Constraints at the transition state of the $\text{D} + \text{H}_2$ reaction: quantum bottlenecks vs. stereodynamics†

F. J. Aoiz,^{*a} V. J. Herrero,^b M. P. de Miranda^c and V. Sáez Rábanos^d

Received 18th June 2007, Accepted 24th July 2007

First published as an Advance Article on the web 14th August 2007

DOI: 10.1039/b709161c

This article presents a quasiclassical trajectory method for the calculation of cumulative reaction probabilities by sampling of the helicity quantum number of the reagents (k). The method is applied to the $\text{D} + \text{H}_2$ reaction at various total angular momentum (J) values, and the helicity-resolved quasiclassical cumulative reaction probabilities are compared to their quantum mechanical counterparts. The agreement between the two sets of results is fairly good. In particular, k -dependent, J -independent reaction thresholds found with quantum methods are reproduced by the quasiclassical calculations. The shift of these thresholds with increasing k , which has been previously attributed to the quantum bottleneck states taking part in the reaction, is revisited and discussed also in terms of the reaction stereodynamics.

1. Introduction

The cumulative reaction probability (CRP) is a quantity that provides a convenient link between the dynamics of an elementary reaction and its rate as described by transition state theory. Its usage was first advocated by Miller, who in the seventies showed that the CRP can be understood as the effective number of reagent states that lead to product formation at a given energy.^{1–5} In general, the CRP is predicted to increase with energy in a more or less smooth but stepwise fashion, with the consecutive steps arising because of the involvement of consecutive, quantized energy levels of the activated complex in the reaction dynamics.⁶ The information about these quantized transition states (the so-called quantum “bottleneck” states) was made more quantitative in later work by Truhlar and coworkers,^{7–10} who have shown that derivative of the CRP with respect to the energy can be associated with the density of reactive states (DRS) and in particular that for the H_3 system the DRS has an undulatory structure that can be assigned to quantized transition states—the quantum bottlenecks.

In a recent series of papers on the role of quantum bottleneck states in the dynamics of direct chemical reactions, Skodje, Yang and co-workers have indicated that their effects on reactive processes might be observable in refined experiments.^{11–16} Indeed, the same authors have recently reported experimental observation of the effects of quantum bottleneck states on the state-to-state dynamics of the $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$

reaction.^{14,15} Their experiments were conducted alternately with $p\text{-H}_2(j = 0)$ or $n\text{-H}_2(j = 0, 1)$ molecules under otherwise identical conditions. This has allowed for the extraction of the differential cross sections of the $\text{D} + \text{H}_2(v = 0, j = 0)$ and $\text{D} + \text{H}_2(v = 0, j = 1)$ reactions, which in turn has allowed for a comparison of the rotational state distributions of HD products scattered in the backward direction by either of the two reactions. The two product rotational state distributions were found to differ, and the differences were attributed to reaction *via* different quantum bottleneck states, with the vibrational angular momentum quantum number of the bottleneck state matching the helicity quantum number of the H_2 reagent.

In this article we revisit that problem using not only quantum but also quasiclassical methods. First, we describe an extension of the methodology recently proposed by Aoiz *et al.*¹⁷ for the determination of CRPs from quasiclassical trajectory data; the purpose of the extension is to allow for calculation of the dependence of the CRP on k , the reagent helicity quantum number. Next, we present results from the application of the quasiclassical method to the $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$ reaction and compare them to accurate quantum results.

Although in the classical treatment there are no bound states at the barrier that can be associated with quantum bottlenecks, the quasiclassical CRPs and DRSs are generally found to be in fairly good agreement with their quantum counterparts. The discussion of this finding gives special attention to the stereodynamical significance of the dependence of the CRP on the reagent helicity and to whether the results of ref. 14 can be rationalized in terms of stereodynamical constraints rather than quantum bottleneck states.

2. Theory and calculations

The main purpose of this section is to describe the quasiclassical method used for the calculation of cumulative reaction probabilities (CRPs). As this method bears several similarities to its quantum counterpart, we start the section with a review of how quantum CRPs are calculated. This is followed by a

^a Departamento de Química Física, Facultad de Química, Universidad Complutense, 28040 Madrid, Spain. E-mail: aoiz@quim.ucm.es

^b Instituto de Estructura de la Materia (CSIC), Serrano 123, 28006 Madrid, Spain. E-mail: vherrero@iem.cfmac.csic.es

^c School of Chemistry, University of Leeds, Leeds, UK LS2 9JT. E-mail: m.miranda@leeds.ac.uk

^d Departamento de Química y Bioquímica, ETSI de Montes, Universidad Politécnica, 28040 Madrid, Spain. E-mail: v.saez@upm.es

† The HTML version of this article has been enhanced with colour images.

presentation of the quasiclassical method that focuses on the distinctions between the quasiclassical and quantum methods.

In either case we will restrict our attention to atom–diatom reactions at a fixed total energy (E). The internal states of reagents and products are described in terms of vibrational, rotational and helicity quantum numbers (v, j and k for reagents, v', j' and k' for products). We will also use the symbols J (total angular momentum quantum number), ℓ (orbital angular momentum quantum number of the reagents) and I (triatomic parity, $I = \pm 1$).

