Isotopic Effects in Ion-Molecule Reactions

Ronald McCarroll

Laboratoire de Chimie Physique-Mat'ere et Rayonnement, Unite Mixte de Recherche n°7614 , Universite Pierre et Marie Curie and CNRS, 11 Rue Pierre et Marie Curie, 75231 Paris Cedex 05, France.
E-mail: ronald.mac_carroll@upmc.fr

Abstract. A review is presented of theoretical methods for the treatment of isotopic exchange in exothermic low energy ion-molecule reactions. These processes play a fundamental role in our understanding of the chemical evolution of interstellar space. While many experimental measurements of the rate coefficients have been carried out over the past 20 years for a wide variety of molecular species, most of these were for temperatures exceeding 200K. At lower temperatures there are very few precise measurements for most of the reactions of interest. And, while the existence of a substantial isotopic effect has been recognized there are even fewer quantitative estimations of the dependence of the rate coefficient on temperature. In this work a statistical model is developed which takes account fully of energy, angular momentum and symmetry constraints to calculate both collision cross sections and rate coefficients.

1. Introduction

This talk is concerned with low energy reactive collisions between ions and molecules, in particular those which involve isotope exchange. In many astrophysical and planetary atmospheres the abundance of molecules containing one or more of the rarer isotopic constituents yields very useful information on the formation mechanisms of the different molecular species [1]. The simplest and most studied example of the problem concerns the formation of the HD isotope [2, 3, 4]. The observational astrophysical evidence indicates that the rate of formation of HD is much more rapid than that of H₂. The formation of H₂ takes place via the association of two H atoms on the surface of an interstellar grain. A similar mechanism will of course be effective for HD formation, but the corresponding rate is insufficient to explain the observations. A more rapid way to form HD is via an indirect chain reaction involving a weak non thermal source of cosmic rays which is responsible for a small but significant fraction (of the order of 10⁻⁴) of H⁺ ions in the interstellar medium. Subsequently, the D atoms are rapidly ionized by the resonant charge exchange reaction with H⁺ ions

\[ H^+ + D \rightarrow H + D^+ \]  

followed by the ion-molecule reaction

\[ D^+ + H_2 \rightarrow HD + H^+ \]  

We observe that since the internal energy of HD is 0.0358 eV lower than that of H₂ the exothermic reaction (2) can occur with a rate coefficient of the order of 10⁻⁹ cm³ s⁻¹ even at the lowest temperature. Similar overabundance of many more complex isotopic deuterated species have been observed. The effect can also be found with heavier species such as ¹³CO. For this reason the isotopic abundances in space, derived from observations of CO may not yield a correct estimation of the ¹²C/¹³C abundance ratio.

The problem of isotopic substitution in ion molecule reaction has attracted little detailed interest in the past 10 years. This stems in part form the difficulty of laboratory experiments at the very low temperatures (10-300K) required for astrophysical applications. Ideally, we would require collision cross section for molecules in a specific rotation state (at the temperatures of interest, most molecules of interest are in their ground vibration state). But even at temperatures as low as 100K, many rotation states can be populated. Most laboratory experiments are carried out at pressures which
ensure a thermal distribution of rotation states and only rate coefficients can be determined. It is clear that the extraction of a state selective collision rate from experimental measurements is at best a highly risky process.

However, in the very low energy regime, theory offers many attractive features, which allows us to investigate state selective cross sections with some degree of confidence. But first of all it is of interest to recall some aspects of statistical mixing models, originally introduced by Langevin [5] proposed for the study of ion mobility in a gas, and first applied to ion-molecule reactions in the 1970’s. See review by Watson [6].

2. Statistical ion-molecule models

First of all, let us recall the basic hypothesis of the simplest Langevin type model, when applied to exothermic reactions involving molecules with no internal rotation. Such a theoretical model is expected to be valid only for temperatures $T < B/k$ where $k$ is the Boltzmann constant and $B$ the rotational constant of the molecule. For relative kinetic energies of the reactants up to about 100 meV, the reactive cross sections collisions are governed by the long range interaction between the reactants. (1 meV corresponds roughly to a temperature of 10K). In the classical statistical model [6] the initial state of the system is characterized by the relative kinetic energy of the reactants $E_i$ and the impact parameter $b$. When, in addition, it is assumed that the interaction potential depends only on the ion-molecule distance $R$, the effective radial potential may be written as

