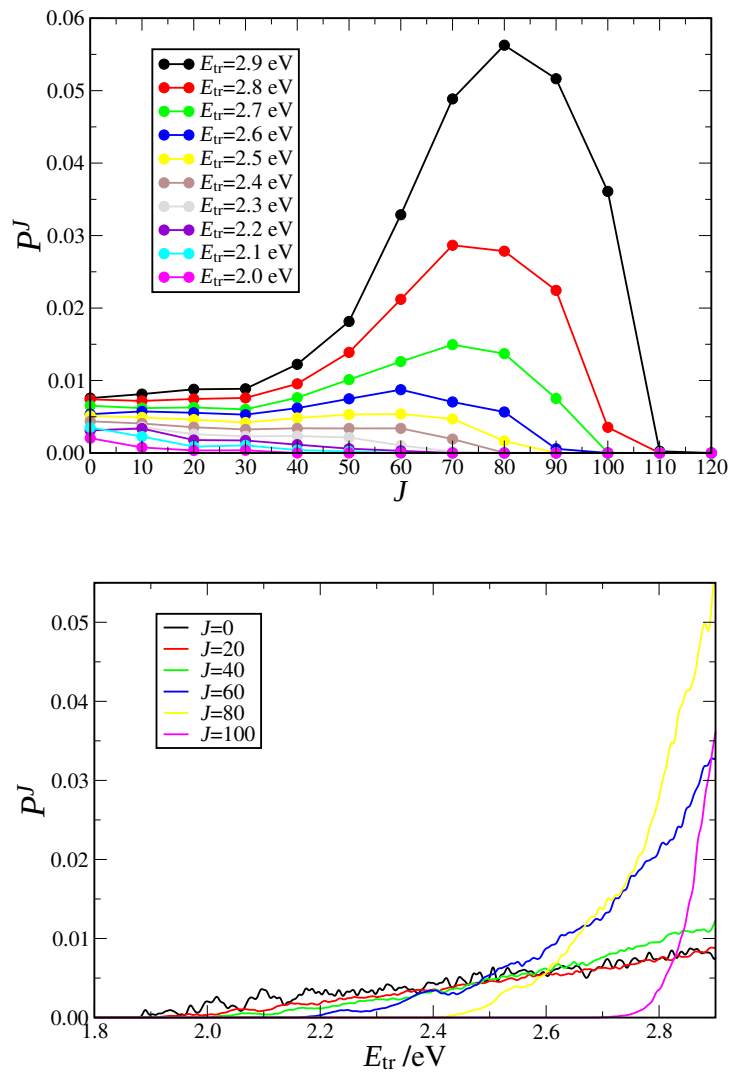


Figure 3.48: CS partial reactive probabilities $P^J(E_{tr})$ calculated at $v=0$ and $j=24$ on the L4 PES plotted as a function of the total angular momentum J (upper panel) and of the collision energy E_{tr} (lower panel).

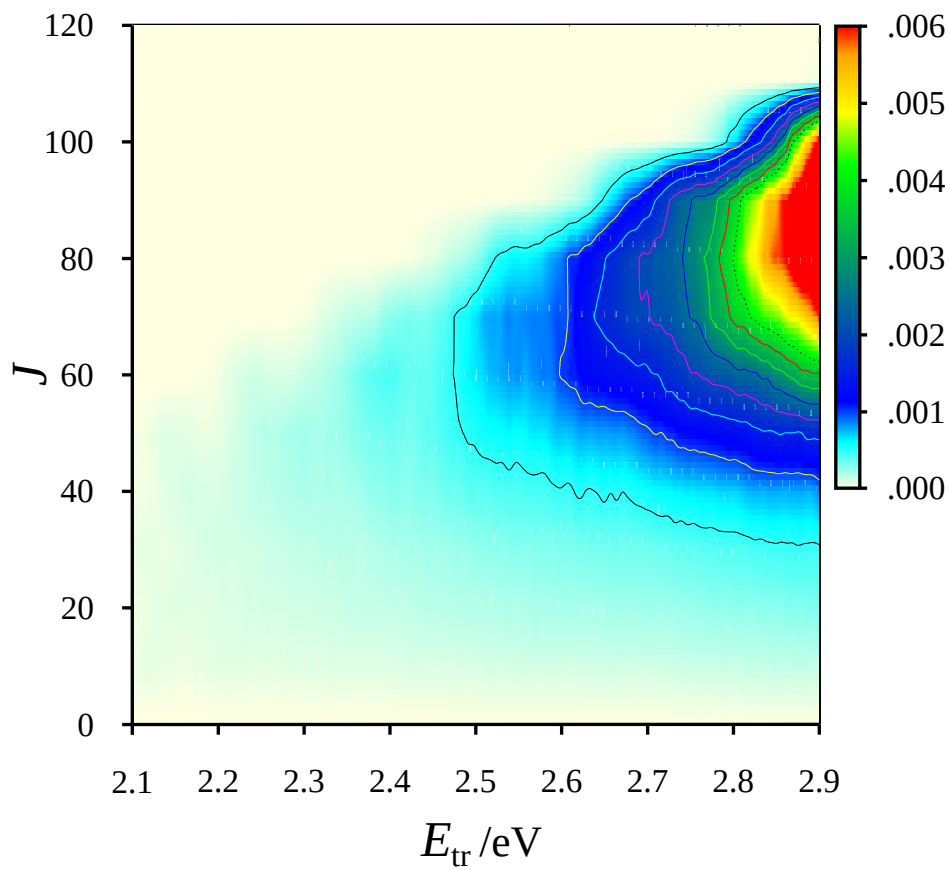


Figure 3.49: CS partial cross section terms, $\sigma^J(E_{tr})$, in a_0^2 , calculated at $v=0$, $j=24$ on the L4 PES plotted as a function of the collision energy E_{tr} and of the total angular momentum J . Contours are plotted in steps of $0.0004 a_0^2$.

probabilities (see Figure 3.48). At the same time, as shown by Figure 3.49, that qualitatively agrees with Figure 3.22, the CS partial cross section terms calculated on the L4 PES are similar to the ones calculated on the L3 PES, except for their shifts of the threshold collision energy.

Finally, the CS state-specific cross sections $\sigma(E_{\text{tr}})$ for $v=0$ and $j=24$ are calculated by summing the CS $\sigma^J(E_{\text{tr}})$ values. The calculated reactive cross sections are plotted in Figure 3.50. The dependence of the CS cross section $\sigma(E_{\text{tr}})$ on the collision energy shows a threshold energy at around 1.9 eV and a significant increase as the collision energy increases. This dependence is qualitatively similar to the one found for the L3 PES (see Figure 3.23). The main difference between the L4 and L3 excitation functions lies in the threshold energy (1.9 eV and 1.2 eV, respectively). Such an increase approximately corresponds to the increase of the saddle energy (see Table 3.7).

Figure 3.50 shows also the cross sections calculated at $v=0$, $j=24$ on the L4 PES using the J -shift approximation. The comparison of the CS cross sections with the J -shift ones evidences large (a factor of about six higher) discrepancies at the highest collision energies considered. A similar disagreement between the CS and J -shift cross sections has been found for the L3 PES (see Figure 3.26).

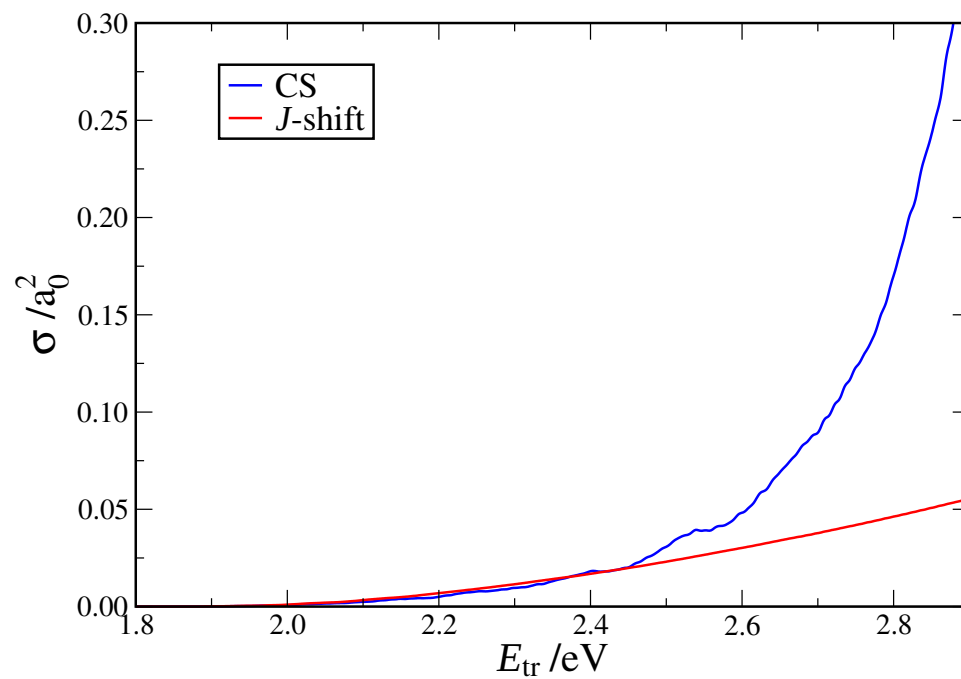


Figure 3.50: CS cross sections, $\sigma(E_{tr})$, calculated at $v=0$, $j=24$ on the L4 PES plotted as a function of the collision energy E_{tr} . J -shift cross sections calculated on the L3 PES are also shown for comparison.

Chapter 4

The CH+H₂ reaction: Theoretical approach

4.1 Time-dependent quantum method

The time-dependent quantum method used for studying the CH+H₂ → CH₂+H reaction in the present Thesis is the real wavepacket (RWP) method developed by Balint-Kurti and Gray [93]. Unlike most wavepacket methods [89], it uses only the real part of the generally complex-valued, time evolving wavepacket, and the effective hamiltonian operator of interest. Time steps in the RWP method are accomplished by a simple three-term Chebyshev iteration, involving per time step just one action of the hamiltonian operator on the current (real) wavepacket. One view of the RWP method is that it is a highly streamline version of the Tal-Ezer and Kosloff's well-known and highly successful Chebyshev expansion of the propagator [148].

The RWP method has also features in common with several other accurate, it-

erative approaches to quantum dynamics, most notable Mandelshtam and Taylor's damped expansion of the time-independent Green operator [122], Kouri and coworkers's "time-independent wavepacket" method [149] and Chen and Guo's Chebyshev propagator [102]. Kroes and Neuhauser also implemented damped Chebyshev iterations in the time-independent wavepacket context for a challenging surface scattering problem [150].

In all the time-dependent quantum approaches one has to choose of representing the wavepacket either on a finite grid, or in a finite basis set, or in a combination of the two. The time-dependent Schrödinger equation which propagates the wavepacket in some set of coordinates x , can be written as:

$$i\hbar \frac{\partial \psi(x, t)}{\partial t} = \hat{H} \psi(x, t) \quad (4.1)$$

where $\psi(x, t)$ is a vector with complex-valued components corresponding to the wavepacket amplitudes on the various grid points and/or associated with the various basis states, and $\hat{H}$ is the corresponding matrix representation of the hamiltonian operator. The $i = \sqrt{-1}$ in eq. 4.1 implies that a full wavepacket is complex-valued. However, as detailed in ref. [93], the knowledge of the time dependence of just the real part of a complex-valued wavepacket is sufficient for the determination of reactive scattering S matrix elements and thus reaction probabilities $|S|^2$ for chemical reactions.

From eq. 4.1, if one knows the wavefunction at an instant t , by simply applying the time evolution operator $\exp(-i\hat{H}\tau/\hbar)$, one can determine the wavefunction at $t + \tau$. Due to the fact that a collision process involves a time independent hamiltonian, the wavepacket at time $t + \tau$ is obtained from the wavepacket at time t through:

$$\psi(x, t + \tau) = e^{-i\hat{H}\tau/\hbar} \psi(x, t) \quad (4.2)$$

It is not an easy job to solve this exponential equation and many methods have been developed to the end to solving it. One of them, which propagates the wavefunction

in an efficient way, is the Chebyshev polynomial expansion method [148]:

$$e^{-i\hat{H}\tau/\hbar} = \sum_{n=0}^N a_n P_n(-i\hat{H}) \quad (4.3)$$

where a_n are the expansion coefficients and P_n are the Chebyshev polynomials. Since the Chebyshev polynomials are confined into the interval $(-1, 1)$, the hamiltonian has to be renormalized by shifting its eigenvalues to this range. Then the normalized hamiltonian operator is represented by:

$$\hat{H}_s = a_s \hat{H} + b_s \quad (4.4)$$

where $a_s = 2/\Delta E$, $b_s = -1 - a_s E_{\min}$ and $\Delta E = E_{\max} - E_{\min}$, with $E_{\min}$ and $E_{\max}$ being the minimum and maximum eigenvalues, respectively.

Using the normalized hamiltonian operator $\hat{H}_s$ the Chebyshev polynomial expansion can be written as:

$$e^{-i\hat{H}\tau/\hbar} = e^{-i(\Delta E/2 + V_{\min})\tau/\hbar} \sum_{n=0}^N (2 - \delta_{n0}) J_n(\Delta E \tau/2\hbar) P_n(-i\hat{H}_s) \quad (4.5)$$

where J_n are the Bessel functions of the first kind and order n . When substituting this expression in eq. 4.2, one has to calculate $P_n(-i\hat{H})\psi(x, t)$. This can be done using the recurrence relationship of Chebyshev polynomials:

$$\phi_{n+1} = -2i\hat{H}_s\phi_n + \phi_{n-1} \quad (4.6)$$

with $\phi_n = P_n(-i\hat{H}_s)\psi(x, t)$. Since for n larger than $\Delta E \tau/2\hbar$ the value of the Bessel functions J_n decreases with n exponentially, their use plays a key role in the convergence of the expansion series. That is why the number N of the total terms which leads to convergence can be set as $N \sim \Delta E \tau/2\hbar$. In other words, the number of terms of the expansion of the exponential of the operator is proportional to the energy interval ΔE defined by the difference between the maximum and the minimum eigenvalues of $\hat{H}$. This means that it is necessary to define the highest eigenvalue of $\hat{H}$ ($E_{\min}$ is already defined through $V_{\min}$) through the definition of a cut off potential energy: $V = V_{\max}$ when $V > V_{\max}$.

4.2 Wavepacket representation

The representation of the wavepacket for a AB + CD four-atom reactive problem is based on the diatom-diatom Jacobi coordinates. These coordinates are shown in Figure 4.1 for the CH + H₂ reaction. The coordinate system is composed of two diatomic units, AB and CD. The distance between the center of mass of AB and CD is R , and the AB and CD bond distances are, respectively, r_1 and r_2 . The angles between the two diatomic units and R , θ_1 and θ_2 respectively, as well as the dihedral angle ϕ complement the three radial coordinates to make a total of six internal coordinates.

To describe the wavepacket a body-fixed (BF) representation is employed, with the Z axis associated with R [151–153]. The theory behind the BF representations and the associated angular momentum function expansions of wavefunction (or wavepacket) in terms of basis parameterized by the relevant constants or quasi-

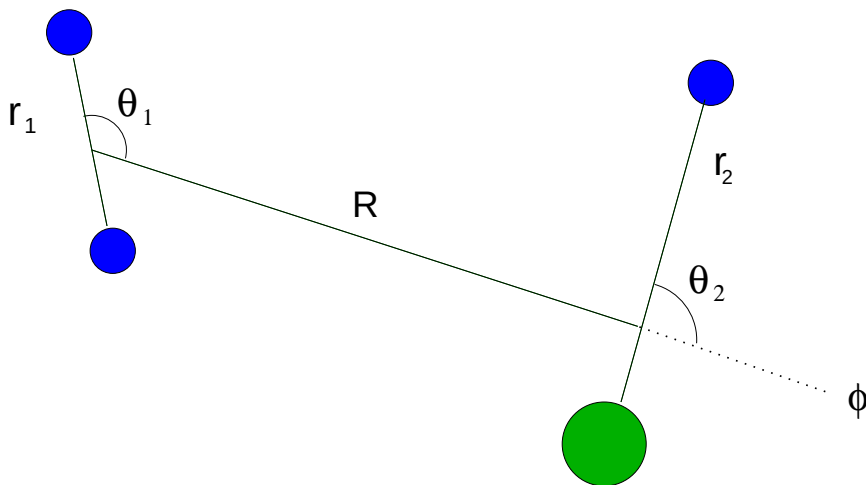


Figure 4.1: Diatom-diatom Jacobi coordinates for the CH+H₂ reaction. Hydrogen atoms are plotted in blue and the carbon one in green.

constants is highly technical and was described in detail for three-atom systems in Chapter 2. The two good constant of motion are the total angular momentum, J , and the parity, p . An approximate constant of motion is the helicity, Ω , that is, the projection of the total angular momentum on the BF Z axis. Furthermore, it is convenient to work in a moving-frame such that only the first two Euler rotations are considered [151]. This is equivalent to setting Ω on the SF Z axis equal to zero. This frame, called "E2" by Gatti *et al.* is discussed extensively in refs. [151, 152].

Here the attention is restricted to the helicity-decoupled or centrifugal sudden (CS) approximation and its application to the $\text{CH} + \text{H}_2 \rightarrow \text{CH}_2 + \text{H}$ reaction. As already discussed in Section 2.9, the CS approximation sets Ω as a constant of motion. When the BF wavefunction ψ^{Jp} is expanded in terms of functions of the six internal coordinates and two Euler angles, β and γ , as follows:

$$\psi^{Jp}(R_\kappa, r_{1\nu}, r_{2\lambda}, \theta_1, \theta_2, \phi, \gamma, \beta, t) = \sum_{j_1 j_2 \Omega_1 \Omega} C_{j_1 j_2 \Omega_1 \Omega}^{Jp}(t) \psi_{j_1 j_2 \Omega_1 \Omega}^{Jp}(R_\kappa, r_{1\nu}, r_{2\lambda}) G_{j_1 j_2 \Omega_1 \Omega}^{Jp}(\theta_1, \theta_2, \phi, \gamma, \beta) \quad (4.7)$$

$\psi_{j_1 j_2 \Omega_1 \Omega}^{Jp}(R_\kappa, r_{1\nu}, r_{2\lambda})$ represents the value of the wavepacket associated with the parity-adapted angular basis function $G_{j_1 j_2 \Omega_1 \Omega}^{Jp}(\theta_1, \theta_2, \phi, \gamma, \beta)$ at the grid point, $R_\kappa, r_{1\nu}, r_{2\lambda}$. In eq. 4.7, κ, ν and λ label the points on the radial coordinate grids, j_1 and j_2 are the rotational quantum numbers of the diatoms, Ω is the projection of the total angular momentum onto the BF Z axis and Ω_1 is the projection of the rotational angular momentum j_1 onto the BF Z axis. Since Ω is fixed, Ω_2 (the projection of the rotational angular momentum j_2 onto the BF Z axis) is not an independent variable and its value is straightly determined by $\Omega_2 = \Omega - \Omega_1$.

The use of parity-adapted angular basis primitives has been suggested by several authors [152, 154, 155]. The parity adaptation means that certain linear superpositions

of primitive functions are used. These parity-adapted basis functions are given by:

$$G_{j_1 j_2 \Omega_1 \Omega}^{Jp}(\theta_1, \theta_2, \phi, \gamma, \beta) = \frac{1}{\sqrt{2 + \delta_{0\Omega} \delta_{0\Omega_1}}} \quad (4.8)$$

$$\times (G_{j_1 j_2 \Omega_1 \Omega}^J(\theta_1, \theta_2, \phi, \gamma, \beta) + (-1)^{J+p} G_{j_1 j_2 -\Omega_1 -\Omega}^J(\theta_1, \theta_2, \phi, \gamma, \beta))$$

with

$$G_{j_1 j_2 \Omega_1 \Omega}^J(\theta_1, \theta_2, \phi, \gamma, \beta) = P_J^{|\Omega|}(\cos \beta) \frac{\exp(i\Omega\gamma)}{\sqrt{2\pi}} \quad (4.9)$$

$$\times P_{j_1}^{|\Omega_1|}(\cos \theta_1) \frac{\exp(i\Omega_1\phi)}{\sqrt{2\pi}} P_{j_2}^{|\Omega-\Omega_1|}(\cos \theta_2)$$

where $P_J^{|\Omega|}$ denotes a normalized associated Legendre function. It should be noted that:

$$P_J^{|\Omega|}(\cos \beta) \frac{\exp(i\Omega\gamma)}{\sqrt{2\pi}} = \left(\frac{2J+1}{4\pi} \right)^{1/2} D_{\Omega 0}^{*J}(\alpha, \beta, \gamma) \quad (4.10)$$

where α, β and γ are the usual Euler angles [156] and $D_{\Omega 0}^{*J}$ the Wigner rotation matrix. This basis is called the "primitive coupled basis" to distinguish it from the j_{12} coupled basis used by Zhang and Zhang in which j_1 and j_2 are coupled together to form j_{12} [114]. This primitive coupled basis is a natural basis for the used algorithm for transforming from a basis to a grid representation when computing the action of the potential energy function.

4.3 Hamiltonian

The four-atom hamiltonian in atomic units (i.e. $\hbar = 1$) can be written as:

$$\hat{H} = -\frac{1}{2\mu} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_1} \frac{\partial^2}{\partial r_1^2} - \frac{1}{2\mu_2} \frac{\partial^2}{\partial r_2^2} \quad (4.11)$$

$$+ \frac{(\hat{J} - \hat{j}_1 - \hat{j}_2)^2}{2\mu R^2} + \frac{\hat{j}_1^2}{2\mu_1 r_1^2} + \frac{\hat{j}_2^2}{2\mu_2 r_2^2} + V$$

where $\hat{J}$ is the total angular momentum operator, $\hat{j}_1$ and $\hat{j}_2$ are the rotational angular momentum operators for each diatom, μ is the reduced mass of the tetratomic

collision complex, while μ_1 and μ_2 are the reduced mass of the diatomic fragments, and V represents the potential energy surface, which is a function of all six internal coordinates.