Presentation of the equations used for calculation of quantum and quasiclassical CRPs is followed by brief discussions of the methods used for determination of densities of reactive states (DRSs) and in the dynamical calculations.

2.1 Quantum CRPs

We start by considering the reaction probability at a fixed total angular momentum, summed over product states but resolved with regard to reagent state. It is related to the elements of the helicity-representation scattering matrix (S) by

$$P_{vjk}^J(E) = \sum_{v',j',k'} |S_{v'j'k',vjk}^J|^2, \quad (1)$$

where the summation runs over all product states that can be produced at the given total energy. Note that we are implicitly assuming a single arrangement for the products; if the number of possible product arrangements is larger the summation of eqn (1) must also run over all product arrangements. For simplicity, we have dropped the arrangement index from the notation.

Cumulative reaction probabilities are obtained by summation of the reaction probability of eqn (1) over reagent states. Summation over all reagent quantum numbers leads to the “standard” CRP,¹⁸

$$C_r^J(E) = \sum_{v,j,k} P_{vjk}^J(E), \quad (2)$$

whereas summation over vibrational and rotational quantum numbers only leads to the helicity-dependent CRP,

$$C_r^{J,k}(E) = \sum_{v,j} P_{vjk}^J(E). \quad (3)$$

In the following it will also prove useful to define parity-dependent CRPs. For this we first need parity-adapted scattering matrices. Their elements, $S_{v'j'k',vjk}^{JI}$, are given by²¹

$$\begin{aligned} S_{v'j'k',vjk}^{JI} &= [(1 + \delta_{k0})(1 + \delta_{k'0})]^{-1/2} [S_{v'j'k',vjk}^J + I(-1)^J S_{v'j'k',v-j-k}^J] \\ &= [(1 + \delta_{k0})(1 + \delta_{k'0})]^{-1/2} [S_{v'j'k',vjk}^J + I(-1)^J S_{v'j'k'-k',vjk}^J], \end{aligned} \quad (4)$$

where $I = \pm 1$ is the triatomic parity and k and k' satisfy

$$0 \leq k \leq \min(j, J), \quad (5)$$

$$0 \leq k' \leq \min(j, J). \quad (6)$$

By inspection of eqn (4), it is easy to show that when k and/or k' equal zero, all S^{JI} elements with $I \neq (-1)^J$ vanish. That is, S^{JI} elements with $k = 0$ and/or $k' = 0$ appear only in the $I = (-1)^J$ parity block.

Using these parity-adapted S elements one can write the parity-dependent CRP as

$$C_r^{J,I}(E) = \sum_{v,j,k} \sum_{v',j',k'} |S_{v'j'k',vjk}^{JI}|^2 \quad (7)$$

where k and k' can only take values lying in the ranges specified by eqn (5) and (6). We also note that taking into account the equations above along with the symmetry and unitary properties of the S matrices²¹ one can show that the parity-dependent and helicity-dependent CRPs are related by

$$C_r^{J,I}(E) = \delta_{I,(-1)^J} C_r^{J,k=0}(E) + \sum_{k=1}^J C_r^{J,k}(E), \quad (8)$$

which is the last of the formulae necessary for calculation of the CRPs we will use here.

2.2 Quasiclassical CRPs

In section 2.1 we have seen that once the reaction probabilities of eqn (1) have been determined, calculation of the CRPs is straightforward, amounting to no more than summation of the reaction probabilities over some of its indices—see eqn (2), (3) and (8). This implies that in order to be able to calculate quasiclassical CRPs all one needs is a method for the determination of the quasiclassical analogues of the reaction probabilities of eqn (1).

The method we use here is similar to that developed in ref. 17 and 19. In those works, the rotational and total angular momentum quantum numbers of the reagents (j, J) are given discrete, integer initial values. For each combination of j and J values, the initial orbital angular momentum quantum number of the reagents is then uniformly sampled with integer values in the $|j - J| \leq \ell \leq j + J$ interval. In the present case, the distinction is that the initial conditions for each trajectory are sampled by quantizing J, j and k rather than J, j and ℓ ; what we do here is choose the helicity quantum number by uniform sampling with integer values in the $-\min(J, j) \leq k \leq \min(J, j)$ interval (the technical details of the sampling procedure are described in the Appendix). With this sampling the reaction probability at a fixed total angular momentum, summed over product states but resolved with regard to reagent state, can be calculated as the ratio between the number of reactive trajectories (N_r) and the total number of trajectories (N) run under the given set of initial conditions (specified by the values of E, J, v, j and k). One has

$$P_{vjk}^J(E) = \frac{N_r(E, J; v, j, k)}{N(E, J; v, j, k)}, \quad (9)$$

which is the quasiclassical counterpart of eqn (1). Once this quantity is determined, the quasiclassical CRPs reported here are calculated from it through use of eqn (2), (3) and (8).