$$V_{\text{eff}}(b, E_i, R) = V(R) + \frac{E_i b^2}{R^2}$$

For $R$ greater than about 5 Bohrs, $V(R)$ is attractive of the form $V(R) = -C_s/R^4$. For low collision energies (of the order of around 100 meV or less), such a potential will lead to orbiting of the reactants at some critical distance $R_{\text{max}}$. The usual procedure is to calculate, for some given $E_i$, the value of $R = R_{\text{max}}$ for which $V_{\text{eff}}(E_i, b, R)$ is maximum. Then considering $R_{\text{max}}$ as a function of $E$ and $b$, we determine the value of $b = b_c$ for which $V_{\text{eff}}(R_{\text{max}}) = E_i$. We observe now that $b_c$ is a function of $E_i$. The critical assumption of statistical models, is that the reaction proceeds with unit probability if $b < b_c$ but is forbidden if $b > b_c$. In other words, the centrifugal barrier can only be crossed if $b < b_c$. Then, the reactive cross section is given by

$$\sigma(E_i) = 2\pi \int_0^{b_c} b P(E_i, b) db = 2\pi b_c^2 \int_0^{b_c} b db = \pi b_c^2$$

This calculation is elementary for interaction potentials of the form $R^{-4}$, when expressions both $R_{\text{max}}$ and $b_c$ can readily be obtained in analytic form.

However, if, the aim is to determine rate coefficients, it is more convenient to characterize the initial state of the collision system by $E_i$ and its angular momentum by $L = b \sqrt{2\mu E_i}$ where $\mu$ is the reduced mass.

$$V_{\text{eff}}(L, R) = V(R) + \frac{L^2}{2\mu R^2}$$

The advantage of this procedure is that it is readily adaptable to a semi classical quantification of the relative angular momentum and, as will become apparent later, makes it much simpler to enforce angular momentum conservation.
As before, we determine, for a given value of $L$ the radial distance $R_{mx}$ for which the effective potential $V_{\text{eff}}(L, R)$ is maximum. In conformity with the capture model, the reaction for any given $L$ is assumed to proceed with unit probability if $E_i > V_{\text{eff}}(L, R_{mx})$ but is forbidden if $E_i < V_{\text{eff}}(L, R_{mx})$. To obtain the cross section, then if $L$ is treated as a continuous variable, we integrate over all possible $L$ to obtain

$$\sigma(E_i) = \frac{\pi}{\mu E_i} \int_{0}^{\infty} L P_L(E_i) dL$$

(6)

where

$$P_L = \begin{cases} 1 & \text{if } E_i \geq V_{\text{eff}}(L, R_{mx}) \\ 0 & \text{if } E_i < V_{\text{eff}}(L, R_{mx}) \end{cases}$$

(7)

For molecules with no internal rotation, a classical description of $L$ is satisfactory since the values of $L$ which contribute most to the cross section are large (of the order of 50-150 a.u.). But when we treat molecules with internal rotation, the rotational quantum number $j$ is quite small (in the range from 0 to15 a.u.) for which a semi-classical quantification is preferable. So, treating $L$ as a semiclassical quantized variable $L_{sc} = L + 1/2$, the effective radial potential may be defined as

$$V_{\text{eff}}(L_{sc}, R) = V(R) + \frac{L_{sc}^2}{2\mu R^2} = V(R) + \frac{(L + 1/2)^2}{2\mu R^2} \approx V(R) + \frac{L(L + 1)}{2\mu R^2}$$

(8)

Then the total cross-section can be expressed as a sum over all possible values of $L$.

$$\sigma(E_i) = \frac{\pi}{2\mu E_i} \sum_{L=0}^{\infty} (2L+1)P_L(E_i)$$

(9)

The expressions (4) and (9), which are not significantly different, correspond to the Langevin capture model. For reactions of ions with non-polar molecules this model predicts qualitatively rate coefficients at room temperature (300-400K). But at lower temperatures (10-200 K), it fails to reproduce correctly the measured temperature dependence. Also, it is unsatisfactory to describe reactions between neutral molecules.