The used internal coordinates fall nicely into two groups: radial and angular. Then the hamiltonian can be partitioned into three general terms:

$$\hat{H}\psi = (\hat{T}_{\text{rad}} + \hat{T}_{\text{a}} + V)\psi \quad (4.12)$$

where $\hat{T}_{\text{rad}}$ is the radial kinetic energy term, $\hat{T}_{\text{a}}$ is the angular or rotational kinetic energy term and V is the potential energy term. Each contribution is treated separately.

The action of the radial kinetic energy operator can be accomplished in a variety of ways. In this work the radial coordinates that break or undergo large changes are treated with a dispersion fitted finite difference (DFFD) method [157]. The advantage of the DFFD method against the commonly used spectral methods such as the fast Fourier transform (FFT) [107] and discrete variable representation (DVR) methods [110] is that it is a local method. In contrast, the FFT and DVR methods are non local in each specific variable. Local methods reduce the amount of communication between processors and therefore vastly improve the scalability of parallel computing algorithms.

The action of the rotational operators in eq. 4.11 is most conveniently accomplished using a parity adapted angular basis set. With this basis, which uses primitive angular momentum functions, there is some minor off-diagonal coupling due to the first rotational term in eq. 4.11 is diagonal in this basis.

Finally, the action of the potential energy on the wavepacket is accomplished by first transforming to an angular grid, a multiplication by the diagonal potential on the grid, and a back transformation to the rotational quantum number basis [154, 158].

4.3.1 Radial coordinates: DFFD and PODVR methods

The three radial coordinates, R , r_1 , and r_2 , are represented on a three dimensional grid. As just mentioned, the action of the radial kinetic energy operator on the wavepacket is accomplished with a dispersion fitted finite difference (DFFD) method [157] to treat R and r_1 . In order to reduce the dimensionality of the problem we assume that r_2 bond does not break and a potential optimized discrete variable representation (PODVR) [159] method is used to treat this coordinate. In this Section, the PODVR and the DFFD methods are outlined.

The PODVR method is a DVR method, that is, the way of solving the Schrödinger equation consists of expanding the wavefunction in a basis of localized functions of the coordinates and solving the resulting matrix equation. The localized functions are approximate eigenfunctions of coordinate operators (see eq. 2.29) and they are orthogonal. The DVR localized functions are obtained from the diagonalization of coordinate matrices calculated using suitable primitive basis sets. The primitive basis functions are usually chosen to be polynomials of a function of the coordinate and do not have information about the potential energy surface. A useful way to reducing the size of basis sets to be used in multidimensional problems is to diagonalize convenient one-dimensional hamiltonians and use the eigenfunctions obtained to build the DVR localized functions. This is the key idea of the PODVR method.

The forms and positions of the DVR localized basis functions depend on the properties of the primitive basis sets. This one-dimensional basis set can be described by:

$$\{\phi_l(x), l = 1, 2, \dots, N_x\} \quad (4.13)$$

In this equation, only a basis set is considered because we have an one-dimensional problem in the r_2 coordinate. Using the primitive functions the corresponding DVR localized basis functions and, in order to obtain localized basis functions that have

some information about the potential energy surface, the PODVR proposes to use the following basis set:

$$\{\phi_l^{\text{PO}}(x), l = 1, 2, \dots, N_x^{\text{PO}}\} \quad (4.14)$$

where PO stands for potential optimized and $\phi_l^{\text{PO}}(x)$ are the eigenstates of a conveniently designed one-dimensional reference hamiltonian $\hat{H}_{\text{ref}}^x$:

$$\hat{H}_{\text{ref}}^x \phi_l^{\text{PO}}(x) = \epsilon_l^x \phi_l^{\text{PO}}(x) \quad (4.15)$$

Then the PODVR localized basis functions can be obtained and, once discarded functions such that the potential is greater than a potential energy cut off, the PODVR hamiltonian matrix can finally be calculated and diagonalized.

It could seem that using the PODVR method the advantage of an easy calculation of the hamiltonian matrix is lost. This is not so, because the eq. 4.15 can be solved using the usual DVR basis functions so that eventually one expresses the new PODVR basis functions in terms of the primitive basis functions of eq. 4.13. Thus the PODVR method can be seen as a transformation from the primitive basis functions of eq. 4.13 to localized basis sets that have some information about the potential energy surface.

The action of the radial R and r_1 kinetic energy operator has been treated using a finite difference (FD) method, in particular the DFFD one [157]. The FD methods are local approximation to derivatives whereas pseudospectral methods (FFT, DVR) are global approximations. In the latter methods, the second derivative matrix is a full matrix whereas in the former the matrix is banded.

FD methods are interested in approximations to the second derivative of some function $y(x)$ in the interval (a, b) defined on a grid as $y_i = y(x_i)$ where $x_i = x_0 + i\Delta$ with $i = 1, 2, \dots, N$ and $\Delta = (b - a)/(N + 1)$. The end points a and b are not among the N grid points, with boundary conditions such that the represented function is zero

at a and b . A $(2n + 1)$ -point FD approximation to second derivative of $y(x)$ is:

$$\mathbf{y}'' = \mathbf{D}'' \mathbf{y} \quad (4.16)$$

where $\mathbf{y}$ denotes the $N \times 1$ column vector of components y_i and $\mathbf{y}''$ denotes the column vector of approximate second derivative components, $y_i'' \approx (\partial^2 y / \partial x^2)_{x=x_i}$.

$\mathbf{D}''$ is a symmetrically banded matrix with nonzero elements of the form:

$$\mathbf{D}'' = \frac{1}{\Delta^2} \begin{pmatrix} d_0 & d_1 & \dots & d_n \\ d_1 & d_0 & d_1 & \dots & d_n \\ \dots & d_1 & d_0 & d_1 & \dots & d_n \\ d_n & \dots & d_1 & d_0 & d_1 & \dots & d_n \\ & d_n & \dots & d_1 & d_0 & d_1 & \dots & d_n \\ & & d_n & \dots & d_1 & d_0 & d_1 & \dots & d_n \\ & & & d_n & \dots & d_1 & d_0 & d_1 & \dots & d_n \\ & & & & d_n & \dots & d_1 & d_0 & d_1 & \dots & d_n \end{pmatrix} \quad (4.17)$$

The dispersion relation, i.e. the relation between the wavenumber and the eigenvalue of the spectrum of $\mathbf{D}''$, is:

$$f(k) = \frac{1}{\Delta^2} \left[d_0 + 2 \sum_{s=1}^n d_s \cos(sk\Delta) \right] \quad (4.18)$$

where k is the wavenumber that for the finite grid representation takes the values of $k = k_j = j\pi / [(N + 1)\Delta]$, with $j = 1, 2, \dots, N$. Since $p_j = \hbar k_j$ corresponds to a momentum, the quantum view of eq. 4.18 is that it yield the momentum representation of $\mathbf{D}''$.

From Fourier transformation theory (i.e. the evaluation of the second derivative using Fourier transforms) or basic quantum mechanics it is known that the continuous limit wavenumber representation of d^2/dx^2 is simply $-k^2$. This suggests that the correct dispersion relation should be:

$$f_{\text{exact}}(k_j) = -k_j^2 \quad (4.19)$$

The standard FD approximations result from Taylor series expanding of eq. 4.18 about $k_j = 0$ and the coefficients can be easily calculated. For example, the 3-point FD has $d_0 = -2$ and $d_1 = 1$ and the 5-point FD has $d_0 = -30/12$, $d_1 = 16/12$ and $d_2 = -1/12$.

The essential idea of the DFFD method is to attempt to fit eq. 4.18 to eq. 4.19 over some range of $K_j = k_j \Delta$ values that leads to a maximum absolute error between eq. 4.18 and eq. 4.19 less than or equal to some pre-specified value, ϵ . More specifically, the reduced variable K_j is defined on a $[0, \pi]$ interval. Generally, the error in an FD approximation increases with K_j . The Taylor series approach is essentially perfect for very small K_j , but quickly deviates from the correct, quadratic dependence of eq. 4.19. The generic behaviour is that the error increases monotonically with K_j . Instead of requiring that the fit be perfect in the limit of very small K_j , the DFFD method requires that the error be no larger than ϵ from $K_j = 0$ up to some $K_{\max}$ determined by ϵ . Still ϵ is chosen to be small, e.g. in the $10^{-3} - 10^{-6}$ range. However, the result is that, while the error on the lower K_j limit is not so quite good as that in the Taylor series approximation, the error for higher K_j is much improved, and, overall, since any given problem involves a large range of K_j values, better results can be obtained for comparable grid spacing.

However, the main advantage of the DFFD method is that it is inherently more suitable for large scale parallel computing because it eliminates the need for large amounts of interprocessor communication. In almost every case, the DFFD method requires only nearest-neighbour communication between processors. For example, let R be discretized in a 100 point grid. The computation over four processors implies that every processor will hold 25 grid points of the wavefunction ψ . If $s = 6$ in eq. 4.18, then $(2s + 1) = 13$ grid points are used to compute the R kinetic energy at each grid point, except for the points close to the grid boundary, and values of the wavefunction at 6 points on each side are needed. Let number processor in ascending

order starting with 1, so that processor 1 holds the 25 first grid points, and processor 4 holds the last 25 points. Then processors 1–3 will pass the values of the wavefunction at their last 6 points to their right neighbours, and processors 2–4 will pass the values of the wavefunction at their first 6 points of their left neighbours. The DFFD edge correction is evaluated at the first 5 points of the processor 1 and at the last 5 points of the processor 4. The evaluation of the radial kinetic energy at points 6 – 19 at each processor is local and does not need data from other processor. Figure 4.2 displays this parallelization scheme.

4.3.2 Rotational basis

The rotational basis described in eq. 4.9 leads to a block diagonal matrix $\mathbf{T}_a$. This matrix is diagonal in j_1 and j_2 and tridiagonal in Ω and Ω_1 :

$$\begin{aligned}
 \langle j_1 j_2 \Omega \Omega_1 | \hat{T}_a | j_1 j_2 \Omega' \Omega'_1 \rangle = & \\
 & \frac{1}{2} \left(\sum_{i=1}^2 \left(\frac{1}{\mu R^2} + \frac{1}{\mu_i R_i^2} \right) j_i(j_i + 1) \right) \delta_{\Omega_1 \Omega'} \delta_{\Omega' \Omega} \\
 & + \frac{1}{2} \frac{1}{\mu R^2} \{ J(J+1) - 2\Omega(\Omega - \Omega_1) - 2\Omega_1^2 \} \delta_{\Omega'_1 \Omega_1} \delta_{\Omega' \Omega} \\
 & + \frac{1}{2} \frac{(-1)^\beta}{\mu R^2} \left\{ -c^-(j_2, \Omega_2) c^-(J, \Omega) \delta_{\Omega'_1 \Omega_1} \delta_{\Omega' \Omega - 1} \right. \\
 & \quad - c^+(j_2, \Omega_2) c^+(J, \Omega) \delta_{\Omega'_1 \Omega_1} \delta_{\Omega' \Omega + 1} \\
 & \quad + c^-(j_2, \Omega_2) c^+(j_1, \Omega_1) \delta_{\Omega'_1 \Omega_1 + 1} \delta_{\Omega' \Omega} \\
 & \quad + c^+(j_2, \Omega_2) c^-(j_1, \Omega_1) \delta_{\Omega'_1 \Omega_1 - 1} \delta_{\Omega' \Omega} \\
 & \quad - c^-(j_1, \Omega_1) c^-(J, \Omega) \delta_{\Omega'_1 \Omega_1 - 1} \delta_{\Omega' \Omega - 1} \\
 & \quad \left. - c^+(j_1, \Omega_1) - c^+(J, \Omega) \delta_{\Omega'_1 \Omega_1 + 1} \delta_{\Omega' \Omega + 1} \right\} \quad (4.20)
 \end{aligned}$$

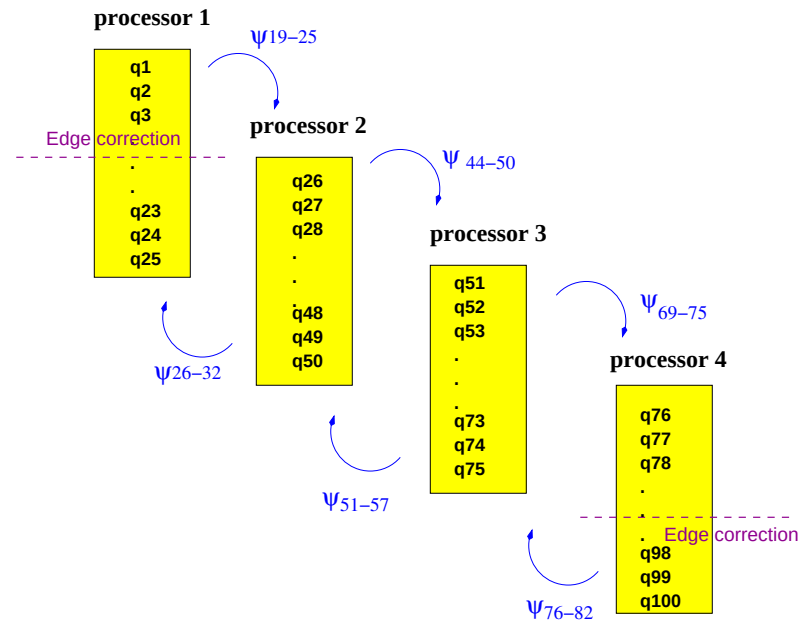


Figure 4.2: Parallelization scheme to treat radial coordinates using DFFD method.

where $c^\pm(n, m) = \eta \sqrt{n(n+1) - m(m \pm 1)}$, $\Omega_2 = \Omega - \Omega_1$, $\eta = 1/\sqrt{2}$, if both Ω and Ω_1 are equal to zero or if both Ω' and Ω'_1 are equal to zero, otherwise $\eta = 1$. The Condon-Shortley phase correction, β , is given by:

$$\beta = (\Omega + \Omega') + \frac{1}{2} (|\Omega| + |\Omega'| + |\Omega_1| + |\Omega_2| + |\Omega'_1| + |\Omega'_2|) \quad (4.21)$$

This Condon-Shortley phase correction to the coefficients of Gatti *et al.* [151, 152] is required because, for reason of convenience, it has not been used Condon-Shortley phases in the basis. The standard definitions of the angular momentum operators used by Gatti *et al.*, however, do assume the Condon-Shortley convention. Thus, when the kinetic energy terms in the hamiltonian are constructed, the transformation into a Condon-Shortley basis has to be done.

4.3.3 Parity adapted rotational basis functions

The use of parity adapted basis functions has several advantages, namely, it allows to use real sine and cosine basis functions for the torsional angle ϕ , it allows to focus only on positive values of Ω , and for the case of $\Omega=0$, it allows to divide the calculation into two smaller calculations for each separate parity block. For all other values of Ω , the two parity blocks are degenerate. Except for the factor η , the expression in eq. 4.20 is identical to the expression for the non parity adapted basis [156], except that only positive values of Ω need to be considered.

When $\Omega=0$, after integrating over the Euler angles, the parity adapted basis functions reduce to

$$\begin{aligned} G_{j_1 j_2 \Omega_1 \Omega}^{Jp}(\theta_1, \theta_2, \phi) = & P_{j_1}^{|\Omega_1|}(\cos \theta_1) P_{j_2}^{|\Omega - \Omega_1|}(\cos \theta_2) \frac{1}{\sqrt{2(1 + \delta_{0\Omega_1})}} \\ & \times \left(\frac{e^{i\Omega_1 \phi}}{\sqrt{2\pi}} + (-1)^{(J+p)} \frac{e^{-i\Omega_1 \phi}}{\sqrt{2\pi}} \right) \end{aligned} \quad (4.22)$$

which results in two separate parity blocks with sine and cosine functions, respectively.

For $\Omega > 0$, however, we must also consider the Euler angles, β and γ :

$$G_{j_1 j_2 \Omega_1 \Omega}^{Jp}(\theta_1, \theta_2, \phi, \gamma, \beta) = P_J^{|\Omega|}(\cos \beta) P_{j_1}^{|\Omega_1|}(\cos \theta_1) P_{j_2}^{|\Omega - \Omega_1|}(\cos \theta_2) \\ \times \frac{1}{\sqrt{2}} \left(\frac{e^{i\Omega\gamma} e^{i\Omega_1\phi}}{2\pi} + (-1)^{(J+p)} \frac{e^{i\Omega\gamma} e^{-i\Omega_1\phi}}{2\pi} \right) \quad (4.23)$$

When $(-1)^{(J+p)} = 1$, the resulting basis function have the form:

$$G_{j_1 j_2 \Omega_1 \Omega}^{Jp}(\theta_1, \theta_2, \phi, \gamma, \beta) = P_J^{|\Omega|}(\cos \beta) P_{j_1}^{|\Omega_1|}(\cos \theta_1) P_{j_2}^{|\Omega - \Omega_1|}(\cos \theta_2) \\ \times \frac{1}{\sqrt{2\pi}} (\cos(\Omega\gamma) \cos(\Omega_1\phi) - \sin(\Omega\gamma) \sin(\Omega_1\phi)) \quad (4.24)$$

Note here that the integration over the Euler angle γ results in two separate blocks in the torsional angle ϕ , one with cosine and one with sine functions. Both blocks, however, contribute to the $(-1)^{J+p} = 1$ calculation. It is easy to see that the other parity case, $(-1)^{J+p} = -1$, leads to an identical energy expression.

4.3.4 Evaluation of the potential term

The straightforward use of the basis set given in eqs. 4.7–4.10 would result in a very large, dense, potential energy matrix. Such matrices are very inefficient, not only because they require huge amounts of memory for storage (a different version of the matrix must be stored for each radial grid point) but also from a computational standpoint [158]. Thus, it is highly desirable to transform to a basis in which the potential matrix is diagonal, i.e. a grid basis in the angular coordinates.

Primarily the primitive coupled basis is chosen because it naturally lends itself to a simple, highly efficient method evaluating action of the potential energy operator.

The potential matrix, $\mathbf{V}$, may be written as a numerical quadrature over the angular grid points in the following matrix form:

$$\mathbf{V} = \mathbf{P}^T \mathbf{V}_g \mathbf{P} \quad (4.25)$$

where $\mathbf{P}$ is a transformation matrix and $\mathbf{V}_g$ is a diagonal matrix with the potential values on the angular grid. Since $\mathbf{V}_g$ is the potential energy as a function of the grid points and $\mathbf{P}$ depends on the angular but not the radial coordinates, eq. 4.25 represents an enormous savings in computer memory. The operation $\mathbf{P}^T \mathbf{V}_g \mathbf{P}$ is equivalent to transforming from the coupled basis to a suitable grid representation, multiplying by $\mathbf{V}_g$, and then transforming back to the coupled basis. The algorithm used starts with the recognition that the problem can be formulated so that the transformation matrix $\mathbf{P}$ reduces to the product of sparse block matrices with submatrices $\mathbf{P}^1$, $\mathbf{P}^2$ and $\mathbf{P}^3$, each of which is a function of only one angular coordinate: θ_1 , θ_2 and ϕ respectively.

The elements of $\mathbf{P}^1$ are given by:

$$P_{ij}^1 = P_{j_1}^{\Omega_1}(x_{1i})\sqrt{w_i} \quad (4.26)$$

where $P_{j_1}^{\Omega_1}$ is a normalized associated Legendre polynomial, $x_{1i} = \cos \theta_{1i}$ is the i th Gauss-Legendre quadrature point and w_i is the corresponding quadrature weight. An analogous definition holds for the $\mathbf{P}^2$. Note that $\mathbf{P}^1$ and $\mathbf{P}^2$ depend on Ω_1 .

When $\Omega=0$, the elements of $\mathbf{P}^3$ for even parity are given by:

$$\begin{aligned} P_{i0}^3 &= \left(\frac{1}{\phi}\right)^{1/2} \\ P_{ij}^3 &= \left(\frac{2}{\phi}\right)^{1/2} \cos(j\phi_i) \quad j > 0 \end{aligned} \quad (4.27)$$

where $\phi_i = (i - 1/2)\pi/n_\phi$ being n_ϕ the number of grid points for ϕ . For odd parity, the elements of $\mathbf{P}^3$ are given by:

$$P_{ij}^3 = \left(\frac{2}{\phi}\right)^{1/2} \sin(j\phi_i) \quad (4.28)$$

where $\phi_i = i\phi/n_\phi$. When $\Omega \neq 0$, there will be a block of sine and a block of cosine basis functions. For $\Omega \neq 0$ and $\Omega_1 \neq 0$, however, the basis functions must be multiplied by $\sqrt{2}$.

The basis to grid transformation is accomplished by a sequence of matrix-vector multiplications involving relatively small matrices. Note that, because $\mathbf{P}^1$ and $\mathbf{P}^2$ depend on Ω_1 , the order of these transformations is important. Schematically, the steps required to compute the potential term of the hamiltonian are as follows:

$$\begin{aligned}
 (1) \quad |j_1 j_2 \Omega_1\rangle & \xrightarrow{\mathbf{P}^1} |\theta_1 j_2 \Omega_1\rangle \\
 (2) \quad |\theta_1 j_2 \Omega_1\rangle & \xrightarrow{\mathbf{P}^2} |\theta_1 \theta_2 \Omega_1\rangle \\
 (3) \quad |\theta_1 \theta_2 \Omega_1\rangle & \xrightarrow{\mathbf{P}^3} |\theta_1 \theta_2 \phi\rangle \\
 (4) \quad |\theta_1 \theta_2 \phi\rangle & \longrightarrow V |\theta_1 \theta_2 \phi\rangle \\
 (5) \quad |\theta_1 \theta_2 \phi\rangle & \xrightarrow{\mathbf{P}^{3T}} V |\theta_1 \theta_2 \Omega_1\rangle \\
 (6) \quad |\theta_1 \theta_2 \Omega_1\rangle & \xrightarrow{\mathbf{P}^{2T}} V |\theta_1 j_2 \Omega_1\rangle \\
 (7) \quad |\theta_1 j_2 \Omega_1\rangle & \xrightarrow{\mathbf{P}^{1T}} V |j_1 j_2 \Omega_1\rangle
 \end{aligned}$$

This method of treating the angular variables combined with the use of the real wavepacket method, the DFFD for the radial variables and parallel computing techniques results in a very efficient prescription for treating four-atom systems using wavepackets.

4.4 Initial wavepacket

The propagation of the wavepacket starts in the asymptotic region in the reactant channel. The initial wavepacket needs a lineal momentum or kinetic energy to move along the interaction region direction. It also must contain the rovibrational information of reactant fragments.

A typical initial wavepacket is an incoming Gaussian wave consistent with particular diatomic vibrational and rotational quantum numbers. The initial wavepacket can be written as:

$$\psi(t=0) = g_{k\alpha}(R) \psi_{v_1}(r_1) \psi_{v_2}(r_2) G_{j_1 j_2 \Omega_1 \Omega}^{Jp}(\theta_1, \theta_2, \phi, \gamma, \beta) \quad (4.29)$$

where $\psi_{v_1}(r_1)$ and $\psi_{v_2}(r_2)$ represent specific diatomic initial vibrational states for the two initial molecules, $G_{j_1 j_2 \Omega_1 \Omega}^{Jp}(\theta_1, \theta_2, \phi, \gamma, \beta)$ are the parity adapted angular basis (see eq. 4.7) and $g_{k\alpha}(R)$ is a Gaussian describing the initial relative motion of the reactants consistent with a collision energy k and with position spread α given by:

$$g_{k\alpha}(R) = \pi^{-1/4} \alpha^{-1/2} \exp\left(\frac{-(R - R_0)^2}{2\alpha^2}\right) \exp(-ik_0) \quad (4.30)$$

where R is the distance between the centers of mass of the two reactant molecules. Note that eq. 4.30 contains equal parts of a Gaussian wavepacket moving inward in R with a wavevector $-k_0$ and outward in R with the a wavevector $+k_0$. The initial wavepacket is centered at $R=R_0$ and it has a certain α spread in space. Accordingly, the smaller α spread, the larger spread in energies will be in the wavepacket (according with the Heissenberg's uncertainty Principle). The spread of the initial wavepacket in the momentum space can be obtained by the Fourier transform of eq. 4.30:

$$\begin{aligned} \bar{g}(k) &= \frac{1}{2\pi} \int_0^\infty \exp[-ikR] g(R) dR \\ &= \sqrt{\frac{\alpha}{2\pi^{3/2}}} \exp(-ik_0) \exp\left(-\frac{\alpha^2(k - k_0)^2}{2}\right) \end{aligned} \quad (4.31)$$

This equation also includes both incoming and outgoing components.

Since the total energy is a constant of motion, each wavepackets can be considered independent one to another and a single wavepacket calculation can yield the desired dynamical information over a wide range of energies (remind that this feature is the main advantage of the time-dependent methods against the time independent

ones). Thus, the time propagation of a wavepacket will yield the information of the reaction probability in the energy range $E = (\hbar k)^2/2\mu + \epsilon_{vj}$ for which $\bar{g}(-k)$ has a significant value.

4.5 Wavepacket absorption

Scattering wavepacket calculations are complicated by the fact that the amplitude can be reflected off boundaries of any grid used to represent a scattering coordinate. One approach to minimize this feature is to periodically absorb amplitude in a small portion of the grid close to the boundary [108, 160, 161]. Interaction representations may also reduce some of the problems [162, 163]. Another approach is to apply an optical potential [161, 164]. In the present work, the former approach has been used. Moreover, in this approach the absorption leads to an useful rule, when one is interested in applying the absorption at every time step τ , with τ not too large. Thus one can define an operator $\hat{A}$ for the absorption. With R denoting the scattering variable, a coordinate representation of $\hat{A}$ might be:

$$\hat{A}(R) = \begin{cases} 1 & \text{when } R \leq R_a \\ \exp[-C_a(R - R_a)^2] & \text{when } R_a < R \leq R_{\max} \end{cases} \quad (4.32)$$

which absorbs the wavefunction in $[R_a, R_{\max}]$, with $R_{\max}$ denoting the maximum value of R on the grid. The preferred absorption is such that per iteration the wavefunction loses only a small amount of amplitude in the absorption region. As one continually iterates, the effect of applying $\hat{A}$ many times eliminates or prevents significant amplitude build up in the absorption region. The absorption procedure here outlined will be detailed in the next Section.

4.6 Real wavepacket propagation

As already mentioned, Balint-Kurti and Gray demonstrated that despite the complex nature of the wavefunction one can propagate only the real part of the wavepacket (RWP) and obtain sufficient information to compute observables associated with the dynamics, including **S** matrices for reactive scattering processes [93]. Let's define τ some arbitrary time step which should (and does) cancel out in any correct formulæ for any observable. From eq. 4.2 and its backwards one can write:

$$\psi(x, t + \tau) = e^{-i\hat{H}\tau/\hbar}\psi(x, t) = [\cos(\hat{H}\tau/\hbar) - i\sin(\hat{H}\tau/\hbar)] \psi(x, t) \quad (4.33)$$

$$\psi(x, t - \tau) = e^{-i\hat{H}\tau/\hbar}\psi(x, t) = [\cos(\hat{H}\tau/\hbar) + i\sin(\hat{H}\tau/\hbar)] \psi(x, t) \quad (4.34)$$

Adding these two equations one obtains:

$$\psi(x, t + \tau) = -\psi(x, t - \tau) + 2\cos(\hat{H}\tau/\hbar)\psi(x, t) \quad (4.35)$$

This expression does not involve the imaginary number i . If one denotes the real part of the wavepacket as $q(x, t)$ and the imaginary part as $p(x, t)$ (that is, $\psi(x, t) = q(x, t) + ip(x, t)$, where $q(x, t) = \text{Re}[\psi(x, t)]$ and $p(x, t) = \text{Im}[\psi(x, t)]$), eq. 4.35 can be written as follows:

$$q(x, t + \tau) = -q(x, t - \tau) + 2\cos(\hat{H}\tau/\hbar) q(x, t) \quad (4.36)$$

$$p(x, t + \tau) = -p(x, t - \tau) + 2\cos(\hat{H}\tau/\hbar) p(x, t) \quad (4.37)$$

where p and q are always real-valued functions. These equations mean that the real and imaginary parts of ψ can be propagated independently each other. In order to evolve just the real part q given some initial condition $\psi(x, t = 0) = q(x, 0) + ip(x, 0)$, one first obtains $q(x, t)$ via eq. 4.35 which leads to:

$$q(x, t = 0) = \cos(\hat{H}\tau/\hbar)q(x, t = 0) + \sin(\hat{H}\tau/\hbar)p(x, t = 0) \quad (4.38)$$

and then eq. 4.36 may be repeatedly applied to obtain $q(x, t)$ in discrete time steps τ .

Equation 4.35 must be modified for scattering applications which use absorption techniques. Absorption of the wavepacket amplitude that approaches the edges of the computational grid can be accomplished by periodically damping out the wavepacket in small regions at the grid edges [160]. Suppose $\hat{A}$ represents the absorption operation. Instead of eqs. 4.33 and 4.34, one has:

$$\psi(t + \tau) = \hat{A} \exp(-i\hat{H}\tau/\hbar) \psi(t) \quad (4.39)$$

$$\psi(t - \tau) = \exp(-i\hat{H}\tau/\hbar) \hat{A}^{-1} \psi(t) \quad (4.40)$$

where for simplicity the set of coordinates x has been dropped. If $\hat{A}$ is "weak" enough such it commutes with $\hat{H}$, then one can obtain:

$$\hat{A}^{-1}\psi(t + \tau) + \hat{A}\psi(t - \tau) \approx 2 \cos(\hat{H}\tau/\hbar)\psi(t) \quad (4.41)$$

and multiplying both sides of this equation by $\hat{A}$ one can obtain:

$$\psi(t + \tau) = \hat{A} \left[-\hat{A}\psi(t - \tau) + 2 \cos(\hat{H}\tau/\hbar)\psi(t) \right] \quad (4.42)$$

which has found to be a more stable iterative scheme. The real part of the wavepacket then satisfies

$$q(t + \tau) = \hat{A} \left[-\hat{A}q(t - \tau) + 2 \cos(\hat{H}\tau/\hbar)q(t) \right] \quad (4.43)$$

This equation represents the first iteration of the RWP idea, but it is not the most efficient. When using time-dependent quantum dynamics to calculate stationary observables, the role of the time lies mainly on the fact that the problem becomes an initial value one and a single calculation provides information over a range of energies. Because time does not enter in any fundamental way into the observables which are to be calculated, it is permissible to replace $\hat{H}$ with $f(\hat{H})$ in the time-dependent Schrödinger equation 4.1 and the modified time evolution equation reads:

$$i\hbar \frac{\partial \chi(u)}{\partial u} = f(\hat{H})\chi(u) \quad (4.44)$$

As long as $f(E)$ is one-to-one mapping, each eigenvalue E of $\hat{H}$ will be mapped onto one unique value $f(E)$. Dynamics of eq. 4.44 can be related to the dynamics of the usual Schrödinger equation 4.1 and its stationary solution is also a stationary solution of eq. 4.44, that is, if $\hat{H}\varphi_n = E_n\varphi_n$, then $f(\hat{H})\varphi_n = f(E_n)\varphi_n$. Therefore, if the initial condition for both eqs. 4.1 and 4.44 is the same, $\chi(0) = \psi(0)$, one has:

$$\psi(t) = \sum_n c_n \varphi_n \exp(-iE_n t/\hbar) \quad (4.45)$$

and

$$\chi(u) = \sum_n c_n \varphi_n \exp(-iE_n u/\hbar) \quad (4.46)$$

where the coefficients c_n are the same in both equations. The difference between these equations is only the time-dependent phase associated with each stationary state.

The corresponding cosine iteration equation (including absorption) for the real part of $\chi(u)$ can be derived following identical arguments which led to eq. 4.43. Accordingly, if $q(u)$ denotes the real part of $\chi(u)$, $q(u) = \text{Re}[\chi(u)]$, the cosine iteration equation reads:

$$q(u + \delta) = \hat{A} \left[-\hat{A}q(u - \delta) + 2 \cos(f(\hat{H})\delta/\hbar) q(u) \right] \quad (4.47)$$

In this work, the particular function chosen for $f(\hat{H})$ is:

$$f(\hat{H}) = -\frac{\hbar}{\delta} \arccos(\hat{H}_s) \quad (4.48)$$

where $\hat{H}_s$ is a scaled and shifted hamiltonian operator (eq. 4.4) such that its minimum and maximum eigenvalues lie between -1 and $+1$. If ψ_E is an stationary state of $\hat{H}$ with eigenvalue E , then it will also be a stationary state of $f(\hat{H})$ with eigenvalue $E_s = a_s E + b_s$. With this particular function, the final cosine iterative equation reads:

$$q(u + \delta) = \hat{A} \left[-\hat{A}q(u - \delta) + 2\hat{H}_s q(u) \right] \quad (4.49)$$

This equation is also called the Mandelstam and Taylor's damped Chebyshev recursion relation [122]. The remarkable feature of using the function of eq. 4.49 is that it solves the propagation problem and it is no necessary to construct any approximation to the exponential propagator. The initial step in the interactive process is:

$$q(u=0) = \hat{H}_s q(u=0) - \sqrt{1 - \hat{H}_s^2} p(u=0) \quad (4.50)$$

where the square root can be evaluated with a Chebyshev polynomial expansion.

To conclude this Section, the relation between the modified Schrödinger equation evolution for $\chi(u)$ (eq. 4.44) and the usual Schrödinger equation (eq. 4.1) will be deduced. The first step to find this relation is to approximate $f(\hat{H})$ via a Taylor series expansion

$$f(\hat{H}) \approx f(\bar{E}) + \left. \frac{df(E)}{dE} \right|_{\bar{E}} (\hat{H} - \bar{E}) \quad (4.51)$$

where $\bar{E}$ is the average energy of the wavepacket. With the particular choice for $f(\hat{H})$ of eq. 4.48 is easy to reduce eq. 4.44 to:

$$i\hbar \frac{\partial \chi(u)}{\partial u} = [\alpha(\bar{E}) + \beta(\bar{E})\hbar\hat{H}] \chi(u) \quad (4.52)$$

where

$$\beta(\bar{E}) = \frac{a_s \hbar}{\delta \sqrt{1 - \bar{E}_s^2}} \quad (4.53)$$

with $\bar{E}_s = a_s + b_s$. A solution of eq. 4.52 is indeed a related solution of eq. 4.1 via a simple phase vector and a time scaling, $u = t/\beta$:

$$\psi(t) \approx \exp[i\alpha t/\beta] \chi(u) \quad (4.54)$$

with the approximate sign being used because of the linear truncation used in eq. 4.51. Equation 4.54 allows to (approximately) equate physical time t and RWP (or Chebyshev) iterations. If u is measured in steps of $k\delta$ with $k = 1, 2, \dots$, then the physically defined time in the RWP propagation can be approximately evaluated by:

$$t \approx \frac{a_s \hbar k}{\sqrt{1 - \bar{E}_s^2}} \quad (4.55)$$

Time does not play any role into the observables which are to be calculated, time only plays an "intermediary" role in the energy dependent observable calculation.

4.7 Wavepacket analysis

After propagation, once the wavepacket is located in one of the possible reaction channels, the wavepacket analysis gives the information needed to obtain the dynamical magnitudes. One analysis technique involves accumulation and Fourier analysis of time-dependent final state amplitudes in the asymptotic product region [126, 165]. Analysis techniques can also be based on calculating the flux through a more general surface (not forced to be in the asymptotic region) [114, 164]. Reference [127] details how the use of the asymptotic product analysis to determine the reaction probability from a real wavepacket propagation is equivalent to a particular limit of flux-based formula.

In this study of the CH + H₂ reaction, the flux analysis approach (as formulated in ref. [127]) has been used to analyse the wavepacket. In this method a surface dividing reactants from products is defined and the flux normal to this surface is saved (as a function of effective energy). The total reaction probability out of some state consistent with the given set of initial quantum numbers $J, p, \Omega, j_1, j_2, \Omega_1$ (which are often dropped for sake of simplicity) is given by:

$$P(E) = \langle \psi(E) | \hat{F} | \psi(E) \rangle \quad (4.56)$$

with $\psi(E)$ being an energy-resolved scattering function. In eq. 4.56 $\hat{F}$ is a flux operator, usually involving some reaction coordinate s (such that the condition $s=s_0$ separates the reactant and products) or other analysis regions:

$$\hat{F} = \frac{\hbar}{2i\mu_s} \left[\delta(s - s_0) \frac{\partial}{\partial s} - \frac{\partial}{\partial s} \delta(s - s_0) \right] \quad (4.57)$$

where μ_s is the reduced mass associated with s . If a scattering process is being studied, one of the diatomic bond distances, r_1 or r_2 (depending on the channel considered), can be used as s . However, in the case of capture probability R is used as s . Insertion of eq. 4.57 into eq. 4.56, then leads to:

$$P(E) = \frac{\hbar}{\mu_s} \text{Im} \left\langle \psi(E) \left| \delta(s - s_0) \frac{\partial}{\partial s} \right| \psi(E) \right\rangle \quad (4.58)$$

The time-independent energy-resolved scattering wavefunction, $\psi(E)$, can be obtained from the propagated wavepackets in time, $\psi(t)$, expanding as:

$$\psi(t) = \frac{1}{2\pi\hbar} \int e^{-iEt/\hbar} \psi^+(E) a_\psi(E) dE \quad (4.59)$$

and Fourier transforming this expression leads to:

$$\psi(E) = \frac{1}{a_\psi(E)} \int e^{-i(E-\hat{H})t/\hbar} \psi(t=0) dt \quad (4.60)$$

where $a_\psi(E) = \langle \psi^+(E) | \psi(t=0) \rangle$ is a normalization constant.

Strictly speaking, however, since the real wavepacket approach is applied and $\hat{H}$ is replaced by $f(\hat{H})$ and ψ by χ , $P(E)$ must be referred as $P(f(E))$. To get from $P(f(E))$ back to $P(E)$, one has to realize that "f" normalized scattering functions are related to E normalized ones by $\chi^+ = \sqrt{|dE/df|} \psi^+$. Thus, if the initial condition for the modified Schrödinger equation is the same as for the ordinary one, $\chi(t=0) = \psi(t=0)$, the amplitude can be calculated with $a_\chi(f) = \langle \chi^+ | \chi(0) \rangle = \sqrt{|dE/df|} a_\psi(E)$.

Since only the real part $q_\chi(t)$ is propagated at discrete times (or iterations) $k\tau$, one can employ Fourier series to evaluate the integrals and $P(E) = |df/dE| P(f)$, the reaction probability (eq. 4.58), can be rewritten as:

$$P(E) = \frac{4\hbar^3}{\mu_s} \frac{a_s^2}{1 - E_s^2} \frac{1}{|a_\psi(E)|^2} \text{Im} \left\langle \sum_k^\infty e^{i\theta(E)k} q_\chi(k\tau) \left| \sum_{k'}^\infty e^{i\theta(E)k'} \left[\delta(s - s_0) \frac{\partial}{\partial s} q_\chi(k'\tau) \right] \right. \right\rangle \quad (4.61)$$

where $\theta(E) = -\arccos(a_s E + b_s)$ and df/dE has been explicitly evaluated.

4.8 Rate coefficients

In order to calculate thermal rate coefficients, one begins with the standard formula for the reaction rate coefficient at a given temperature T , which involves a Boltzmann distribution over the cumulative reaction probability:

$$k(T) = \frac{\sigma}{2\pi Q_{\text{react}}(T)} \int e^{-E_{\text{tr}}/k_{\text{B}}T} N(E) dE \quad (4.62)$$

where σ is an overall electronic degeneracy factor for the reaction, E is the total energy of the system and $Q_{\text{react}}(T)$ is the partition function of the reactants and k_{B} is the Boltzmann constant. $N(E)$ is the cumulative reaction probability given by:

$$N(E) = \sum_{J=0}^{J_{\text{max}}} (2J+1) N^J(E) \quad (4.63)$$

where $N^J(E)$ is the sum of all possible reactive transition probabilities. Clever methods based on focusing directly on $N(E)$, including time-independent Green's operator techniques, [166], the transition state wavepacket method [167, 168] and thermal flux operator approaches [169] can reduce the required computational effort.

At the temperatures to be considered in the present work, the reactants will be in their vibrational ground state, so that $Q_{\text{react}}(T) = Q_{\text{tr}}(T)Q_{\text{rot}}(T)$. For a reaction of two diatomic molecules, we may rewrite the expression for the rate coefficient in terms of a Boltzmann weighted average over state-specific reaction probabilities as follows:

$$k(T) = \frac{\sigma}{2\pi\hbar Q_{\text{tr}}(T)} \sum_{J=0}^{J_{\text{max}}} (2J+1) \sum_j \frac{e^{-E_{\text{rot}}/k_{\text{B}}T}}{Q_{\text{rot}}(T)} \int_0^\infty e^{-E_{\text{tr}}/k_{\text{B}}T} P(E, J, j) dE_{\text{tr}} \quad (4.64)$$

where $P(E, J, j)$ is the reaction probability for each specific state with quantum numbers $J, \Omega, j_1, j_2, \Omega_1, p$. These are collectively denoted by J, j with J being as

usual the total angular momentum, Ω the projection of J onto the BF Z axis, j_1 and j_2 the rotational angular momentum of, respectively, H_2 and CH , Ω_1 the projection of j_1 onto the BF Z axis, and p the parity. The total energy is given by $E = E_{\text{tr}} + E_{\text{rot}} + E_{\text{vib}}$, where E_{tr} is the relative translational energy, $E_{\text{rot}} = B_1 j_1(j_1 + 1) + B_2 j_2(j_2 + 1)$ is the rotational energy of the isolated diatoms and E_{vib} is the combined zero point of the vibrational energies of the reactants.

An exact calculation of the thermal rate coefficient $k(T)$ of the $\text{CH} + \text{H}_2$ reaction though in the realm of possibility, is so expensive and time consuming to be at present unfeasible. In fact, the number of both the initial rovibrational states and the collision energies needed becomes rapidly unmanageable as the temperature increases. Moreover, an exact calculation of the probabilities $P(E, J, j)$ is not an easy task because of the explosive growth in the number of allowed states as J increases. For this reason, in the present work the rate coefficients for the $\text{CH} + \text{H}_2$ reaction were calculated using statistical models specifically designated for complex-forming reactions. In particular, the Capture Phase Space Theory (C/PST) model with a Monte Carlo sampling procedure to select the initial reactant quantum states was used. The obtained C/PST rate coefficients were then compared with those calculated using the simplest version of the Phase Space Theory (PST) and quasiclassical trajectory (QCT) methods.