One obvious weakness of the simple Langevin model is the neglect of the anisotropic contribution to the interaction potential. A more precise representation of the interaction potential is given by [7, 8]

$$V(R, \theta) = -\frac{\mu_d}{R^2} \cos \theta + \frac{Q(3\cos^2 \theta - 1)}{2R^3} - \frac{1}{6R} \left[ 3\alpha + (\alpha_i - \alpha_p) (3\cos^2 \theta - 1) \right]$$

(10)

where $\mu_d$ is the dipole moment of the molecule, $Q$ is the quadrupole moment, $\alpha$ is the isotropic polarizability and $\alpha_i, \alpha_p$ are the anisotropic components of the polarizability parallel and perpendicular to the molecular axis. The anisotropic terms of (10) can be taken into account using the statistical adiabatic channel model of Troe [7, 8] or variants thereof [9-14]. The main corrective term in (10) is only present in the case of polar molecules. In this work, we shall only be concerned with non-polar molecules such as $H_2$, the main corrective term arises from the quadrupole term. This term is not expected to be dominant, but its inclusion will give a measure of the accuracy of the theoretical model.

3. Calculation of the rate coefficient at very low temperatures

The rate coefficient can always be defined, but it is only when the reactants are in thermal equilibrium that a practical calculation can be made. In this section, we determine the rate constant
when only the ground rotational state \((j = 0)\) of the molecule is significantly populated. In this case the kinetic energy of the reactants, \(E_i = E\).

We first define the transition rate \(K_0(E)\) at a specific energy \(E\),

\[
K_0(E) = \sqrt{\frac{2E}{\mu}} \sigma_0(E)
\]  

(11)

The rate coefficient at a temperature \(T\) is then given by integrating (11) over the Maxwell distribution of \(E\). Then, we obtain, using (8)

\[
K_0(T) = \frac{1}{2\mu kT} \left(\frac{8}{\pi \mu kT}\right)^{1/2} \int_0^\infty \sum_{L=0}^\infty (2L+1)P_L(E) \exp\left(-\frac{E}{kT}\right) dE
\]

(12)

and permuting the integration over \(E\) with the sum over \(L\), we have

\[
K_0(T) = \left(\frac{2\pi}{\mu kT}\right)^{1/2} \sum_{L=0}^\infty (2L+1)\exp(-E_L^* / kT)
\]

(13)

This expression (13) was first used to calculate reaction rates in [15]. We may remark that it is identical to the result of the statistical capture model [7, 8] based on the assumption that the reaction proceeds via an energetically accessible transition state. For every value of \(L\), there exists a quasi-stationary transition state, and if accessible, the reaction proceeds with unit probability. However, the formula (13) is only valid at very low temperatures \(T\) for which \(T < B / k\). So even for a molecule such as \(\text{H}_2\), which has a large rotation constant of 60.4 cm\(^{-1}\) (13) is not expected to be valid for temperatures exceeding 50K when the population of excited rotational states becomes significant.

4. Calculation of the rate coefficients including rotation

Other considerations become important when the reactant molecule has internal rotational energy. In section 3, the reactant molecule has no internal rotation energy and the relative angular momentum of the system \(L\) is conserved. But when the molecule possesses an internal angular momentum \(j\), the conservation of the total angular momentum imposes additional constraints. For a general discussion of this problem see [16-18] and for an application to reactive collisions involving neutral molecules see [19].

Fortunately, in the asymptotic region, where the interaction potential is purely radial, the internal rotation is not coupled to the relative angular momentum and so, in this region the initial relative angular momentum \(L\) is still conserved. Consequently, as in the preceding section, the transition states can be labelled by a value of \(L\) from 0 up to \(L_{\text{max}}\) and their energies are determined uniquely by the asymptotic potential and \(L\). All transition states which contribute effectively to the reaction are defined by the asymptotic potential. Energy conservation is ensured by the condition that the collision energy must exceed the centrifugal barrier. So, when the energy \(E\) and the angular momentum \(L\) are such that the centrifugal barrier can be crossed, and the reactive region, where the interaction is no longer isotropic, becomes accessible. But, whereas the \(j, L\) states are uncoupled in the asymptotic region, they become strongly coupled in the reactive region. Then, neither \(j\) nor \(L\) is conserved in the reaction process.