4.9 Statistical models for complex-forming reactions

It is well known that for reactions involving a stable intermediate complex exact quantum cross sections and rate coefficients are difficult to calculate. Unlike direct abstraction reactions, these processes are often dominated by deep potential wells that support a large number of quantum states. Paradoxically, the reasons that causes the difficulties in an exact quantum treatment, namely, the formation of long-lived

complexes, may make converged quantum calculations of the highly oscillatory reaction probabilities unnecessary because the formation and decay of the complexes can be reasonably described by statistical arguments. As a consequence, statistical models may offer a much less-expensive but reasonably accurate way to the solution of the problem of calculating cross sections and rate coefficients.

Statistical models for collision processes were first proposed in the context of nuclear collisions in the 1950s [170] and subsequently they were introduced into molecular collisions in 1960s by Bernstein [171] and Light [172–175]. According to the general statistical model, the state-to-state reaction probability $P(E)$ of a complex-forming reaction at specified values of J and p is calculated simply by [170, 171, 173, 174, 176]:

$$P(E) = \frac{P_{\text{react}}(E)P_{\text{prod}}(E)}{\sum_{\text{react,prod}} (P_{\text{react}}(E) + P_{\text{prod}}(E))} \quad (4.65)$$

where $P_{\text{react}}(E)$ is the capture probability (the probability of forming the collision complex) from the reactant channel, $P_{\text{prod}}(E)$ is the capture from the product channel, and the sum in the denominator runs over all open reactant and product channels at energy E which are compatible with the given values of J and p . An important feature of the model is that it fully respects all the quantum mechanical symmetries of the collision problem, including the conservation of total energy E , total angular momentum J and quantum mechanical parity p .

Equation 4.65 is based on two assumptions. The first one is that all the reactive collisions proceed via the collision complex (i.e., there is no possibility of a direct reactive process). The second assumption is that the collision complex is sufficiently long-lived to allow to treat its formation and decay as independent events. Taken together, these two assumptions imply that the reaction probability $P(E)$ will be given by the product of the reactant capture probability and the fraction of collision complexes that decay into the product channel. But since the complex formation and

decay probabilities from and to a given channel are the same by detailed balance, this fraction is simply $P_{\text{prod}}(E) / \sum_{\text{react,prod}} (P_{\text{react}}(E) + P_{\text{prod}}(E))$.

Extensive work has been carried out on this idea for triatomic complex-forming reactions on both time-dependent and time-independent quantum dynamics. Manolopoulos *et al.* developed the so-called Coupled-Channel Statistical model (CCS) in which the intermediate complex states are assumed to be distributed statistically and the reactant and product channels dynamics are treated within a time-independent quantum formalism [177, 178]. Similarly, Huo *et al.* proposed a wavepacket-based statistical model (WPS) differing from the CCS one in that asymptotic channels dynamics are computed within a time-dependent quantum approach [179, 180]. Both CCA and WPS models, unlike the exact quantum scattering calculations, only require inelastic collision calculations in both entrance and exit channels.

Recently a PST approach based on the Langevin capture model has been applied to the complex-forming reactions $A + H_2 \rightarrow AH + H$ with $A \equiv C(^1D)$, $N(^2D)$, $O(^1D)$ and $S(^1D)$ [181]. This PST theory has shown to achieve an excellent agreement for detailed dynamical magnitudes (state-resolved integral and differential cross sections) with the (more "exact") CCS statistical model and experimental counterparts.

In addition to these statistical approaches, recently a statistical quasiclassical trajectory model (SQCT) has been presented for the $H^+ + H_2$ and $H^+ + D_2$ insertion ionic reactions [182] (also studied using wavepacket methods [183]). In the SQCT model, quasiclassical trajectories are propagated in the entrance and exit channels. SQCT differential cross sections well compare with the CCS ones.

In the best of our knowledge, statistical models have not been applied to estimate the rate coefficients of complex-forming tetratomic reactions. In this work, the capture phase space theory model developed by Goldfield and Gray [68] has been applied to the reaction $CH + H_2 \rightarrow CH_2 + H$. Since this reaction involves three

equivalent atoms for the complex formation, one would expect that the PST statistical assumption will be a good approximation to obtain accurate cross sections and rate coefficients. At the same time, the reaction has the form $AH + H_2 \rightarrow AH_2 + H$ and therefore can be considered as the tetratomic counterpart of the triatomic $A + H_2 \rightarrow AH + H$ reaction. Accordingly, on the base of the results of ref. [181] for several triatomic reactions of this type one would expect that the statistical model works well for the tetratomic reaction $CH + H_2$.

4.9.1 C/PST rate coefficients

In the statistical Capture Phase Space Theory (C/PST) model used in this work, the complex-forming reaction probability is estimated by:

$$P(E, J, j) = P_{\text{cap}}(E, J, j) P_{\text{diss}}(E, J) \quad (4.66)$$

where $P_{\text{cap}}(E, J, j)$ is the probability of forming the complex at a given energy and quantum state and P_{diss} is the probability for the complex to dissociate weighing all available channels equally.

The probability of formation of any given product from the intermediate complex is proportional to the ratio of the phase space available to that product divided by the total phase space consistent with conservation of the energy and total angular momentum. Accordingly, P_{diss} can be calculated simply by statistical arguments as the ratio between the number of product states and the total number of both reactant and product states energetically accessible and compatible with the conservation of total angular momentum. This ratio can be expressed as:

$$P_{\text{diss}}(E, J) = \frac{N_{\text{prod}}(E, J)}{N_{\text{prod}}(E, J) + N_{\text{react}}(E, J)} \quad (4.67)$$

with $N_{\text{prod}}(E, J)$ and $N_{\text{react}}(E, J)$ being, respectively, the total number of product and reactant internal states available at total energy E and at total angular momentum

quantum number J . $N_{\text{react}}(E, J)$ is obtained by counting the rovibrational states of the reactants having energy less than E whereas $N_{\text{prod}}(E, J)$ is obtained by counting the rovibrational states of the products that having an energetic content smaller than $E - E_{\text{endo}}$ (E_{endo} is the endothermicity of the reaction).

At this point it is worth mentioning that equations 4.66 and 4.67 are conceptually equivalent to equation 4.65. However, the C/PST model uses some approximations to estimate the capture probability from reactants and products, i.e., the probability for the formation and decay of the complex. In fact, while the formation probability is calculated accurately using a time-dependent quantum method, the decay probability is estimated by simply counting the open channels for reactants and products. For this reason, in eq. 4.67 the symbol N is used rather than the generic probability P , used in eq. 4.65.

As just mentioned, the capture probability $P_{\text{cap}}(E, J, j)$ is computed using a four-atom wavepacket method. Shortly, in this method a wavepacket associated with a particular initial state is launched towards the entrance channel. As the wavepacket arrives to the complex well, it is absorbed. Figure 4.3 shows the three absorption regions used. Two absorption regions are placed around the potential energy well of the surface and the third one is placed at the asymptotic reactant region, as usual for non-reactive processes. The wavepacket propagation leads to a flux passing through the analysis line located at R_c and this flux is evaluated using eq. 4.61. In this way, the flux captured by the potential well is evaluated.

Even though the calculation of each capture probability $P_{\text{cap}}(E, J, j)$ is not terribly time consuming, as we have already pointed out, the number of initial states $(J, \Omega, j_1, j_2, \Omega_1, p)$ to be considered (thousands even at low energy) make the complete calculation unfeasible. For this reason, in this work a sampling method to select the initial states was used. This rotational sampling procedure reproduces, at each

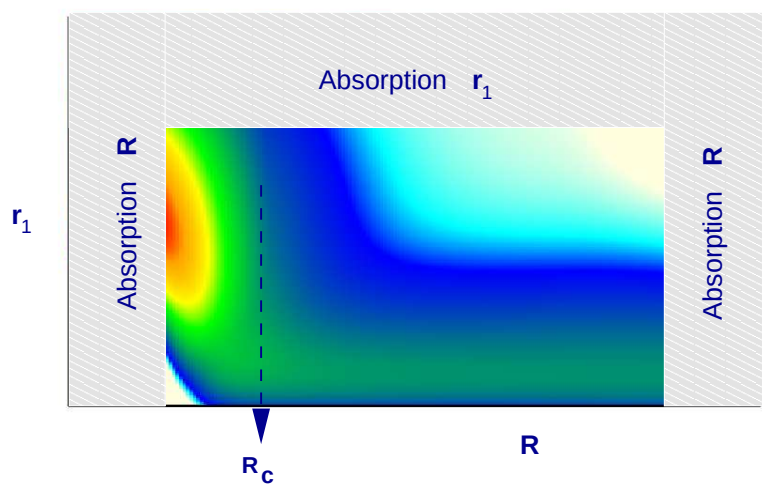


Figure 4.3: Schematic representation of the three absorption regions used to compute the capture probability.

temperature, a realistic J distribution, a good Boltzmann distribution for each j_1 and j_2 rotational quantum numbers and a reasonable distribution for Ω and Ω_1 . Each initial state needs six quantum numbers. The first three, J , j_1 and j_2 , can be picked independently while Ω , Ω_1 and p obey some restrictions. The ensemble of initial states is chosen to be large enough to converge the reaction coefficient at the given temperature.

The values of the initial rotational quantum number for a diatomic molecule, for example j_1 , are selected by the Boltzmann weighing at the temperature T :

$$\mathcal{P}_{j_1}(T) = \frac{g_{j_1}(2j_1 + 1) \exp\left(\frac{-B_1 j_1(j_1+1)}{k_B T}\right)}{Q_{\text{rot}}(1)} \quad (4.68)$$

where B_1 refers to the spectroscopic rotational constant and g_1 refers to the rotational degeneracy factor. In this work, the degeneracy factor is 1 for even rotational states and 3 for odd rotational states of the H_2 molecule. Probabilities of eq. 4.68 are computed within an interval of rotational states ranging up to a maximum value with negligible probability at the considered temperature.

The values of the total angular momentum quantum number are selected by:

$$\mathcal{P}_J = \frac{(2J + 1)}{(J_{\text{max}} + 1)^2} \quad (4.69)$$

In this equation the denominator represents the total number of possible J, Ω quantum states compatible with J_{max} while the numerator arises from the $(2J + 1)$ degeneracy factor (see eq. 4.64) due to the number of possible SF Z axis projections of the total angular momentum. The maximum total angular momentum J_{max} is determined according to dynamical considerations and therefore it requires test calculations to determine the largest J that contributes significantly to the capture probability.

Once the quantum numbers J , j_1 and j_2 are chosen, Ω and Ω_1 are then selected by picking randomly one of the microstates compatible with them. In most cases,

$J \geq j_1 + j_2$ and there are $(j_1 + 1)(j_2 + 1)$ possible combinations of Ω and Ω_1 microstates. In this case, the probability of choosing a particular microstate with quantum numbers $J, \Omega, j_1, j_2, \Omega_1$ is:

$$\mathcal{P}_{Jj_1j_2\Omega\Omega_1}(T) = \frac{\mathcal{P}_J \mathcal{P}_{j_1}(T) \mathcal{P}_{j_2}(T)}{(j_1 + 1)(j_2 + 1)} = \frac{(2J + 1)}{(J_{\max} + 1)^2} \frac{g_{j_1} \exp(-E_{\text{rot}}/k_B T)}{Q_{\text{rot}}} \quad (4.70)$$

with $E_{\text{rot}} = B_1 j_1(j_1 + 1) + B_2 j_2(j_2 + 1)$. When $J \leq j_1 + j_2$, there are fewer than $(j_1 + 1)(j_2 + 1)$ microstates compatible, so that the probability of choosing a particular microstate is somewhat larger than what would be computed using eq. 4.70. This introduces a slight bias into the rotational sampling. However, due to the initial states with $J \leq j_1 + j_2$ account for only 5% in the ensemble, the error introduced by this bias is typically $\leq 1\%$ and therefore the eq. 4.70 was used for all cases.

We note several subtle points, however, regarding the Ω and Ω_{HH} (Ω_1). By permitting both projection quantum numbers to attain both positive and negative values, we account for both parity states. In the case of $\Omega=0$, a negative value of Ω_{HH} is considered to correspond to odd parity. For $\Omega \neq 0$, even and odd parity initial conditions give rise to identical results. Therefore, if our ensemble includes both $\{J, j_{\text{HH}}, j_{\text{CH}}, \Omega, \Omega_{\text{HH}}\}$ and $\{J, j_{\text{HH}}, j_{\text{CH}}, -\Omega, -\Omega_{\text{HH}}\}$ we would only compute one $P(E, J, j)$ but count it twice. The second consideration is whether to eliminate the possibility of choosing a given set of initial conditions more than once. In the limit of very large ensembles, one would allow this possibility. Otherwise, by eliminating highly probable initial conditions from consideration, one would bias the sample in favour of less probable ones. In the limit of rather small ensembles, however, where one might want as much variety as possible, one might not allow it. In our particular case, we determined that each alternative gave rise to nearly identical results.

Using the C/PST model with the rotational sampling, the expression of eq. 4.64

for the thermal rate coefficients can be rewritten as follows:

$$k(T) = \frac{\sigma}{2\pi\hbar Q_{\text{tr}}} \sum_{J=0}^{J_{\text{max}}} (2J+1) \sum_i \frac{g_i e^{-E_{\text{rot}}(i)/k_{\text{B}}T}}{Q_{\text{rot}}} \tilde{P}_i(T, J, j) \quad (4.71)$$

Thus, for each i state in the ensemble we compute $P_i(E, J, j)$ and then integrate over the translational energy to obtain $\tilde{P}_i(T, J, j)$:

$$\tilde{P}_i(T, J, j) = \int_0^\infty e^{-E_{\text{tr}}/k_{\text{B}}T} P(E, J, j) dE_{\text{tr}} \quad (4.72)$$

For an ensemble of N states, the reaction rate is then computed as follows:

$$k(T) = \frac{\sigma}{2\pi\hbar Q_{\text{tr}}} \frac{(J_{\text{max}}+1)^2}{N} \sum_{i=1}^N \tilde{P}_i(T, J, j) \quad (4.73)$$

where $\sum_{i=1}^N \tilde{P}_i(T, J, j)/N$ corresponds to the average of the reactive probability calculated using N states. This average is then multiplied by the total number of states compatible with J_{max} (i.e., $(J_{\text{max}}+1)^2$) in order to estimate the total reactive probability.

In eq. 4.73 the rotational weighing factors and the partition functions have disappeared with respect to eq. 4.71 because they are accounted for in the sampling procedure. At the same time, the factor $(2J+1)$ present in eq. 4.71 has also disappeared in eq. 4.73 as a consequence of the factor $(2J+1)/(J_{\text{max}}+1)^2$ in eq. 4.70. Accordingly, the estimation of the rate coefficient through eq. 4.73 implies the $(J_{\text{max}}+1)^2$ factor, which plays a similar role to the b_{max}^2 (being b_{max} the maximum impact parameter) factor in the quasiclassical expression for the rate coefficient.

4.9.2 PST rate coefficients

As already mentioned, the statistical C/PST model estimates the rate coefficients by calculating accurately the probability of the complex formation from the reactants

and by approximating the calculation the complex decay. The simplest version of the statistical PST model consists in calculating the capture probability from the reactants using the same ideas than those used for the complex decay in the C/PST model. This PST method requires to consider the minimum energy path as a function of the distance between the centers of mass either the reactants and the products. Accordingly, this PST method is much more computational saving than the C/PST one. Moreover, the space fixed angular momentum representation (in contrast to the body fixed representation used in the quantum dynamics calculations) is used because is more intuitive and convenient.

In the simplest version of the PST model, following ideas in refs. [181, 184, 185], the rate coefficient is estimated by:

$$k_{\text{PST}}(T) = \frac{\sigma}{2\pi\hbar Q_{\text{tr}}(T)} \sum_{J=0}^{J_{\text{max}}} (2J+1) \int_0^\infty \frac{N_{\text{react}}^J(E) N_{\text{prod}}^J(E)}{N_{\text{react}}^J(E) + N_{\text{prod}}^J(E)} e^{-E/k_{\text{B}}T} dE \quad (4.74)$$

where $N_{\text{react}}^J(E)$ and $N_{\text{prod}}^J(E)$ are the sum of reactant and product states compatible with J and E .

The reactant sum of states is taken to be:

$$N_{\text{react}}^J(E) = \sum_{j_1} \sum_{j_2} \sum_j \sum_L \theta(\epsilon_{\text{react}} - V_{\text{react},L}^*) \quad (4.75)$$

The sums over j_1 and j_2 range from 0, 1, 2, The range of the j sum is determined by angular momentum addition of the $\mathbf{j}_1$ and $\mathbf{j}_2$ to make $\mathbf{j}$ to be from $|j_1 - j_2|$ to $(j_1 + j_2)$. Similarly, the range of the L sum, based on adding $\mathbf{j}$ and $\mathbf{L}$ to make $\mathbf{J}$, is from $|J - j|$ to $(J + j)$. For a given set of reactant quantum numbers, the translational energy is $\epsilon_{\text{react}} = E - E_{\text{react}}^{\text{rot}}(j_1, j_2) - E_{\text{react}}^{\text{vib}}(v_1 = v_2 = 0)$ (the temperatures that will be considered in this work are such that excited vibrational states do not appreciable contribute to the thermal rate coefficient). The step function $\theta(x)$ is equal to zero when $x=0$ and one otherwise. It ensures that the translational energy ϵ_{react} is

larger than the centrifugal barrier in the reactant channel, $V_{\text{react},L}^*$. This centrifugal barrier for the orbital angular momentum quantum number L is the maximum of $V_{\text{react}}(R) + L(L+1)\hbar^2/2\mu R^2$, where $V_{\text{react}}(R)$ denotes the minimum energy path for the complex formation starting from reactants as a function of R , the distance between the centers of mass of CH and H₂, being $\mu = m_{\text{CH}}m_{\text{H}_2}/(m_{\text{CH}} + m_{\text{H}_2})$. The minimum energy path was determined as outlined in [68].

The product sum of states is taken to be:

$$N_{\text{prod}}^J(E) = \sum_{v'_1, v'_2, v'_3} \sum_{j_{\text{CH}_2}} \sum_{\Omega_{\text{CH}_2}} \left(2 - \delta_{0\Omega_{\text{CH}_2}}\right) \sum_L \theta(\epsilon_{\text{prod}} - V_{\text{prod},L}^*) \quad (4.76)$$

where v'_1, v'_2, v'_3 are the vibrational numbers of the CH₂ product molecule, $j_{\text{CH}_2}=0, 1, 2, \dots$ and $\Omega_{\text{CH}_2}=0, 1, 2, \dots, j_{\text{CH}_2}$. The angular momentum addition of $\mathbf{j}_{\text{CH}_2}$ and $\mathbf{J}$ determines $\mathbf{L}$ and its range going from $|J - j_{\text{CH}_2}|$ to $(J + j_{\text{CH}_2})$. In this case, the product translational energy is determined by $\epsilon_{\text{prod}} = E - E_{\text{prod}}^{\text{rot}}(j_{\text{CH}_2}, \Omega_{\text{CH}_2}) - E_{\text{prod}}^{\text{vib}}(v'_1, v'_2, v'_3)$. A prolate symmetric rotor can be assumed for the product rotational energy. For CH₂ the rotational constants are $A=73.811 \text{ cm}^{-1}$ ($9.15 \times 10^{-3} \text{ eV}$) and $\bar{B}=7.187 \text{ cm}^{-1}$ ($0.89 \times 10^{-3} \text{ eV}$). At the same time, an energy of 942.8 cm^{-1} (0.117 eV) is employed for the lowest CH₂ vibrational state [67].

The centrifugal barrier $V_{\text{prod},L}^*$ for a given orbital quantum number in the CH₂ + H product channel were obtained by finding the maximum of $V_{\text{prod}}(\tilde{R} + L(L+1)\hbar^2/(2\tilde{\mu}\tilde{R}^2))$, where $\tilde{R}$ is the distance of H from the center of mass of CH₂ and $\tilde{\mu} = m_{\text{H}}m_{\text{CH}_2}/(m_{\text{H}} + m_{\text{CH}_2})$. The potential $V_{\text{prod}}(\tilde{R})$ is determined by assuming H approaches CH₂ along the bisector of the CH₂ angle, equating the two CH bond distances and minimizing the full potential with respect to the remaining degrees of freedom.

As is noted in ref. [68], the endothermicity calculated for the potential energy surface is 0.055 eV higher than an accurate experimentally-based estimate. To correct

for this feature we note that:

$$\begin{aligned}\Delta H(0 \text{ K}) &= E_{\text{prod}}^{\text{vib}}(0, 0, 0) - E_{\text{react}}^{\text{vib}}(0, 0) \\ &= (V_{\text{endo}} + \text{ZPE}_{\text{prod}}) - \text{ZPE}_{\text{react}}\end{aligned}\quad (4.77)$$

with V_{endo} being the bare potential energy difference between reactants and products and ZPE denoting zero-point-energy. We use an energy scale such that the reactants bare potential is zero, i.e., $\text{ZPE}_{\text{react}} = E_{\text{react}}^{\text{vib}}(0, 0)$. The product vibrational energies required in the computation of eq. 4.76 can be written as:

$$\begin{aligned}E_{\text{prod}}^{\text{vib}}(v'_1, v'_2, v'_3) &= \Delta E(v'_1, v'_2, v'_3) + \text{ZPE}_{\text{prod}} + V_{\text{endo}} \\ &= \Delta E(v'_1, v'_2, v'_3) + \Delta H(0 \text{ K}) + \text{ZPE}_{\text{react}}\end{aligned}\quad (4.78)$$

where eq. 4.77 has been used and $\Delta E(v'_1, v'_2, v'_3) = E_{\text{prod}}^{\text{vib}}(v'_1, v'_2, v'_3) - E_{\text{prod}}^{\text{vib}}(0, 0, 0)$. Use of 4.78 with the ab initio values for $\Delta E(v'_1, v'_2, v'_3)$ and $\text{ZPE}_{\text{react}}$, but with the empirical value $\Delta H = 0.145 \text{ eV}$ [68], corrects for the ab initio error in the endothermicity.

4.10 Potential energy surface

For the complex-forming study carried out in this work a recently published potential energy surface for the CH₃ system has been used. This potential energy function is detailed in ref. [67]. Basically the potential energy function is an accurate fit to over 75000 multireference configuration interaction electronic structure points sampling the CH₃(X²A₂''), CH₂(X³B₁) + H and CH(²Π) + H₂ regions and the regions connecting them.

The electronic structure calculations were done using the MOLPRO package [147]. The Dunning augmented correlation consistent polarized valence triple zeta

basis set were used [186–188]. The calculations employed the internally contracted, singles and doubles multi-reference, configuration interaction (MR-CI) formalism of Werner and Knowles [189, 190]. The orbitals were optimized using the complete active space, self consistent field (CASSCF) methodology [191, 192]. In the calculations the CASSCF reference wavefunction consisted of seven active orbitals and seven active electrons. The effects of higher order excitations were approximated using a multireference Davidson correction.

MR-CI calculations were carried out at 79000 symmetry single points. Of these, approximately 2000 were discarded because they were more than 18.37 eV larger than the CH_3 minimum. The remaining 77000 points were least-square fitted to a full, 6th order, direct product, multinomial in Morse variables for the six internuclear distances [193]. A total of 924 terms, of which only 196 are symmetry unique, were used. The resulting fit, V_G , had a root mean square (rms) error of 0.23 eV.

In order to improve the accuracy of the surface in the vicinity of the CH_3 minimum and both the $\text{CH} + \text{H}_2$ and the $\text{CH}_2 + \text{H}$ asymptotes, three additional fits were done using subsets of the 77000 points. The fits near the CH_3 minimum (V_{CH_3}), the $\text{CH} + \text{H}_2$ asymptote ($V_{\text{CH}+\text{H}_2}$), and the $\text{CH}_2 + \text{H}$ asymptote, ($V_{\text{CH}_2+\text{H}}$) included 10000, 20000 and 35000 points respectively and these fits yielded rms errors of 0.003 eV or less.

The final analytic function consists of the four fits described above connected by switching functions:

$$V = V_G(1 - S_{\text{CH}_3} - S_{\text{CH}_2+\text{H}} - S_{\text{CH}+\text{H}_2}) + S_{\text{CH}_3}V_{\text{CH}_3} + S_{\text{CH}_2+\text{H}}V_{\text{CH}_2+\text{H}} + S_{\text{CH}+\text{H}_2}V_{\text{CH}+\text{H}_2} \quad (4.79)$$

where the switching functions S_{CH_3} , $S_{\text{CH}_2+\text{H}}$ and $S_{\text{CH}+\text{H}_2}$ are detailed in ref. [67].

On this surface, the $\text{CH} + \text{H}_2 \rightarrow \text{CH}_2 + \text{H}$ reaction is barrierless along the

minimum energy path (MEP), with a bare endothermicity of 0.18 eV and a zero-point corrected endothermicity of 0.20 eV.

The plot of the MEP for the CH₃ complex formation from CH + H₂ is shown in the Figure 4.4. It was obtained by varying the separation between the CH and H₂ center of masses, R , and minimizing the potential with respect to the remaining internal coordinates. The depth of the CH₃ well is 4.8 eV relative to the energy of the isolated CH and H₂ at their equilibrium bond distances. The MEP shown in Figure 4.4 corresponds always to planar geometries but the relative orientation of the two diatomic molecules varies suddenly at $R \approx 2.51$ a₀. In fact, at $R > 2.51$ a₀, the orientation which minimizes the energy is a parallel orientation (in agreement with an early work of Brooks and Schaefer [44]) whereas at $R < 2.51$ a₀ the preferred orientation corresponds to a perpendicular insertion (C_{2v} geometry) of the CH bond into the H₂ bond, with the carbon atom nearest to the H₂ bond.

A more global picture of the PES is shown in Figures 4.5 and 4.6 where the isoenergetic contours maps of the PES for the parallel and perpendicular geometries are shown. Both contour plots are calculated as a function of the distance between the center of mass of the two reactant molecules, R , and of the internuclear distance of the H₂ molecule, r_{HH} . The internuclear distance of the CH molecule has been set at its equilibrium distance, 2.12 a₀. In both contour plots the planar geometry has been considered.

As apparent from the Figures 4.5 and 4.6, at long distances the energy for the parallel orientation is lower than that for the perpendicular orientation. Moreover, when the reactant molecules approach each other a barrier arises for perpendicular geometries. The maximum point of the barrier is 1.01 eV and it is located at $R = 4.28$ a₀ and $r_{HH} = 1.7$ a₀. On the contrary, for parallel geometries there is not a barrier as reactants approach each other to form the CH₃ complex. The most stable

geometry of the complex corresponds to a perpendicular geometry with $R = 2.07 \text{ a}_0$ and $r_{\text{HH}} = 3.55 \text{ a}_0$ being the depth associated 4.8 eV relative to the energy of the isolated CH and H_2 at their equilibrium bond distances. For comparison, the most stable configuration of the complex for the perpendicular geometry is located at $R = 1.96 \text{ a}_0$ and $r_{\text{HH}} = 3.39 \text{ a}_0$ being the depth associated 0.5 eV.

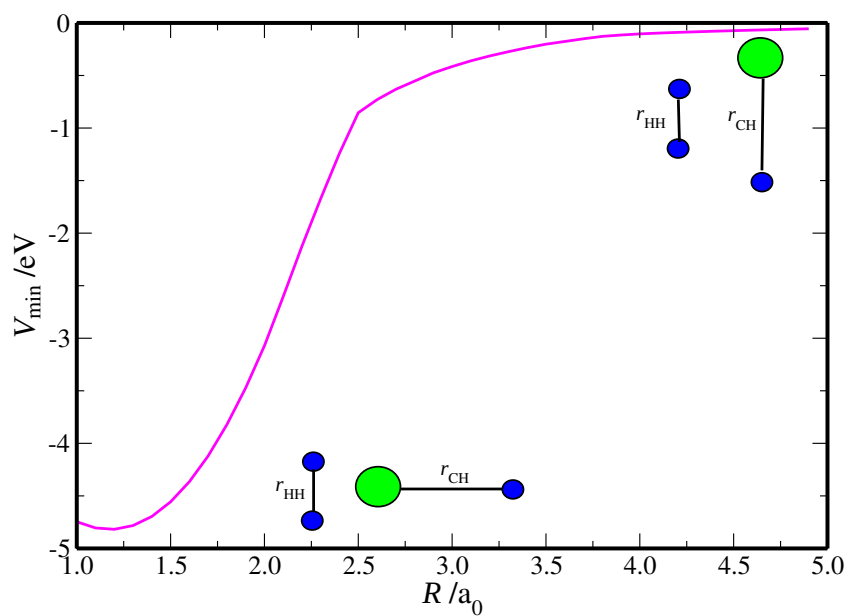


Figure 4.4: Energy along the MEP corresponding to formation of CH₃ from CH and H₂ fragments plotted as a function of the distance R between the H₂ and CH fragments.

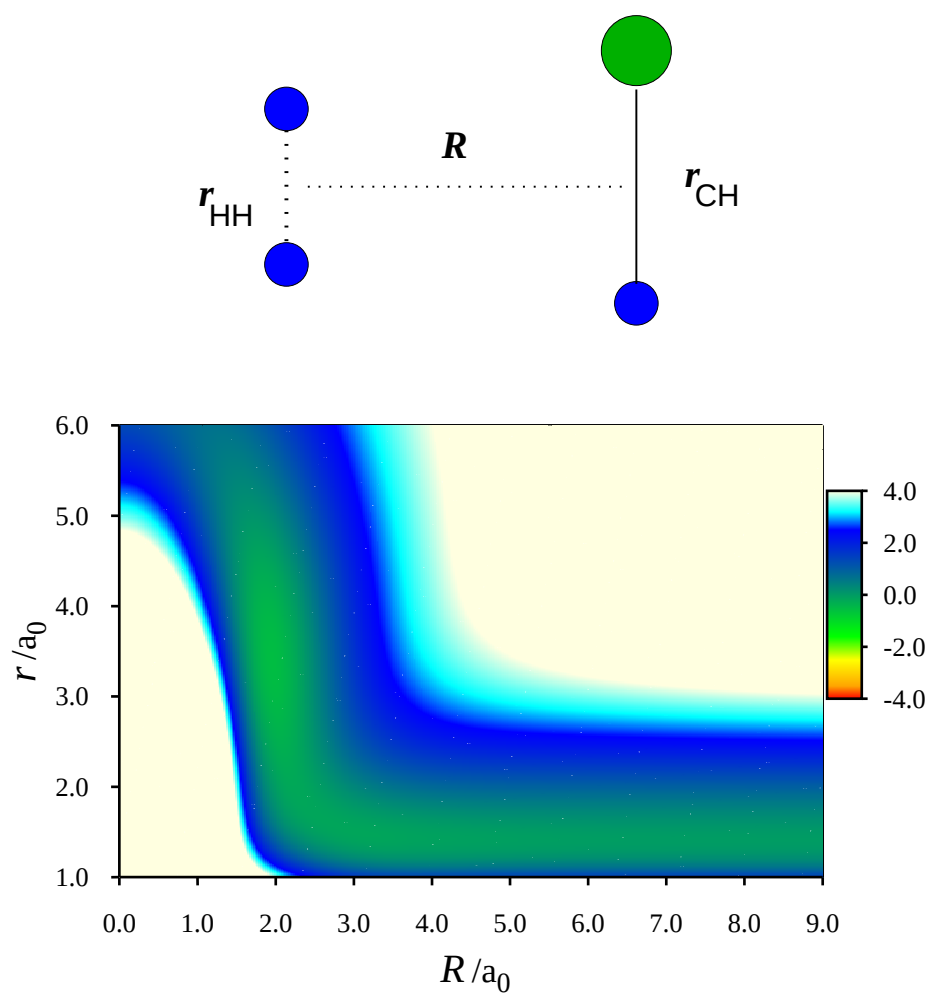


Figure 4.5: Isoenergetic contour maps for the parallel approach of the reactant CH to the H_2 molecule plotted as a function of R and r_{HH} (with r_{CH} set at its equilibrium value).

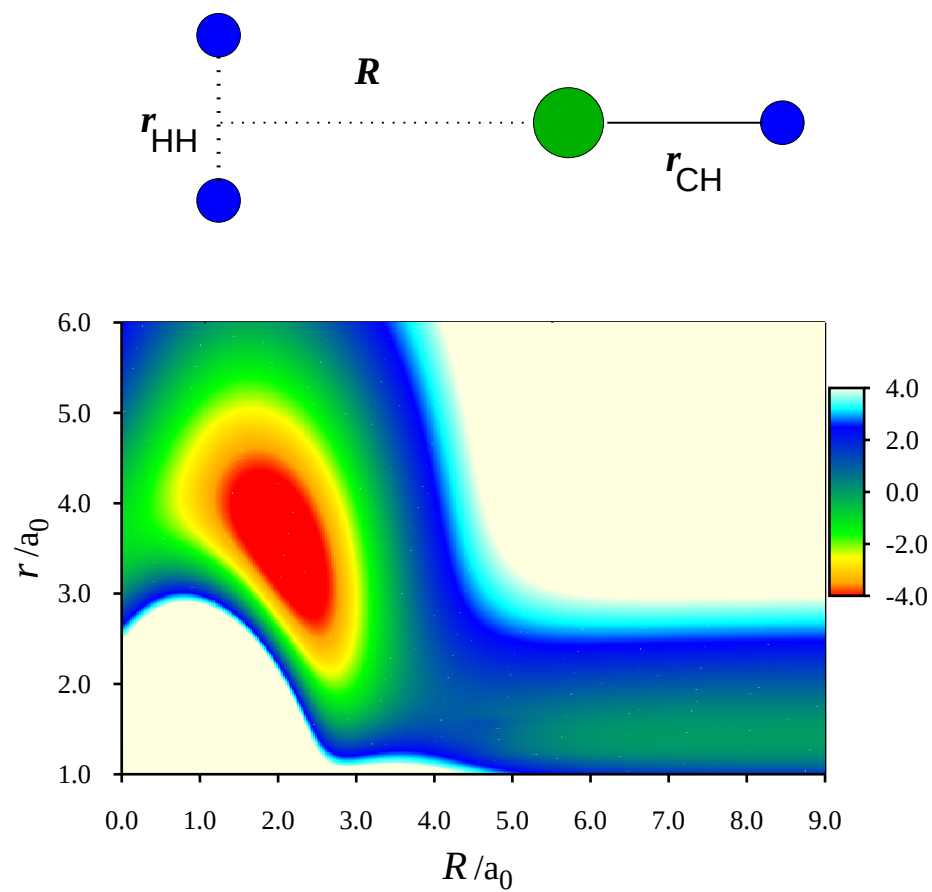


Figure 4.6: Isoenergetic contour maps for the perpendicular approach of the reactant CH to the H₂ molecule plotted as a function of R and r_{HH} (with r_{CH} set at its equilibrium value).

Chapter 5

The CH+H₂ reaction: Calculations and results

The experimental information for the reaction $\text{CH} + \text{H}_2 \rightarrow \text{CH}_2 + \text{H}$ is confined to thermal rate coefficients. For this reason, our study was devoted to obtain an estimate of this kinetic property to compare with. In particular, thermal rate coefficients in the range 202–584 K were calculated.

Tetratomic reactions are next in complexity to the atom-diatom problems. As a matter of fact, the more structured potential energy surface and the larger number of degrees of freedom represent a limiting factor to the study of four-atom reactions. This makes still unfeasible a full dimensional quantum calculation of the rate coefficient for a tetratomic system. For this reason, in the present work we used the C/PST model developed by Goldfield and Gray [68] to estimate the rate coefficient of the $\text{CH} + \text{H}_2 \rightarrow \text{CH}_2 + \text{H}$ diatom-diatom reaction.

To calculate the capture probabilities needed to estimate the rate coefficient, the

four-atom real wavepacket (RWP) method described in Chapter 4 was used. Both $J = 0$ and $J > 0$ quantum calculations were performed. In the later case the centrifugal sudden (CS) approximation was applied. The calculations were also restricted to reactants in their ground vibrational states. The interval of total energy investigated ranged from 0.44 to 1.60 eV in steps of 0.005 eV.

5.1 Calculations at zero total angular momentum

5.1.1 Capture probabilities

As detailed in Chapter 4, the TD capture probabilities were computed by absorbing the wavepacket as it arrives at the complex well. It is also assumed that the CH bond of the reactant CH does not break. This allowed us to use a potential-optimized discrete variable representation. This choice does not affect the accuracy of the calculated capture probabilities since the subsequent dynamics of the CH₃ complex dynamics is neglected. Since the related calculations involve only the entrance channel in which the coupling between various degrees of freedom is relatively weak, the required basis set is smaller than that for the full quantum calculations (see Table 1 in ref. [68]) though a rather large rotational basis is still required to reach convergence.

The capture probabilities were computed directly from a flux analysis at a value of R corresponding to R_c in Figure 4.3. As long as R_c is not too close to the absorption region, the results are independent of its value. The results were also insensitive to the choice of the absorption parameters.

Numerical parameters for the $J=0$ capture wavepacket calculations are given in the Table 5.1. In Figure 5.1 the calculated capture probabilities, P_{cap} , are plotted as a function of the initial translational energy for three different initial conditions:

Table 5.1: Computational details for capture wavepacket calculations with total angular momentum $J = 0$. Distances are given in atomic units.

$R_{\min}, R_{\max}, N_R$	0.5,14.0,176
$r_{\text{HHmin}}, r_{\text{HHmax}}, N_{\text{HH}}$	1.0,5.0,48
Number of r_{CH} PODVR points	1
Largest value of j_{HH}	$12^a, 13^b$
Largest value of j_{CH}	18
Absorption parameters ^c : $R_{\text{abs}}, C_{\text{abs}}$ for R :	10.5, 0.005
Absorption parameters: $R_{\text{abs}}, C_{\text{abs}}$ for r_{HH} :	2.0, 0.005
Absorption parameters in the interaction region: $R_{\text{abs}}, C_{\text{abs}}$ for R :	2.0, 0.1
Incoming gaussian function: $\hbar^2 k_0^2 / 2\mu(\text{eV}), R_0, \alpha$	0.3,9.0,0.3

^a The rotational basis for H_2 with initial $j_{\text{CH}} = j_{\text{HH}} = 0$. Note that the basis contains only functions of the even values of j_{HH} .

^b The rotational basis for H_2 with initial $j_{\text{CH}} = j_{\text{HH}} = 1$. Note that the basis contains only functions of the odd values of j_{HH} .

^c The absorption potential has the form $\exp[-C_{\text{abs}}(R - R_{\text{abs}})^2]$, with $R \geq R_{\text{abs}}$ except in the interaction region where it is applied for $R < R_{\text{abs}}$.

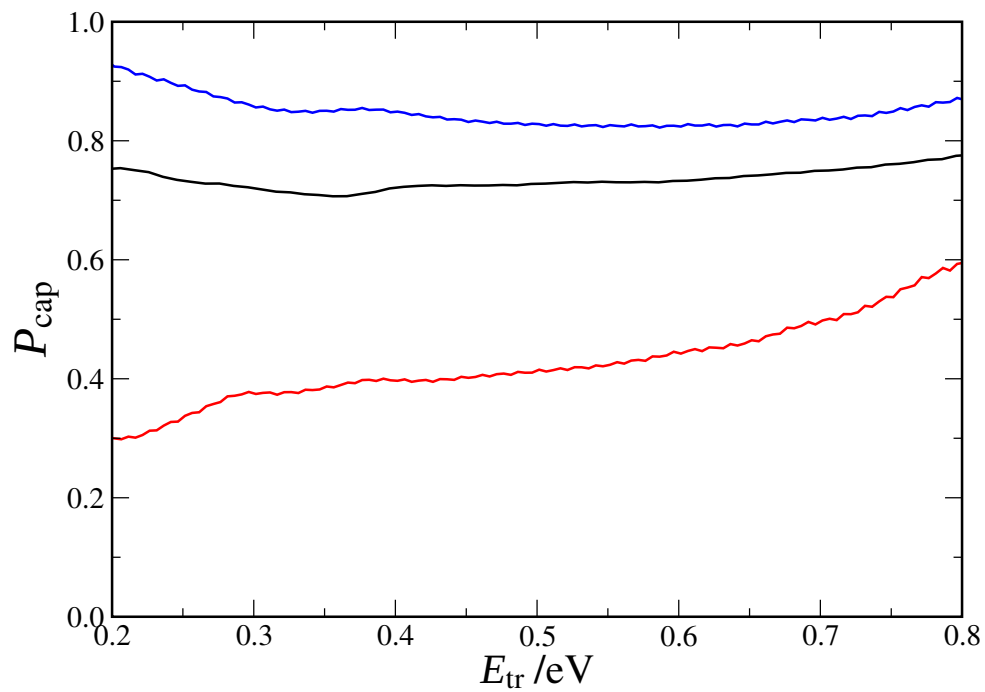


Figure 5.1: Capture probability plotted as a function of the collision energy for three different initial conditions: $j_{HH}=j_{CH}=0$ (black line); $j_{HH}=j_{CH}=1$, $|\Omega_{HH}|=|\Omega_{CH}|=0$ (red line); $j_{HH}=j_{CH}=1$, $|\Omega_{HH}|=|\Omega_{CH}|=1$ (blue line).

$$j_{\text{HH}}=j_{\text{CH}}=0; j_{\text{HH}}=j_{\text{CH}}=1, |\Omega_{\text{HH}}|=|\Omega_{\text{CH}}|=0; j_{\text{HH}}=j_{\text{CH}}=1, |\Omega_{\text{HH}}|=|\Omega_{\text{CH}}|=1.$$

The potential of the $\text{CH} + \text{H}_2 \rightarrow \text{CH}_2 + \text{H}$ reaction is barrierless along the minimum energy path (see Figure 4.4). Thus, one might expect the capture probability P_{cap} to be one at all translational energies. However this turns out not to be the case. In fact, for example, the capture probabilities calculated at $j_{\text{HH}}=j_{\text{CH}}=0$ (the black line of Figure 5.1) falls in the 70–74% range for the whole interval of investigated collision energy interval. The reason for this is that the entrance channel is relatively narrow with respect to the possible orientations of CH and H_2 . To rationalize this feature, isoenergetic contours calculated at $R=4.8 \text{ a}_0$ and both r_{CH} and r_{HH} at their equilibrium values are plotted in Figure 5.2 as a function of θ_{HH} and θ_{CH} . The Figure shows that the optimum relative orientation for reaction is the one in which the diatoms approach parallel each other and perpendicular to R . When both CH and H_2 are initially in the ground rotational state, there is a broad angular distribution in the entrance channel and the calculations show that there is a significant portion of the wavepacket reflected back before entering the complex-forming region. That means, indeed, that P_{cap} is a function of the initial orientations of the diatoms.