So let us now consider the cross section when the reacting molecule is in a specific initial rotation state \(j\). If no restriction is introduced on the nature of the coupling between states \(j\) and \(L\), we might expect statistical mixing of the \((2j+1)(2L+1)\) degenerate states of the entry channel. But this is incorrect since such a statistical mixing of all the \((2j+1)(2L+1)\) states of the \((j, L)\) entry channel would violate angular momentum conservation. The \((j, L)\) entry channel does not correspond to just one.
specific total angular momentum (as in section 3). Rather, it corresponds to a superposition of \((2j+1)\) total angular momentum states \(J\) where
\[
|L - j| \leq J \leq L + j
\]  
(14)
The net results of this constraint that since there is only a probability of \(1/(2j+1)\) of forming a complex of total angular momentum \(J\) and since there is only a statistical mixing of states with a given \(J, M_j\) we find that
\[
P^j_L = \begin{cases} 
\frac{1}{2j+1} & \text{if } E_i \geq V_{\text{eff}}(L, r_{\text{mx}}) \\
0 & \text{if } E_i < V_{\text{eff}}(L, r_{\text{mx}})
\end{cases}
\]  
(15)
where \(E_i\) is the relative kinetic energy of the system, initially in rotational state \(j\). It then follows that
\[
\bar{\sigma}_j(E_i) = \frac{\pi}{2\mu E_i} \left( \frac{1}{2j+1} \sum_{L=0}^{\infty} (2L+1)P^j_L(E_i) \right)
\]  
(16)
We may observe that this result is due to the fact that there is only a fractional probability of forming a \(J\) state from any given couple \((j, l)\). No probability is lost since other \(J\) states can be formed from other \((j, l)\) couples. And, when we sum over \(L\), it is easy to verify that all possible values of \(J\) have been taken into account. The result (16) is, of course, only valid for randomly oriented molecules. It would require modification in the case of an aligned reactant.

The rate constant for a reactant in state \(j\) is then given by
\[
K_j(T) = \frac{1}{2\pi Q_T} \frac{1}{2j+1} \int_0^\infty \left( \sum_{L=0}^{\infty} (2L+1)P^j_L(E_i) \exp\left( -\frac{E_i}{kT} \right) \right) dE
\]  
(17)
where \(Q_T\) is the partition function of the translation motion given by:
\[
Q_T = \left( \frac{2\pi}{\mu kT} \right)^{-3/2}
\]  
(18)
We note that when there is no internal rotation, that is for \(j = 0\), the result is identical to expression (10). As before, permuting the integration over \(E_i\) with the sum over \(L\), we obtain
\[
K_j(T) = \frac{1}{2\pi Q_T} \frac{1}{2j+1} \sum_{L=0}^{\infty} (2L+1)\exp\left( -\frac{E_L^*}{kT} \right) E_L^* = V_{\text{eff}}(L, R_{\text{mx}})
\]  
(19)
The total reaction rate, summed over all \(j\) is then given by:
\[
K(T) = \frac{1}{Q_T(T)} \sum_{j=0}^{\infty} K_j(T)(2j+1)\exp(-E_j/kT) = \frac{S_v(T)}{2\pi Q_T Q_T(T)} \sum_{L=0}^{\infty} (2L+1)\exp(-E_L^*/kT)
\]  
(20)
where
The rate coefficient given by formula (20) differs from the result of Liao and Herbst [20]. To our knowledge, the formulae (20) and (21) do not seem to have been used before to calculate rate coefficients.

In the case of a diatomic molecule whose electronic ground state is of \( \Sigma \) symmetry, \( Q_r(T) \) is defined as

\[
Q_r(T) = \frac{1}{\sigma_r} \sum_{j=0}^{\infty} (2j+1) \exp \left( - \frac{E_j}{kT} \right)
\]

where \( E_j \) is the energy of the \( j \)th rotational level and \( \sigma_r = 2 \) for symmetric diatomic molecules and is unity for non-symmetric species.

It may be observed that an analogous expression to (20) has been successfully used by a number of applications [21,22] to take account of the statistical mixing of fine structure levels in atom-molecule reactions at low temperatures. It may also be remarked that the expression (20) ensures detailed balance.

6. Calculation in the statistical adiabatic channel method (SACM)

The modifications introduced in the SACM approach can be implemented in a relatively simple way. The main initial requirement is the determination of the adiabatic channel potentials which are given by the eigenvalues of the ion molecule system at fixed \( R \). These eigenvalues are labelled as \( V_{j|m}(R) \) where \( j,m \) are the rotational quantum numbers of the molecule. So it then becomes necessary to compute the orbiting radius, not only for each \( L \), but all possible values of \( L,j,m \).