To test the effect of the initial orientation we computed the $J=0$ capture probability with initial $j_{\text{CH}}=j_{\text{HH}}=1$. When $J=0$, the quantum numbers for the projection of the rotational angular momentum of the diatoms onto the BF Z axis (or the R vector), Ω_{CH} and Ω_{HH} , are equal in magnitude and opposite in sign. Whereas, for the initial condition $j_{\text{CH}}=j_{\text{HH}}=1$ the magnitude of Ω_{HH} can be either 0 or 1. If $|\Omega_{\text{HH}}|=|\Omega_{\text{CH}}|=0$, both diatoms are aligned with the R axis so that CH and H_2 approach each other collinearly. If, instead, $|\Omega_{\text{HH}}|=|\Omega_{\text{CH}}|=1$ then for both H_2 and CH, the initial rotational even parity wavefunction is given by $\sin \theta \cos \phi$. Thus the two diatoms face each other and are perpendicular to R . As apparent from Figure 5.1, perpendicular orientation leads to larger P_{cap} values (blue line) while the collinear orientation leads to smaller ones (red line).

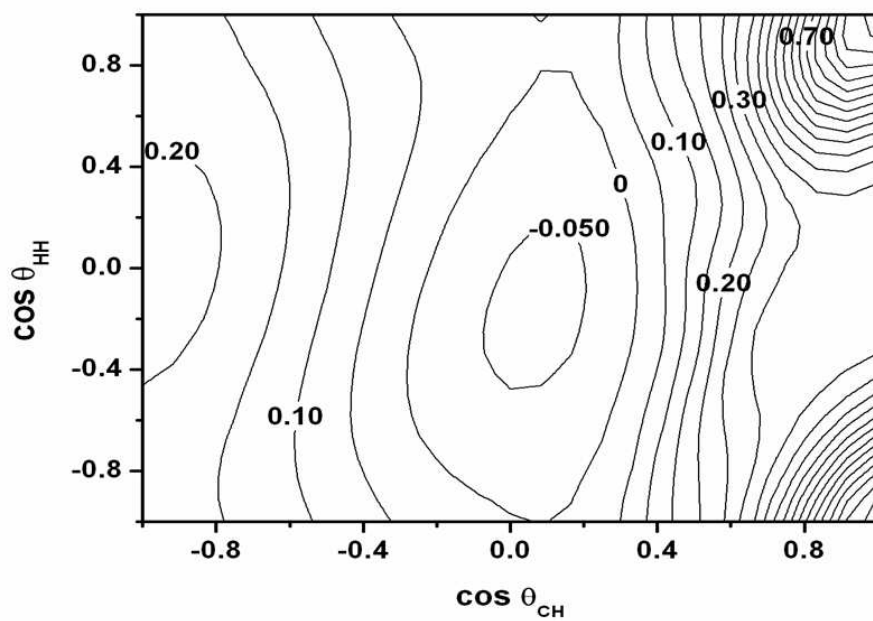


Figure 5.2: Isoenergetic contours maps of the potential energy surface plotted as a function of θ_{HH} and θ_{CH} for $R=4.8 a_0$, $\phi = 0$ (i.e. coplanar approach) and the CH and H₂ bond lengths being at their equilibrium values. Contours range from -0.05 to 1 eV.

5.1.2 Reaction probabilities

The total reaction probabilities were estimated from the calculated capture probabilities by multiplying them for the dissociation fraction. The reaction probabilities calculated at $j_{HH}=j_{CH}=0$ (and $v_{HH}=v_{CH}=0$) are plotted in Figure 5.3. As apparent from the Figure, the C/PST probabilities (black line) show a threshold energy of 0.2 eV. The reactivity increases with the collision energy an enhancement of the reactivity occurs though more steply for the just-past-the-threshold energies. At the highest collision energy values considered, the probability reaches a value of about 0.3.

Figure 5.3 shows also the QM reaction probability values calculated by Mayneris, González and Gray [68] using the same RWP method as the one used in the C/PST calculations. However, they propagate the wavepacket all the way along up to the product region where it is absorbed and state-to-state reaction probabilities are calculated directly. Like for the C/PST RWP calculations, the QM calculations assume that the initial CH bond does not break. Such an assumption lowers the accuracy of the QM calculations while it introduces no significant errors in the C/PST calculations. Actually, QM probabilities are likely to be overestimated. For this reason, they were systematically corrected.

As already mentioned, the simplest evaluation of the statistical dissociation probability $P_{\text{diss}}(E)$ for the complex reads as:

$$P_{\text{diss}}(E) = \frac{N_{\text{CH}_2}(E)}{N_{\text{CH}_2}(E) + N_{\text{CH}_2+\text{H}_2}(E)} \quad (5.1)$$

where N_{CH_2} and $N_{\text{CH}_2+\text{H}_2}$ are respectively the total number of product and reactant internal states available at total energy E . Thus the calculation of P_{diss} involves enumerating all the possible states in one particular reactant channel, say $\text{CH}_a + \text{H}_b$, H_c . Similarly, it involves enumerating all the possible states in one product channel, say, $\text{H}_a\text{CH}_b + \text{H}_c$. Considering hydrogen exchanges, there are actually three equiv-

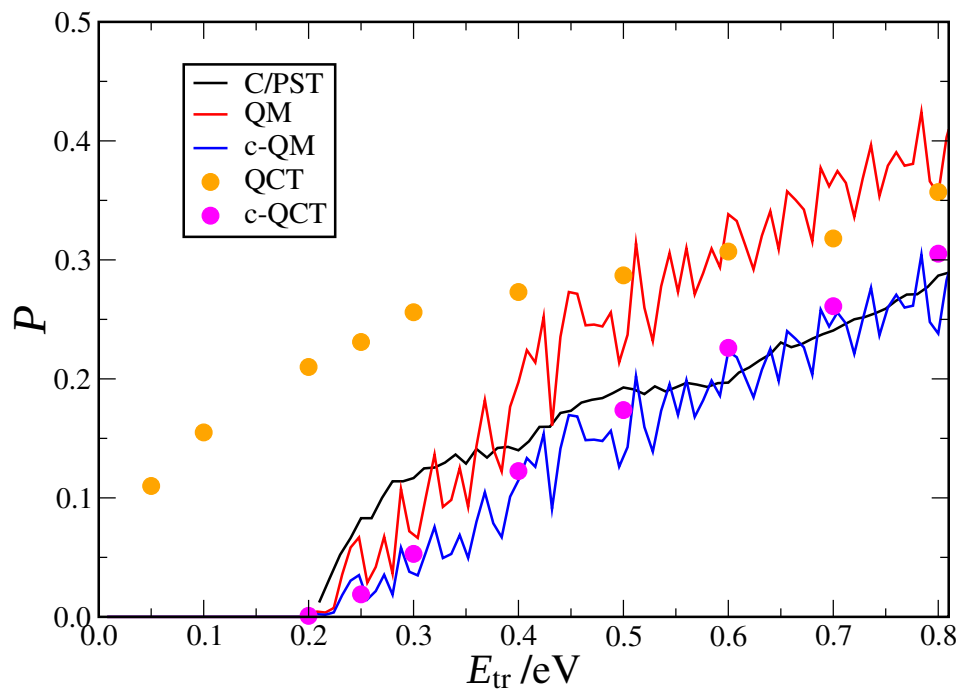


Figure 5.3: Total angular momentum $J=0$ reaction probabilities calculated at $j_{HH}=j_{CH}=0$ plotted as a function of the collision energy. Capture/phase space theory model (black line), quantum model (red line), corrected quantum results (blue line), quasiclassical trajectories (orange circles) and corrected quasiclassical trajectories (magenta circles).

alent reactant channels and three equivalent product channels. However, in the QM calculation, starting from the $\text{CH}_a + \text{H}_b\text{H}_c$ channel, the fragment CH_a is not allowed to dissociate and therefore only one of the three reactant channels $\text{CH}_a + \text{H}_b\text{H}_c$ and only two of the three products channels (namely $\text{H}_a\text{CH}_b + \text{H}_c$ and $\text{H}_a\text{CH}_c + \text{H}_b$) are actually taken into account. Accordingly, the QM calculations has only $2 N_{\text{CH}_2}/3$ of the possible product states and $N_{\text{CH}+\text{H}_2}/3$ of the possible reactant states making the QM probabilities overestimated. For example, if the probability of forming complexes was unity and the number of reactant channels significantly exceeding the number of product channels ($N_{\text{CH}+\text{H}_2} \gg N_{\text{CH}_2}/3$), then one would predict that the QM probability is overestimated by a factor 2 ($[2N_{\text{CH}_2}/3]/[N_{\text{CH}+\text{H}_2}/3] = 2$). For non-unity P_{cap} it is possible to obtain a better correction factor of the calculated QM probabilities as follows. First, one assumes that the corrected QM probability, $\bar{P}$, can be expressed as:

$$\bar{P} = P_{\text{cap}} \bar{P}_{\text{diss}} \quad (5.2)$$

where P_{cap} is the calculated capture probability (see Figure 5.1) and $\bar{P}_{\text{diss}}$ is given by:

$$\bar{P}_{\text{diss}} = \frac{(3/2)P}{(3/2)P + 3P_{\text{nr}(\text{stat})}} \quad (5.3)$$

with P being the original QM probability based on the limited number of available channels and $P_{\text{nr}(\text{stat})}$ being the statistical part of the total nonreactive probability, P_{nr} . Since $P_{\text{nr}} = (1 - P_{\text{cap}}) + P_{\text{nr}(\text{stat})} = 1 - P$, one obtains $P_{\text{nr}(\text{stat})} = P_{\text{cap}} - P$, and eq. 5.2 then becomes:

$$\bar{P} = P_{\text{cap}} \frac{P}{2P_{\text{cap}} - P} \quad (5.4)$$

For example, with $P_{\text{cap}} = 0.74$ and $P = 0.3$, the corrected reaction probability is 0.19, that is, 1.6 times smaller than the original value.

The original (QM) and the corrected quantum dynamics (c-QM) probabilities are compared in Figure 5.3 as red and blue lines, respectively. As just discussed, the

QM results overestimate the "true" (C/PST) reaction probability while the C/PST and the corrected QM results are in reasonable accord at moderate and high energies and show larger discrepancies in the 0.2–0.44 eV range. Assuming that the corrected QM results are a reasonable representation of the situation, the results support the idea that the CH₃ complexes, once formed, behave statistically. The zigzag structure of the QM probabilities is caused by the large number of overlapping resonances occurring (this feature is common to the QM probabilities of several complex-forming chemical reactions such as H + O₂ [194, 195]). The details of the zigzag patterns are sensitive to the value of various parameters and are difficult to converge [195]. An even finer structure may result from the use of a denser energy grid.

Figure 5.3 shows also the probabilities calculated using a quasiclassical trajectory method (details of the calculations will be given in the next Section). QCT results (orange circles) are in general higher than C/PST and QM ones, with the largest discrepancies occurring for collision energies near and below the QM threshold for reaction, ~ 0.2 eV. It turns out that there is no clear QCT threshold for the reaction because the reactant zero-point energy (ZPE) (0.44 eV) lies always below the minimum energy path (there is, in fact, no barrier to reaction other than the endoergicity (0.18 eV)). Due to attraction of the tail of the deep well located in the interaction region, and to the excess energy associated with the fact that the ZPE of CH₂ (0.29 eV) larger than the process endoergicity, many trajectories starting from the ground rovibrational states and collision energy smaller than 0.18 eV react. Several recipes have been reported in the literature to correct ZPE violation (see refs. [196–199]). Here we discard the trajectories with an internal energy lower than the ZPE of the CH₂ molecule. The corrected QCT probabilities (c-QCT) are shown in Figure 5.3 as magenta circles. As apparent from the Figure, the c-QCT results well agree with the C/PST probabilities and even better with the c-QM ones.

5.1.3 QCT lifetimes

Thinking classically, one might divide reactive collisions in two subsets: those entering the complex region and those not entering it. The former trajectories form a highly excited CH_3 complex that is expected to end up into one of the six possible exit channels (three equivalent reactive channels and three equivalent nonreactive channels) in a statistical manner. One would expect that the related distribution of trajectory lifetimes would be broad and that all three hydrogens would have an equal chance of ending up bound to the carbon atom. Trajectories not entering the complex region, however, would all be nonreactive, have a short lifetime and not exchange the H atoms. To confirm this behaviour a specific quasiclassical trajectory study was performed.

The QCT calculation were carried out using a version of VENUS96 [200] customized to incorporate the potential and evaluating numerically derivatives. A further modification was introduced by limiting the calculations to trajectories with $v_{\text{CH}}=v_{\text{H}_2}=j_{\text{CH}}=j_{\text{H}_2}=0$ and zero total angular momentum (zero impact parameter). The initial and final separations of the collision fragments were set at $12 a_0$. The time step was chosen to be 0.05 fs in order to guarantee the accuracy of the calculations. Collision energy was varied in the range 0.05 to 1.00 eV, integrating for each collision energy a sufficient number of trajectories to yield reaction probabilities with statistical error $\leq 2\%$. At the lowest collision energies this required the integration of up to 12000 trajectories.

Since, as already mentioned, we were interested in characterizing the mechanism of the $\text{CH} + \text{H}_2$ reaction using a classical approach, the distribution of trajectory lifetimes was plotted in Figure 5.4. The lifetime distributions of reactive and nonreactive trajectories that exchange H atoms are broad with very few of them having a lifetime ≤ 0.2 ps. In contrast, 57% of the nonreactive trajectories that do not exchange H

atoms fall in the ≤ 0.2 ps range, representing 21% of the total number of trajectories. (If one assumes that these trajectories are not "captured", then the quasiclassical capture probability is 0.79, somewhat higher than the quantum capture probability of 0.74). We further assessed the statistical nature of the break up of the collision complex by comparing the number of reactive trajectories exchanging hydrogens with that of the non exchanging ones. (Please, note that the exchange channel is not included in the wavepacket calculations.) If the break up of the complex is statistical, then 1/3 of all reactive trajectories should be in the exchange channel. For all the energies considered here, this condition is largely satisfied.

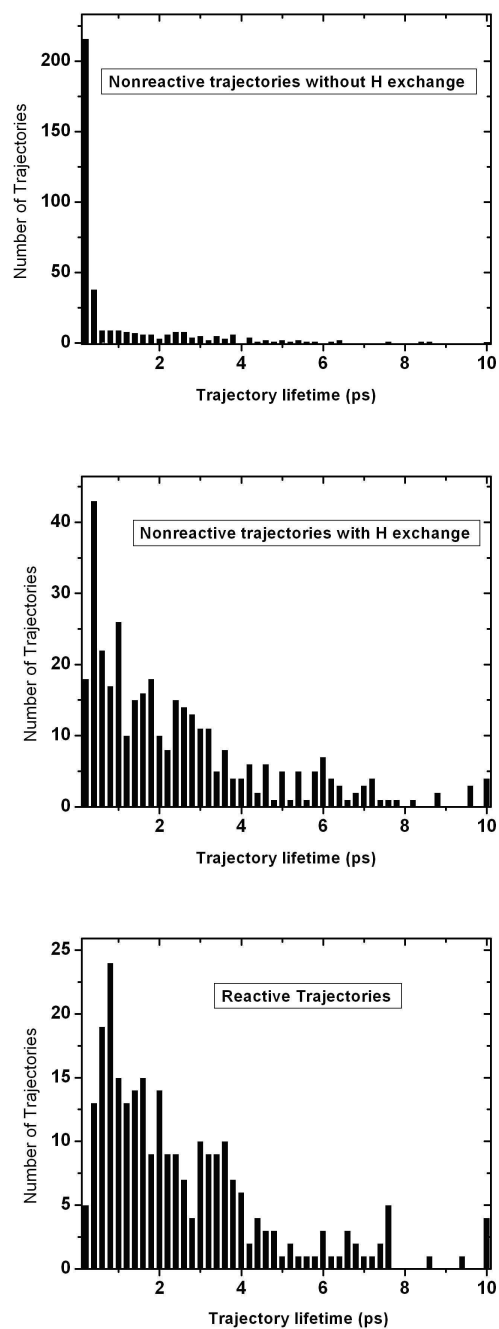


Figure 5.4: Lifetime distributions from the QCT calculations.

5.2 Calculations at non-zero total angular momentum

Extensive $J > 0$ four-atom wavepacket calculations were performed in order to calculate the capture probabilities. In the calculations, the Coriolis coupling was ignored, by treating so far Ω as a good quantum number. Since all the dynamics takes place in the entrance channel, this approximation is fully justified.

More than 300 initial states were needed to converge the rate coefficients. The five quantum numbers characterizing the system, namely $J, \Omega, j_{\text{HH}}, j_{\text{CH}}, \Omega_{\text{HH}}$, were selected using the already described rotational sampling. The sampling corresponded to a temperature T of 300 K and a maximum total angular momentum value J_{max} of 32 (this implies a total of $(32 + 1)^2 = 1089$ quantum states) were considered. The range of collision energy investigated goes from 0.18 to 0.40 eV in steps of 0.005 eV. As for the $J=0$ calculations, the calculations were restricted to reactants in their ground vibrational states. The numerical parameters for the $J > 0$ wavepacket calculations are given in Table 5.2. It is worth noting that a different set of parameters was used for the $0 < J \leq 25$ and $25 < J \leq 32$ cases.

5.2.1 Capture probabilities

In this Section, we shall discuss the role played by the rotational excitations in determining the capture probability. In general, the capture probability is a quite complex function since it depends on all the five initial quantum numbers $J, \Omega, j_{\text{HH}}, j_{\text{CH}}$ and Ω_{HH} . However, a few considerations on the influence of the initial rotations of the diatoms and of their relative orientation on the capture probabilities are in order.

First, the influence of the value of the quantum number Ω (the relative orientation of the H₂ and CH diatoms) is analysed. As already pointed out before for $J=0$, there

Table 5.2: Values of computational parameters* for the capture wavepacket calculations performed at total angular momentum $J > 0$. Distances are given in atomic units.

	$0 < J \leq 25$	$25 < J \leq 32$
$R_{\min}, R_{\max}, N_R$	0.5,17.0,216	0.5,20.0,255
$r_{\text{HHmin}}, r_{\text{HHmax}}, N_{\text{HH}}$	1.0,6.0,48	1.0,6.0,48
Number of r_{CH} PODVR points	1	1
Largest value of j_{HH}	18	18
Largest value of j_{CH}	12, 13	12, 13
Absorption parameters: $R_{\text{abs}}, C_{\text{abs}}$ for R :	13.5, 0.005	16.5, 0.005
Absorption parameters: $R_{\text{abs}}, C_{\text{abs}}$ for r_{HH} :	2.0, 0.005	2.0, 0.005
Absorption in the interaction region: $C_{\text{abs}}, R_{\text{abs}}$ for R :	2.0, 0.1	2.0, 0.1
Incoming gaussian function: $\hbar^2 k_0^2 / 2\mu(\text{eV}), R_0, \alpha$	0.35,12.0,0.3	0.35,14.0,0.3

* See Table 5.1 for further explanations

is a strong angular effect in the entrance channel of the potential. The diatoms are optimally oriented when they approach each other in a nearly parallel fashion and perpendicularly to R . It turns out that, due to this orientation of preference, if all other things are equal, larger Ω will generally result in larger capture probabilities at the energies relevant to this study especially at high J values. To illustrate this point, some representative examples (picked up from the 300 states generated in 300 K ensemble) are shown in Figure 5.5. To understand this Figure, it is important to realize that there is a "hidden" quantum number, $\Omega_{CH} = \Omega - \Omega_{HH}$, i.e. the projection onto the BF Z axis of the rotational quantum number of the diatom CH. As apparent from the Figure, when Ω (and accordingly Ω_{CH}) increases, the capture probability generally increases (sometimes even dramatically). This can be related to the fact that the initial rotational wavefunctions j_{HH} and j_{CH} are given by a product of associated Legendre functions written as:

$$P_{j_{HH}}^{\Omega_{HH}}(\cos \theta_{HH}) P_{j_{CH}}^{\Omega_{CH}}(\cos \theta_{CH})$$

Optimal orientation occurs when Ω_{HH} and Ω_{CH} reach their maximum values, i.e. $j_i = \Omega_i$, because then the associated Legendre functions are proportional to $\sin^\Omega(\theta)$ which peaks at $\theta = \pi/2$. The orientation is less than optimal when $\Omega_i = 0$, and becomes increasingly more optimal as Ω_i gets larger.

To further analyse the effect of the orientation of the H₂ and CH diatoms on the capture probability, reduced density plots of the wavepacket along the direction of its motion towards the well associated with the formation of the complex have been drawn. The calculated reduced densities are plotted in Figure 5.6 as a function of R and $\cos \theta_{CH}$ after averaging over the remaining coordinates. In particular, the Figure shows the reduced density plots of the wavepacket calculated at $J=10$, $j_{HH}=1$, $j_{CH}=3$, $\Omega_{HH}=1$ for $\Omega_{CH}=2$ and $\Omega_{CH}=3$ (this means also $\Omega=3$ and $\Omega=4$ respectively) after 1200 and 1500 time steps. Time step of 1200 corresponds approximately to the time when the wavepacket reaches the complex well and time step of 1500 corre-

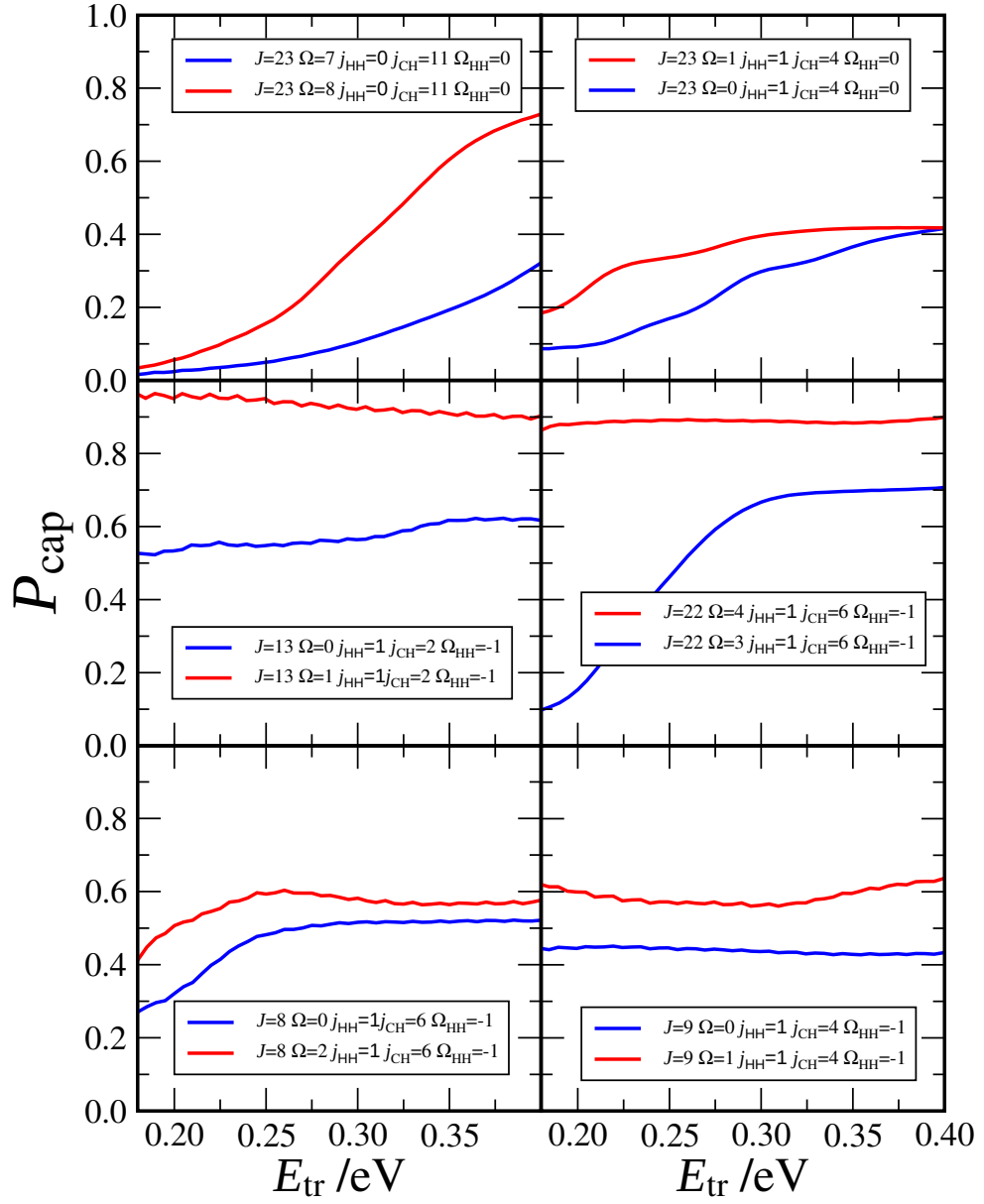


Figure 5.5: Capture probabilities calculated at different values of Ω and plotted in pairs of values of J , j_{HH} , j_{CH} and Ω_{CH} as a function of the collision energy.

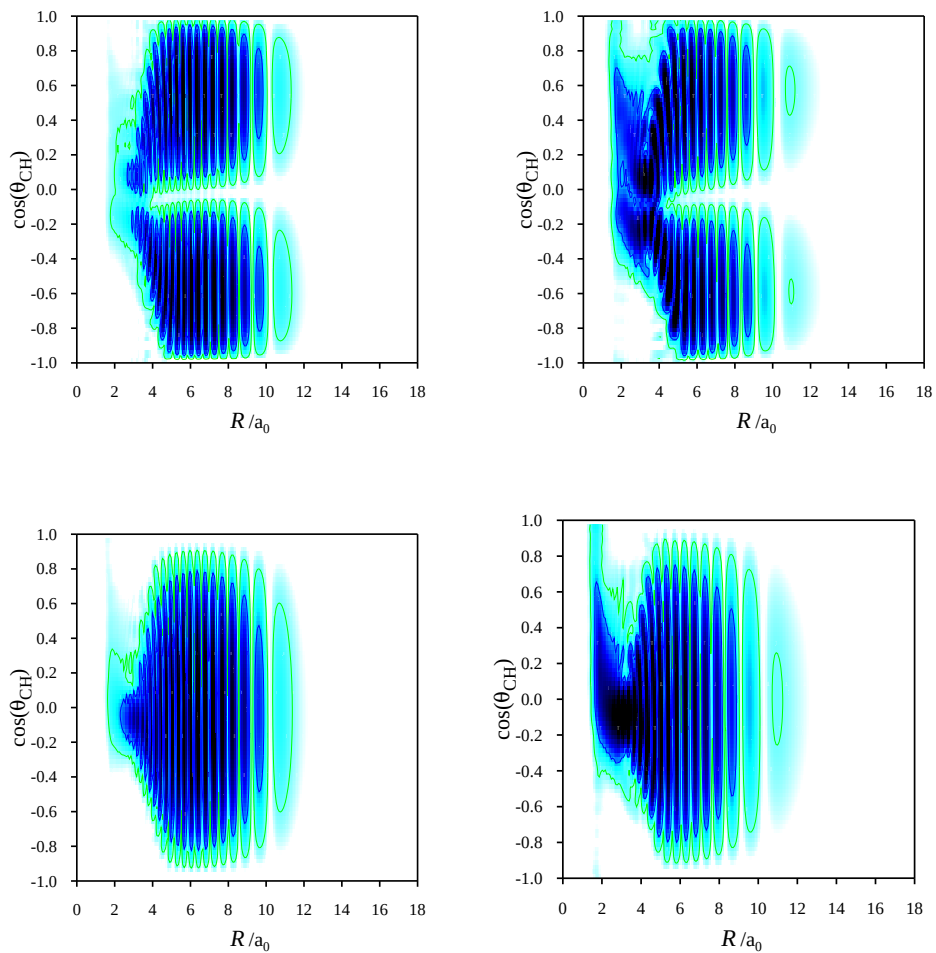


Figure 5.6: Reduced density plots of the wavepacket calculated at $J=10$, $j_{HH}=1$, $j_{CH}=3$, $\Omega_{HH}=1$ for $\Omega_{CH}=2$ (upper panels) and $\Omega_{CH}=3$ (lower panels) after 1200 (left panels) and 1500 (right panels) time steps represented as a function of $\cos \theta_{CH}$ and R .

sponds approximately to the time when the wavepacket has already fully covered it. The Figure tells us that as Ω_{CH} (or equivalently Ω) increases, larger density accumulates near $\cos \theta_{\text{CH}}=0$ facilitating the formation of the CH_3 intermediate complex.

A somewhat surprising (but completely consistent with the above considerations) result is shown in Figure 5.7 with "all else being equal", higher CH rotational excitation reduces the capture probability. This is the case of the $\text{CH} + \text{H}_2$ system since, at a fixed value of $\Omega_{\text{CH}} < j_{\text{CH}}$, an increase of j_{CH} leads to a larger divergence between the values of Ω_{CH} and j_{CH} , and thus to a larger desalignment of the related orientations. In these cases, it has also to be noted that a loss of symmetry with respect to the $\cos(\Omega_{\text{CH}})=0$ case ($\cos(\Omega_{\text{CH}})=-1$) corresponds to an attack to the carbon atom end of the CH diatom while $\cos(\Omega_{\text{CH}})=1$ corresponds to an attack to the other end (the hydrogen atom one).

Till now, we have concentrated our attention on the role of Ω_{CH} . Moreover, similar remarks could be made on Ω_{HH} though, due to its large rotational constant, H_2 tends to stay in low rotational states and not lead to a significant variation of j_{HH} and Ω_{HH} . Despite that, we have been able to find evidence of the above mentioned effect and draw some conclusions on the impact of j_{HH} and Ω_{HH} on the capture probability.

The effect of j_{HH} on the capture probability is illustrated in Figure 5.8. In the Figure, the j_{HH} rotational quantum number is incremented (from $j_{\text{HH}}=0$ to $j_{\text{HH}}=1$) being "all else" equal. As apparent from the Figure, the capture probability is slightly different at high translational energies whereas it is significantly different at low translational energies. Especially at low temperatures these differences are important and therefore it can be concluded that this effect significantly affects the value of the calculated rate coefficient.

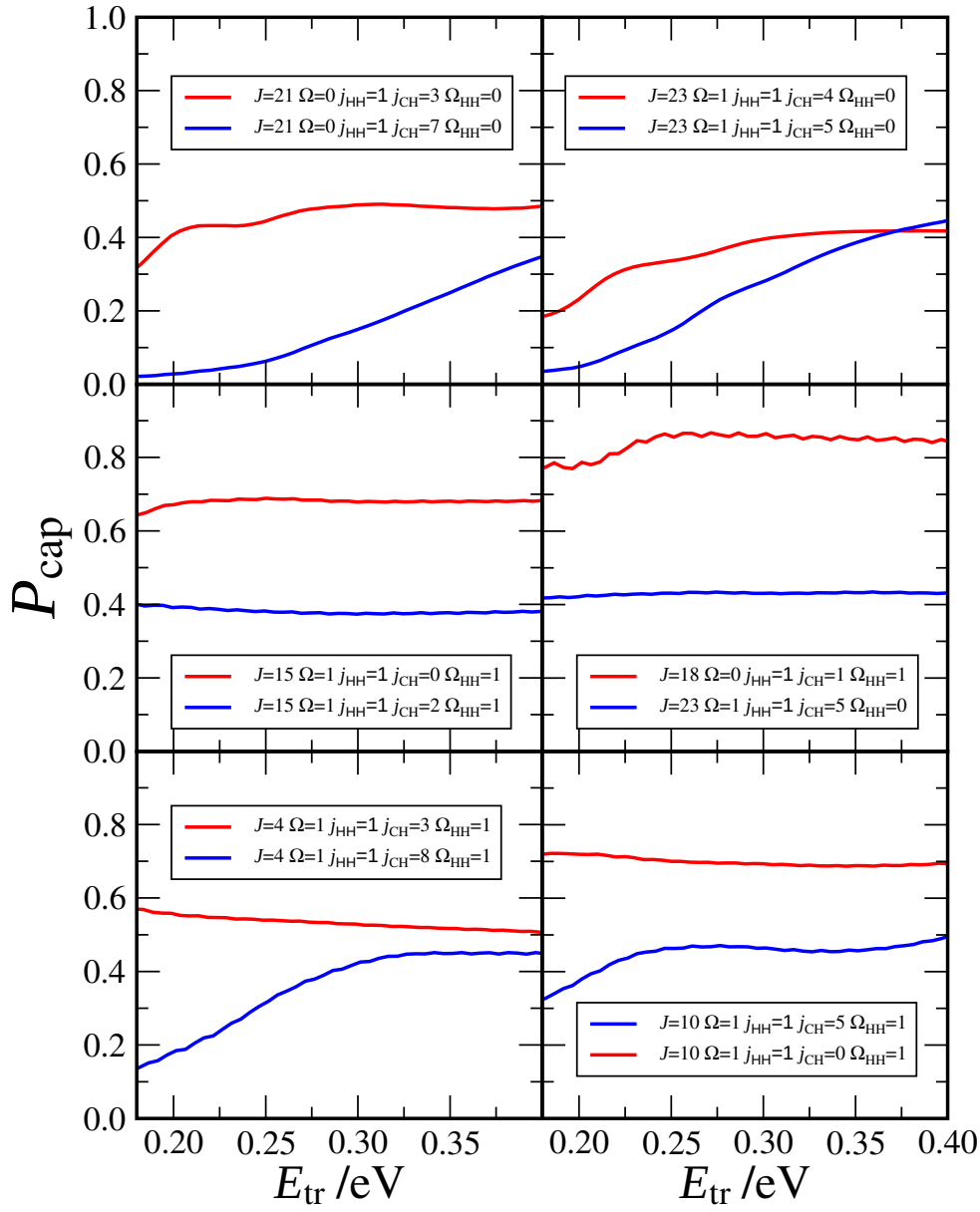


Figure 5.7: Capture probabilities calculated at different values of j_{CH} and plotted in pairs of values of J , Ω , j_{HH} and Ω_{HH} as a function of the collision energy.

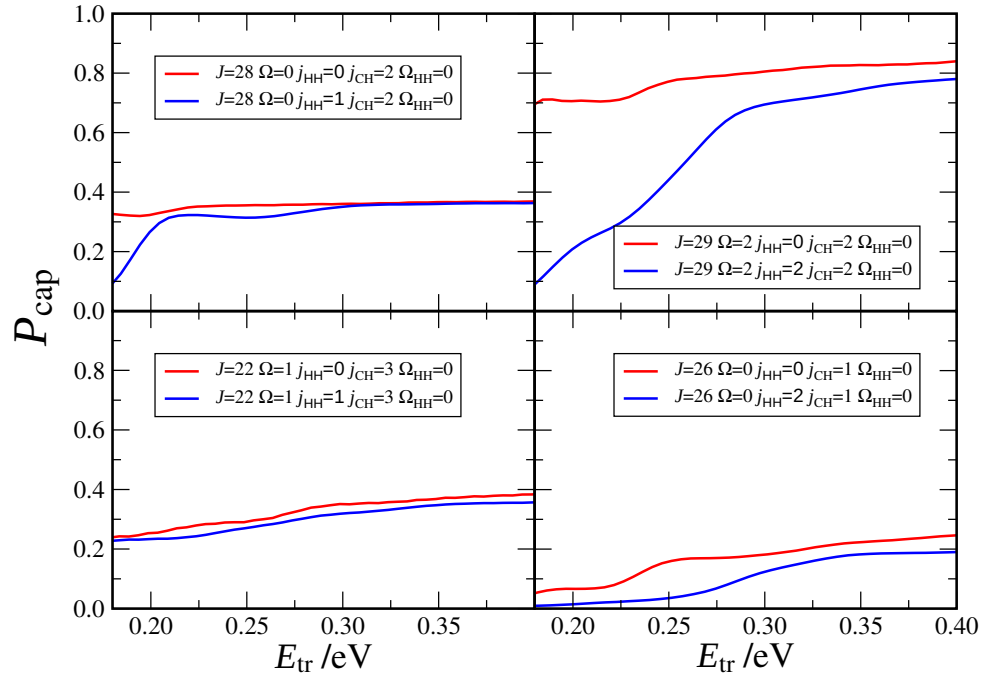


Figure 5.8: Capture probabilities calculated at different values of j_{HH} and plotted in pairs of values of J , Ω , j_{CH} and Ω_{HH} as a function of the collision energy.

5.2.2 Rate coefficients

As is well known, the calculation of thermal rate coefficients requires first the calculation of the cross section for the relevant interval of collision energy and all the appreciably populated rovibrational initial states and then its integration over E_{tr} and averaging over rovibrational initial states. The evaluation of the cross section needs in turn the calculation of partial reaction probabilities for all the values of J appreciably contributing to reaction. Unfortunately, as already mentioned, high J values calculations bear insurmountable difficulties. The maximum value of J needed for the converged calculation of the cross section is directly proportional to the mass of the system. Since in the present study three light atoms are involved, the maximum value of J ends up to be not so large to make the calculation impossible. However, things are made more difficult by the fact that being the system consists of two diatoms. Therefore, at $J > 0$ for each rotational state of one diatom, all the energetically accessible rotational states of the second diatom need to be computed. This makes the number of initial states to be considered too large to allow an exact calculation of the rate coefficient. At the same time, however, the use of drastic approximations, like the J -shift quantum and all J QCT ones, leads to quite inaccurate estimates of the rate coefficients. In this Section, we give first a short description of the J -shift and the QCT methods used and then the C/PST and PST results are presented.

The usual J -shift approximation to the calculation of the thermal rate coefficients relies on the identification of a "bottle neck" geometry (such as a transition state). For reactions proceeding through a deep well and having no "bottle neck" geometry, like the corresponding atom-diatom O + H₂ complex-forming one, the shifting model was found not to work and a "capture J -shift model" is known to work better [201]. Using the capture J -shift model one can determine, on the basis of the potential energy cut along the MEP and the associated $J(J+1)/2\mu R^2$ centrifugal term, various centrifugal barriers before entering the region of the complex formation. For the CH

+ H₂ reaction, one can then proceed as in reference [201] by simply assuming the reaction probability for any total angular momentum J be of the same form as the $J=0$ one yet shifted in energy to account for the "bottle neck" effect of the centrifugal barrier. These probabilities can then be used to compute the reactive cross section and/or the thermal rate coefficients. The thermal rate coefficients calculated in this way at 300 and 1000 K are respectively two and one order of magnitude smaller than the experimental value.

On their side, QCT calculations carried out using the VENUS96 program [200] led to better results. In QCT calculations, the appropriate Boltzmann distributions of collision energies and reactants rotational states were adopted. The reactants were kept in their vibrational ground states (that should be adequate for the temperatures considered) and at each temperature, a number of trajectories leading to a statistical error smaller than 2% (corresponding to 31000 and 90000 trajectories at the investigated temperatures of 300 and 1000 K) was run. The rate coefficient is computed from the total number of reactive trajectories using the expression [202]:

$$k(T) = g_{\text{el}} \sqrt{\frac{8k_{\text{B}}T}{\pi\mu}} \pi b_{\text{max}}^2 \frac{N_{\text{r}}}{N}$$

where N_{r}/N is the fraction of the reactive trajectories, b_{max} is the maximum impact parameter, and μ is the reduced mass of the system in the H₂ and CH arrangement. The electronic degeneracy factor, g_{el} , was set equal to 1/2 to take into account that only one of two spatial components of the Π state of CH in the reactant arrangement correlates with the CH₃ and the H + CH₂ product channels. To converge the calculations a $b_{\text{max}}=5.5$ Å had to be chosen. As apparent from Fig. 6 of ref. [68], the high temperature QCT results agree with the experiment while the low temperature ones appreciably deviate from the measured slope since they are essentially flat. This feature can be attributed to the unrealistic ability of trajectories to react at collision energies near or below the quantum mechanical threshold due to the missing correction for the zero point energy (ZPE) (see Figure 5.3). However, when reactive

trajectories with internal energy lower than the ZPE are discarded also QCT estimates of the thermal rate coefficients underestimate the experimental results by more than order of magnitude though showing a clear dependence on the temperature.

To obtain the C/PST estimate of the rate coefficient the wavepacket needs to be propagated in time for an ensemble of initial states (defined by five quantum numbers, $J, \Omega, j_{\text{HH}}, j_{\text{CH}}, \Omega_{\text{HH}}$) large enough to ensure convergence. The initial states were chosen by sampling the complete Boltzmann rotational ensemble at 300 K and considering $J_{\text{max}}=32$ (that means 1089 possible states).

The value of J_{max} was set at 32 because at this J value the reactive probability becomes zero at the minimum collision energy considered (0.18 eV). The Figure 5.9 offers a clear illustration of the effect of the centrifugal barrier and of its rise with J . In fact, while the capture probabilities calculated at total angular momenta lower than $J=25$ are independent of the collision energy, at higher values of J the centrifugal barrier determines a decrease of the reactivity at low collision energy (remember that a minimum of 0.18 eV of collision energy is needed to overcome the endothermicity of the reaction). Moreover, for the highest considered J value the collision energy threshold increases significantly (for example, 0.40 eV at $J=40$).

The convergence of the calculations of the rate coefficient at $T=300$ K with respect to the number of the initial states considered is shown in Figure 5.10. As apparent from the Figure, the calculated value of the rate coefficient oscillates significantly but from 200 states on it begins to converge at the final value. The value of $2.76 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ calculated in this way is in excellent agreement with the one given by Brownsford *et al.* [61] ($2.57 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Note that by choosing initial conditions according to their statistical weights, we reached convergence using a small fraction of all possible initial states.

One might wonder if an ensemble chosen at one temperature can be used to

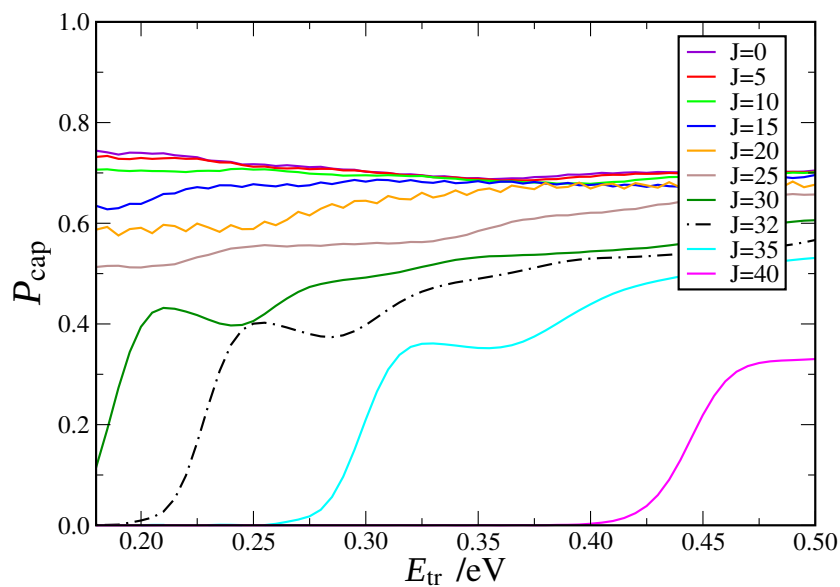


Figure 5.9: Capture probabilities calculated at $\Omega=j_{\text{HH}}=j_{\text{CH}}=\Omega_{\text{HH}}=0$ and several values of J plotted as a function of the collision energy.