The calculation of \( V_{j|m}(r) \) for all \( j,m \) over the range of \( r \) is much simpler than it might at first appear, since we only require \( V_{j|m}(r) \) in the asymptotic region, where perturbation theory can be applied. The first order term vanishes for \( j=0 \), but for \( j \geq 1 \) it gives rise to a term varying as \( R^{-3} \). The main contribution comes from the second order term, which is proportional to \( Q^2/B \) and varies as \( R^{-6} \). So in the SACM approach we may write \( V_{j|m}(r) \) in the form

\[
V_{j|m}(r) = -\frac{\alpha}{2R^4} + \frac{C_3(j,m)}{R^4} + \frac{C_6(j,m)}{R^6}
\]

The results can be summarized in Table 1, where we give the \( C_3 \) and \( C_6 \) coefficients for the \( H_2 \) molecules with the following values of the quadrupole moment and rotation constant: \( Q=0.9462 \) a.u., \( B=60.4 \) cm\(^{-1}\).

A cursory examination of Table 1 indicates that the inclusion of the anisotropic potential has only a fairly weak influence on the rate coefficient at very low temperatures. Not only are the \( C_3 \) coefficients small, but they also tend to be positive for \( m \leq j/2 \) but negative for large \( m > j/2 \). As for the \( C_6 \) coefficients they are only negative for \( m = j \) or \( j-1 \). So the net effect of the anisotropic potential is only of any real importance for \( j < 2 \). Of course the influence on the state selective reactive cross sections for \( j < 2 \) does indeed, increase as higher collision energies. But, then, as the temperature increases, more highly excited rotation states contribute to the rate coefficient. So the net influence on the averaged rate coefficient tends to remain weak at thermal energies.
Table 1. Coefficients $C_j(j, |m|)$ and $C_6(j, |m|)$ in atomic units

| $j, |m|$ | $C_j(j, |m|)$ | $C_6(j, |m|)$ |
|---|---|---|
| 0,0 | 0 | -107.5 |
| 1,0 | 0.378 | -49.7 |
| 1,1 | -0.189 | -33.2 |
| 2,0 | 0.270 | -73.6 |
| 2,1 | 0.135 | -28.2 |
| 2,2 | -0.270 | -14.1 |
| 3,0 | 0.252 | 23.9 |
| 3,1 | 0.189 | 9.90 |
| 3,2 | 0.000 | -16.3 |
| 3,3 | -0.315 | -7.24 |
| 4,0 | 0.245 | 12.8 |
| 4,1 | 0.209 | 8.60 |
| 4,2 | 0.098 | -1.55 |
| 4,3 | -0.086 | -10.0 |
| 4,4 | -0.344 | -4.20 |

5. Applications

We give here a brief discussion of one of the most studied reactions involving isotope exchange, namely the reaction $D^+ + H_2 \rightarrow HD + H^+$. On the experimental side the reaction rates were first obtained by ion flow tube techniques in the 200-300K range by Henchman et al. [2] and in the 400-2000K by Villinger et al. [3]. Both these experiments find the rate coefficient to increase as the temperature decreases. More recently ion-trap experiments by Gerlich [4] using specially designed to produce very low energy ions do not seem to exhibit any very strong temperature dependence, of the rate coefficient. But in such ion-trap experiments, the rotation temperature of the molecule may be quite different from the ion temperature. So the measured rate coefficient does not correspond to a truly thermalized rate. Of course, it is easily possible to deduce the corresponding rate if the rotational temperature of the molecule is known. But for this reason, it is difficult to make a direct comparison of theory and experiment.

A selection of theoretical results is summarized in the figure. Results are given separately for para-H$_2$, ortho-H$_2$, and for a thermal average of para and ortho H$_2$. Under most laboratory conditions, the ortho and para states are populated statistically. But it should be borne in mind that this condition may not be satisfied in all applications. For example, under interstellar conditions, the conversion of ortho to para H$_2$ proceeds via the reaction $H^+ +$ ortho-H$_2 \rightarrow H^+ +$ para-H$_2$, rather analogous to the reaction studied here.