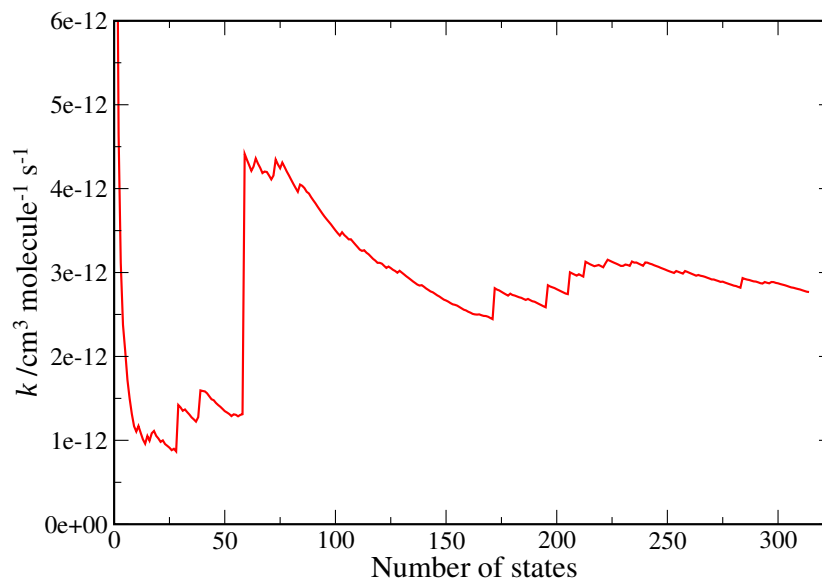


Figure 5.10: C/PST rate coefficient calculated at $T=300$ K and plotted as a function of the number of initial states included in the calculation.

compute the rate coefficient at other temperatures. To do this there are two main important consideration to make: (1) the $J_{\max}$ will increase with temperature and (2) the range of translational energies in eq. 4.72 will also increase. These factors are easily taken into account and we computed $k(T')$, being $T' \neq 300$ K, from our 300 K ensemble in the following manner. Employing the $P_i(E, J, j)$ already obtained, we computed $\tilde{P}_i(T', J, j)$ using 4.72. Then, the proper value of $J_{\max}$ for each temperature was determined analysing the capture profiles and finally $k(T')$ was calculated via eq. 4.73. One might also think that the weights for each member of the ensemble as given in eq. 4.70 should be adjusted for each particular temperature. However, in this work, because all the temperatures considered fall in the range 202–584 K distributions do not differ significantly from that at 300 K. This allowed us to keep the weights calculated for $T=300$ K also at the other temperatures.

In order to determine $J_{\max}$ for a given T' , we first determined the maximum value of the relative translational energy E_{tr} appreciably contributing to the integral of eq. 4.72. (The minimum E_{tr} is the amount needed to overcome the reaction endothermicity and is a function of initial states of the diatoms.) Table 5.3 shows the maximum collision energy for the temperatures used in this study and a value of $E_{\text{tr}}=0.40$ eV was set.

We then performed many test calculations at high J to determine the highest J in which there is significant capture probability for the relevant range of collision energy. As shown in Figure 5.9, at a given collision energy the capture probability decreases as J increases and the collision energy threshold increases significantly as J increases in such a way that a value of $J_{\max} < 40$ is sufficient to take into account most of the contributions to the capture probability at collision energies lower than 0.40 eV. It is important not to determine the value of $J_{\max}$ based on the contributions of a few initial states. For this reason, several tests considering mainly the most favourable oriented initial states were performed and, as a result of the tests, the

Table 5.3: Values of $J_{\max}$ and of the maximum E_{tr} relevant to the C/PST calculations at different temperatures.

Temperature (K)	Maximum E_{tr} (eV)	$J_{\max}$
202	0.15	30
294	0.20	32
300	0.20	32
364	0.30	35
484	0.35	38
584	0.40	39

values of $J_{\max}$ corresponding to the maximum collision energy for the temperatures used in this study were obtained. These values are also reported in the Table 5.3.

The values of C/PST rate coefficients calculated in the interval of temperatures ranging from 202 to 584 K, are plotted in Figure 5.11 and compared with the experimental results. As can be easily seen from the Figure, the agreement with the experiment is excellent. This suggests that the main contribution to the temperature dependence of the thermal rate coefficient comes from the two quantities given in Table 5.3: the maximum value of translational energy and the maximum value of the total angular momentum appreciably contributing to the rate coefficient. It should be noted that in general larger values of the translational energy result in larger values of the total energy, thus enhancing the ability of the CH_3 complex to overcome the reaction endothermicity.

Finally, it is of interest to compare the quantum C/PST rate coefficients with the more standard PST approach described in Chapter 4. In such an approach the capture probability is inferred from considerations on whether or not the centrifugal barrier of the reactant channel can be surmounted. As apparent from the Figure 5.11, for $T >$

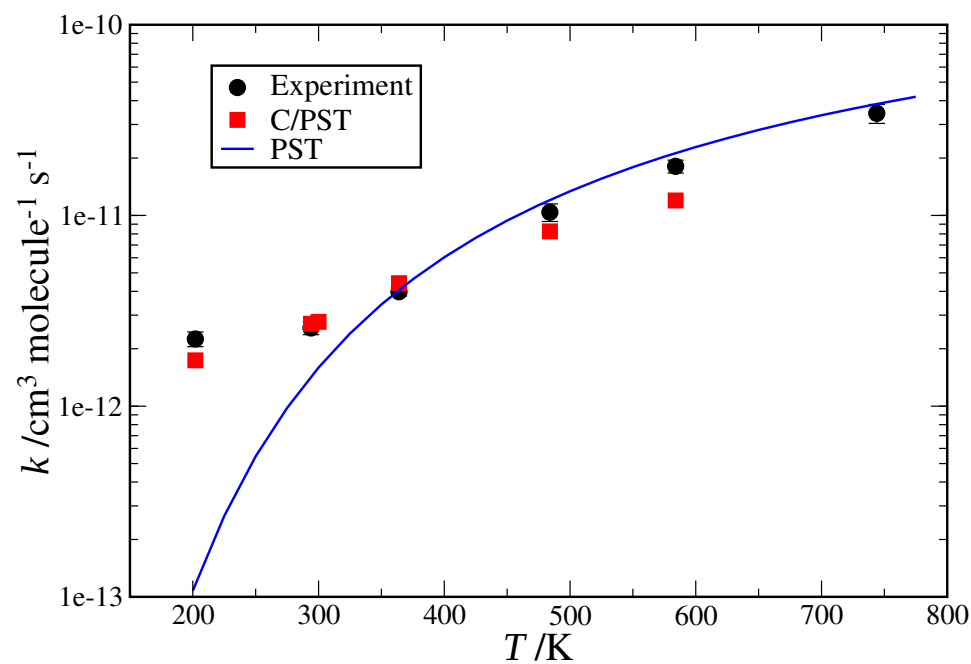


Figure 5.11: C/PST rate coefficients plotted as a function of the temperature. Experimental and PST results are also shown for comparison.

350 K PST is also in good accord with the experiment. For $T < 350$ K, however, the standard PST rate coefficient underestimates the rate coefficient. Near $T=200$ K, for example, it is more than a factor of ten lower than the experiment whereas quantum C/PST results are in much better accord. We have also investigated the effect of incorporating tunneling contributions into the PST calculation by replacing the step functions in eqs. 4.75 and 4.76 with tunneling probabilities based on parabolic or Eckart tunneling formulations. The correction led to a factor of two increase in the rate coefficient at the lowest temperatures in Figure 5.11 suggesting that there are other contributions (such as orientation) coming into play.

Chapter 6

Conclusions

The main objective of this work was to calculate quantum rate coefficients for both the triatomic reaction $\text{N} + \text{N}_2$ and the tetratomic reaction $\text{CH} + \text{H}_2$. Accurate estimates of the rate coefficients of these reactions are part of the necessary database for the modeling of complex environments in atmospheric chemistry, combustion, astrochemistry, cold plasmas, spacecrafts reentering, etc.

Reaction probabilities (the first step to evaluate more averaged properties like cross sections and rate coefficients) were calculated using quantum time-dependent methods. The time-dependent approach allows to solve in a single run the Schrödinger equation for a given initial state of the reactants and a range of collision energies. To carry out the calculations the code developed by Skouteris and Laganà (RWAVEPR) for triatomic reactions and the RWP code developed by Goldfield for tetratomic reactions were used.

The reactions tackled are intrinsically difficult to study using quantum dynamical methods. The triatomic reaction $\text{N} + \text{N}_2$ involves three non hydrogen atoms and

therefore several hundreds of initial states have to be considered to compute the rate coefficient at relatively high temperatures. At the same time, a large number of total angular momentum states has to be considered. The $\text{CH} + \text{H}_2$ reaction is a tetratomic one and this implies a larger number of degrees of freedom.

The most possible rigorous quantum methods were used to calculate the kinetic and dynamic properties. For the triatomic $\text{N} + \text{N}_2$ reaction, rate coefficients were calculated using the popular J -shift approximation while (converged) cross sections were computed using the centrifugal sudden approximation and a limited study of the reaction probabilities were carried out using an "exact" treatment. For this reaction also high-level ab initio calculations were performed and a new potential energy surface was proposed. For the tetratomic complex-forming $\text{CH} + \text{H}_2$ reaction, (converged) centrifugal sudden calculations were performed to calculate the capture probabilities as a first step to estimate accurate rate coefficients. The choice of calculating capture probabilities rather than the state-to-state ones is due to the averaged nature of the rate coefficients.

Once outlined the methods and the calculations performed, the main conclusions are detailed, beginning for the exchange reaction $\text{N} + \text{N}_2$.

The reactive probabilities calculated at $v=j=J=0$ on several PESs (namely, the LEPS, L0, L1 and L3 PES) have allowed us to investigate the effect of modifying the geometry of the system at the saddle to reaction and the height of the saddle. Thus, the bending of the saddle geometry leads to an increase of the collision energy threshold and a consequent decrease of reactivity at fixed energy. At the same time, the lowering of the saddle leads to a decrease of the threshold and a significant increase of the reactivity. The study of these effects provides a solid quantum basis to the well-known Polanyi's rule linking the efficiency of various degrees of freedom in promoting reactivity.

The reactive probabilities calculated at $v=1-5$ and $j=J=0$ indicate a significant efficiency of vibrational energy in promoting reactivity on bent PESs and a consequent larger than that of collinearly dominant PESs.

Hereafter, the conclusions of the study on the $N + N_2$ reactive system refers only to the LEPS PES that is a collinearly dominant surface and the L3 PES that has a bent geometry and a lower saddle.

The PVDs calculated at $v=0-5$ and $j=J=0$ on both LEPS and L3 PESs indicate a substantial vibrational adiabaticity of the reaction although it progressively deteriorates as v increases populating higher product vibrational states.

The reactive probabilities calculated at $v=0-3$, $J=0$ and several values of j indicate that for the LEPS the rotational excitation scarcely modifies the threshold collision energy while for the L3 it is shifted to lower energy. Moreover, this effect is also accompanied by a simultaneous increase of the reactive probability. These results confirm that on the bent dominant PESs the interconversion of rotational energy to collision energy is efficiently exploited.

The reactive probabilities calculated at $v=j=0$ and $J=0-70$ on both LEPS and L3 PESs show a clear regular shift in the collision energy as J increases and a linear dependence when they are plotted as a function of $J(J+1)$. Therefore, the assumptions of the J -shift model are fulfilled and the rotational constants derived acceptably agree with those corresponding to the geometry at the reaction saddle. It is worth to recall that on the LEPS a linear rotor is assumed while on the L3 surface the rotor is assumed to be a prolate symmetric top. This issue and the related larger value of the rotational constant calculated for the L3 PES implies that the shift in energy for the LEPS probabilities is lower than that for the L3 ones.

Calculations of the reactive probabilities at $J=0$ for the 242 lower rovibrational

states were performed in order to cover all the significant contributions to the rate coefficient at the highest temperature considered (4000 K). The probabilities at $J > 0$ (and subsequently the cross sections) were then calculated by applying the J -shift approximation.

The calculated partial cross section terms, $\sigma_{vj}^J(E_{\text{tr}})$, show that, as expected, the threshold collision energy increases as J increases. A more interesting feature found is that the partial cross section terms show a maximum at J values as high as 100 and become negligible at $J > 160$. On the other hand, the values calculated on the LEPS surface are significantly larger than those calculated on the L3 surface due to the smaller energy shift mentioned above.

The analysis of the J -shift cross sections calculated for the 242 lowest rovibrational states show that at all the vibrational states considered here the largest cross section corresponds to the ground rotational state of the reactants. At the same time, when the rotational quantum number j increases, the cross section decreases becoming independent of the initial rotational state at high values of j . At the same time, the vibrational excitation increases significantly the cross sections. As to the comparison between the LEPS and the L3 cross sections, the former are clearly larger than the latter as one would expect due to a smaller energy shift.

J -shift thermal rate coefficients, calculated in the range of temperatures 1000–4000 K, show a dependence on the temperature similar to the experimental one. On the other hand, the LEPS rate coefficients at lower temperatures are slightly higher than the L3 ones while they agree at higher temperatures. However, the rate coefficients calculated on both surfaces fall slightly short of the measured data. This suggested that the PES has to be moulded to better reproduce the ab initio information especially in the transition state region.

Calculations using the CS approximation of the cross sections were performed

at the $v=0, j=14$ and $v=0, j=24$ (the most populated states at the temperatures of the experiment, $T=1273$ K and $T=3400$ K) on the L3 PES for total angular momentum quantum numbers up to $J=100$ (half those needed for the J -shift calculations) in order to reach convergence. For each J value, all the Ω quantum numbers allowed were considered.

A first analysis of the CS reaction probabilities indicates that they are nearly independent on Ω at low Ω values while they progressively decrease as the value of Ω increases to vanish at the highest values of Ω . This behaviour suggests that an attack by the atom to the molecule rotating in a plane parallel to the velocity vector is preferred.

The calculated CS partial cross section terms, $\sigma^J(E_{\text{tr}})$, show a clear different dependence on the total angular momentum J at the lower and higher collision energies. At the lower collision energies, the cross section terms decrease near linearly from $J=0$ as J increases while at higher collision energies they present a maximum value at total angular momentum as high as 60–70. The value at the maxima is significantly larger than that for $J=0$ and it increases as the collision energy increases. On the other hand, the dependence of the cross section terms on the collision energy varies at the lower and higher total angular momenta. Thus, as J increases both an increase of the threshold energy for the reaction and a dramatic enhancement of the reactivity in the just-past-the-threshold region are observed. Minor differences between the results for the $v=0, j=14$ and $v=0, j=24$ states are found.

The calculated CS cross sections for the $v=0, j=14$ and $v=0, j=24$ states exhibit a similar dependence on the collision energy, a threshold energy and thereafter an exponential increase. However, a smaller threshold energy for the $v=0, j=24$ state and a larger cross sections at the higher collision energies for the $v=0, j=14$ state are found.

The comparison of the partial cross section terms, $\sigma^J(E_{tr})$, obtained from the CS and the J -shift approximations shows appreciable differences especially at high values of J . In fact, in these cases, the CS terms exhibit larger thresholds and more pronounced increases at the just-pass-the-threshold collision energies.

The comparison between the CS and J -shift cross sections shows a clear discrepancy at the higher collision energies for which the CS cross section is twice the J -shift ones. On the contrary, at the lower collision energies the J -shift cross sections are slightly larger than the CS ones despite the fact that the related threshold energies are almost coincident.

Calculations aimed at investigating the effect of the Coriolis coupling (neglected in the CS calculations) were performed on the L3 PES for the $v=0, j=24$ rovibrational state and for a limited cases of the total angular momentum because of the huge computational effort they require.

The investigation of the effect of raising the level of coupling on the reactive probability shows that it is more effective at the higher values of Ω considered, that is when the velocity vector is parallel to the axis of rotation of the diatomic molecule. On the other hand, the neglect of the Ω coupling leads to an underestimation (overestimation) at high (low) collision energy. Moreover, the fact that the underestimation increases with Ω confirms the important role played by the coupling at high values of Ω .

The comparison of the "exact" (considering the coupling among all allowed Ω states) and CS partial cross section term at $J=5$ shows that the "exact" results are higher than the CS ones and that the differences can become as large as 17%. Accordingly, it looks like the Ω coupling further enhances the exploitation of coupling collision energy to promote the reactivity of the system.

Calculations were performed also on a new potential whose construction was motivated by the drawbacks of results obtained on the LEPS and L3. The new PES is based on high-level ab initio calculations. A limited number of calculations were performed. In particular, ab initio calculations were devoted to characterize the transition state region, to figure out its dependence on the bond angle and to determine the minimum energy path at several bond angles. The calculated ab initio energies show the existence of a double barrier connected by a shallow well between reactants and products although the double barrier structure tends to disappear as the bond angle moves away from that of the transition state. The double barrier structure at the transition state found in our calculations coincides with the one described in ref. [35]. However, no other features could be compared because the surface is not available for distribution and its details are not given in the paper.

The new PES (called L4) was generated using the LAGROBO functional (previously developed in our group). Substantial modification to the LAGROBO function were inserted in order to describe accurately the most complex topology characterized by the new ab initio data. Nevertheless, only twenty parameters were used for the new L4 PES. The main difference between the L4 and L3 PESs, apart from the double barrier structure, is the height of the saddle. In fact, the height of the saddle of the L4 PES (and of the ab initio results) is 0.73 eV higher than that of the L3 PES.

The first dynamical study on the new L4 PES was aimed at calculating the J -shift cross sections (from the exact $J=0$ reactive probabilities) for the two rovibrational states $v=0, j=14$ and $v=0, j=24$. The calculated cross sections exhibit a threshold energy and a moderate increase as the collision energy increases. However, when these results are compared with those obtained on the L3 PES a significant shift of the threshold energy is observed. The shift roughly coincides with the difference between the heights of the related saddles.

Another dynamical study on the new L4 PES was aimed at calculating the CS cross sections only for the rovibrational state $v=0$, $j=24$. Total angular momentum quantum numbers up to $J=100$ and all the allowed Ω projections were included in the calculation in order to reach convergence. The calculated cross sections show a dependence with the collision energy similar to that found on the L3 PES. However, as just mentioned, the threshold energy is significantly shifted to higher collision energy. At the same time, as for the L3 PES, at high collision energy the CS cross sections are significantly larger than the J -shift ones.

For the tetratomic reaction $\text{CH} + \text{H}_2$ the conclusions are as follows.

The capture probabilities calculated at $j_{\text{HH}}=j_{\text{CH}}=J=0$ are in the 70–74% range for all collision energies considered. This feature was explained as a consequence of the narrow width of the entrance channel with respect to the possible orientations of the CH and the H_2 . The effect of the orientation of the diatoms was confirmed from the results of the calculations performed at $j_{\text{CH}}=j_{\text{HH}}=1$. In fact, when the diatoms are oriented on a perpendicular (parallel) fashion the capture probability increases (decreases).

The C/PST reaction probabilities calculated at $j_{\text{HH}}=j_{\text{CH}}=J=0$ show a threshold energy of 0.2 eV (similar to the reaction endothermicity) and at the highest collision energy considered, the probability reaches a value of near 0.3. These values underestimate the probabilities calculated directly with a RWP method [68], even though the excitation functions have a similar shape. However, the agreement improves if the quantum probabilities are corrected to overcome the restriction that the initial CH bond does not break. At the same time, a good agreement is found when QCT reaction probabilities are corrected for the zero point energy violation.

The mechanism of the $\text{CH} + \text{H}_2$ reaction was characterized by investigating the distribution of trajectory lifetimes. Thus, the number of trajectories with long life-

time (those that forming the CH_3 complex) well correlates with the quantum capture probabilities. Moreover, the break up of the quasiclassical complex is found to be one third, that is, it is statistical.

The capture probabilities calculated at $J > 0$ for several initial quantum states increase with Ω and larger values of Ω imply that $\Omega_{\text{CH}} \rightarrow j_{\text{CH}}$ and $\Omega_{\text{HH}} \rightarrow j_{\text{HH}}$, or, in other words, that the diatoms approach each other in a parallel fashion and perpendicularly to the relative velocity vector.

The rotational excitation of CH (at all the remaining quantum states equal) reduces the capture probability. This feature was attributed to a loss of the optimal orientation caused by an increased difference between Ω_{CH} and j_{CH} .

The capture probabilities calculated at $\Omega=j_{\text{HH}}=j_{\text{CH}}=\Omega_{\text{HH}}=0$ and $J=0-40$ show a centrifugal barrier only for $J > 25$. Moreover, a value of $J_{\text{max}}=32$ is found to be large enough to guarantee the convergence for the rate coefficient calculations at $T=300$ K.

The C/PST rate coefficient calculated at $T=300$ K selecting three hundred (of the 1089 possible) initial quantum states ($2.76 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is in excellent agreement with the experimental value ($2.57 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [61].

The C/PST rate coefficients calculated in the range of 202–584 K were derived from the capture probabilities by adjusting the value of J_{max} . The results show an excellent agreement with the experimental values.

The rate coefficients calculated using a standard PST model slightly overestimate the experimental results at the higher temperatures considered. However, as the temperature decreases this difference increases significantly. This loss of reactivity

can be understood in terms of the omission of the orientational effects in the PST model.

A last comment is deserved by the computational aspects underlying the calculations of the present Thesis and occasionally treated in the text. The deployment of the COMPCHEM virtual organization [78] within the EGEE production grid infrastructure [77] has been the key move that has significantly enhanced the possibility of carrying out extended calculations using three tridimensional quantum methods. The possibility in fact of distributing the individual computational task over many nodes of a grid infrastructure has been vital for the success of the computations required by the present Thesis. The other key requirement is to have access to 64 bits machines (like ARINA at the SGI/IZO-SGIker of the Basque Country University [203]) in order to be able to deal with the high memory demand of "exact" partial wavepacket calculations.

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