There are several interesting features of these results. First of all, we observe that the rate coefficient for p-H$_2$ exhibits a fairly rapid decline by a factor of 2 between 50 and 200K, whereas the o-H$_2$ rate coefficient remains fairly constant. This is mainly a consequence of the fact that the j=2 level of H$_2$ is significantly populated for T greater than 50K, whereas the first excited ortho state is not significantly populated until much higher temperatures. This explains why the average over para and ortho H$_2$ the temperature variation is less pronounced than for p-H$_2$.
On the other hand, the inclusion of the anisotropic terms on the potential leads to a significant increase of the rate coefficient by less than 20% but the temperature dependence is similar. So the effect of the anisotropic contribution is minor compared with the case of a reaction of a polar molecule with a permanent dipole moment.

Finally, a few comments should be made on the interaction potential used in this work. The potential used in this work is asymptotically correct and should be accurate for distances greater than about 5-6 Bohr. This is not the case for many ab-initio calculated potentials, such as the one used in recent quantum calculations [23] on the \( \text{H}^+ + \text{D}_2 \) reaction presents a non-physical potential barrier around 10 Bohr. We have therefore consistently verified that at all temperatures given here, the orbiting resonance corresponding to the largest value of \( L \) which contributes to the reaction rate occurs at values of \( R \), where the asymptotic representation (23) is accurate. Of course the inner part of the potential would be required to verify the validity of the strong statistical mixing approximation of the allowed reaction channels. However, the excellent agreement between the theoretical and experimental rate coefficients provides strong evidence that statistical mixing approximation is satisfactory for collision energies investigated here.

We may also observe that the procedure outlined here to obtain cross sections or rate coefficients is exceedingly rapid. Of course the calculations involve a sum over a large number of \( j,L \) angular momentum states (generally up to about \( j=6 \) and \( L \) up to about 80 au.) but the convergence with respect to \( j,L \) and the dependence of the computed rate coefficients on the interaction potential can be easily tested.

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**Figure 1.** Isotope exchange reaction \( \text{D}^+ + \text{H}_2 \rightarrow \text{H}^+ + \text{HD} \)
References

[1] D. Gerlich and S. Schlemmer, Planetary and Space Science 50, 1287 (2002)
[2] M.J. Henchman, N.G. Adams and D. Smith, J. Chem. Phys 75, 1201 (1981)
[3] H. Villinger, M.J. Henchman and W. Lindinger, J. Chem. Phys. 76, 1590 (1982)
[4] D. Gerlich, J. Chem. Soc. Faraday Trans. 89, 2199 (1993)
[5] P. Langevin, Ann. Chim. Physique, 5, 245 (1905)
[6] W.D. Watson, Rev. Mod. Phys. 48, 513 (1976)
[7] J. Troe, Chem. Phys. Lett. 122, 425 (1987)
[8] J. Troe, J. Chem Phys. 87, 2773 (1987)
[9] K. Sakimoto, Chem. Phys. 63, 419 (1981)
[10] D.R. Bates, Proc. R. Soc. Lond. Ser. A 384, 289 (1982)
[11] D.C. Clary, Mol. Phys. 54, 605 (1985)
[12] D.C. Clary, in Rate Coefficients in Astrochemistry, edited by T.J. Millar and D.A. Williams (Kluwer, Dordrecht, 1988)
[13] M.L. Dubernet and R. McCarroll, Z. Phys.D 13, 255 (1989)
[14] M.L. Dubernet, M. Gargaud and R. McCarroll, Astron. Astrophys. 259, 373 (1992)
[15] M. Ramillon and R. McCarroll, J. Chem. Phys. 101, 8697 (1994)
[16] J.C. Light, Disc. Faraday Soc. 44, 14 (1967)
[17] M. Quack, Mol. Phys. 34, 477 (1977)
[18] R.D. Levine, Molecular Reaction Dynamics, (Cambridge University Press 2009)
[19] R. McCarroll, J. Phys. Chem.A, 113, 14845 (2009)
[20] Quing Liao and E. Herbst, Astrophys. J. 444, 694 (1995)
[21] M.M. Graff and A.F. Wagner, J. Chem. Phys 92, 2423,(1990)
[22] F. Dayou and A. Spielfiefel, J. Chem. Phys. 119, 4237 (2003)
[23] P.G. Jambrina, F.J. Aoz, N. Bulut, S.C. Smith, G.G. Balint-Kurti and M. Hankel, Phys. Chem. Chem. Phys. 12, 1102 (2010)