2.3 Quantum and quasiclassical DRSs

The DRS is the derivative of the CRP with respect to the energy. Quantum or quasiclassical, all DRSs reported here were obtained through numerical differentiation of the corresponding CRPs. They will be denoted by $\rho_r^J(E)$, $\rho_r^{Jk}(E)$ or $\rho_r^{JI}(E)$ depending on whether they were obtained *via*

differentiation of $C_r^J(E)$, $C_r^{Jk}(E)$ or $C_r^{Jl}(E)$. These are, respectively, the CRPs of eqn (2), (3) and (8).

2.4 Dynamical calculations

All dynamical calculations were run with the BKMP2 potential energy surface by Boothroyd *et al.*²⁰ For the quantum scattering calculations we have used the coupled-channel hyperspherical coordinate method of Skouteris *et al.*²¹ Converged CRPs were obtained for $J = 0-3$ at total energies up to 1.77 eV and with a basis set including all $D + H_2$ and $HD + H$ channels with diatomic energies up to $E_{\max} = 3.2$ eV; this implied $v_{\max} = 7$ and $j_{\max} = 25$.

The QCT calculations were done in batches of 10^6 trajectories, for selected J values and with total energy values in the 0.5–1.75 eV range. Each individual trajectory was integrated between initial and final points at which the distance between the atom and the center of mass of the diatomic was 8 Å; the integration time step (0.05 fs) was such that energy conservation was better than 1 in 10^5 . The initial rovibrational energies were calculated semiclassically using the asymptotic diatomic potential energy of the PES; they agree with their exact, quantum counterparts to within four significant figures.

3. Results and discussion

As this is the first publication reporting quasiclassical helicity-dependent CRPs, we start the presentation of our results with a comparison between the k -dependent and l -dependent quasiclassical CRPs (the latter were obtained as described in ref. 17). This is done in Fig. 1, where we have plotted the $J = 1$ cases of the two CRPs and their derivatives (the DRSS).

Fig. 1 Quasiclassical CRPs (top) and DRSS (bottom) obtained for the $D + H_2$ reaction at $J = 1$ using orbital angular momentum (J, l) or helicity (J, k) quantization.

Fig. 2 Quantum and quasiclassical $k = 0$ helicity-dependent CRPs (top) and DRSS (bottom) of the $D + H_2$ reaction at $J = 3$. Open circles and solid line: QM results. Solid line with error bars: QCT results.

Within statistical error, the quasiclassical CRPs and DRSSs calculated with l or k quantization are found to be identical.

We now turn to the comparison between quantum and quasiclassical data, starting with the $k = 0$ helicity-dependent CRPs and DRSSs at $J = 3$; they are shown on Fig. 2. The main finding here is that the two theoretical approaches result in very similar CRPs. In either case one observes a monotonic rise with an unpronounced step-like modulation. As seen in the lower panel of the figure, the DRS also exhibits a rise, albeit with an oscillatory structure superimposed on it. The structure in the quantum DRS is very similar to that previously obtained for $\rho_r^J(E)$, the DRS summed over helicity states,^{10,12,17} whose maxima have had their locations identified with the energies of the reaction's quantum bottleneck states.¹⁰ The quasiclassical oscillations reproduce approximately the trend of the quantum results, although the positions and intensities of the maxima and minima are not entirely coincident.

Fig. 3 is similar to Fig. 2, except that the value taken for the helicity quantum number is $k = 2$. Quantum and quasiclassical CRPs and DRSSs relate to each other as in the previous case, the only clear distinction being that all curves (CRPs and DRSSs, quantum and quasiclassical) have their threshold shifted by about 0.2 eV toward higher energies. We also note the very good agreement between the classical and quantum DRSSs, which except for the energy shift have structures rather similar to those found for $k = 0$.

We extend the QM-QCT comparison by presenting in Fig. 4 all the helicity-dependent CRPs of the $D + H_2$ reaction at $J = 2$ and $J = 3$. It is seen that the agreement between quantum and quasiclassical data is consistently good. In particular, the smooth step-like structure of the CRPs and their shifts in energy with growing k value are almost identical

Fig. 3 As for Fig. 2 but with $k = 2$.

in the two sets of calculations. The largest disagreement is found when $k = 0$; in this case the quantum CRPs are slightly larger than their quasiclassical counterparts.

In order to further stress the relevance of the helicity quantum number for the reaction dynamics, we show on Fig. 5 all quantum and quasiclassical CRPs at $J = 0-3$.

Fig. 4 The quantum and quasiclassical helicity-dependent CRPs of the $D + H_2$ reaction at $J = 2$ (top) and $J = 3$ (bottom).

Quantum CRPs are plotted on the top panel, quasiclassical CRPs on the bottom one. What this figure reveals most clearly is the striking resemblance between the various helicity-dependent CRPs for a given k value: the four curves for $k = 0$ (corresponding to $J = 0-3$) are nearly indistinguishable, as are the three curves for $k = 1$ (corresponding to $J = 1-3$) and the two curves for $k = 2$ (corresponding to $J = 2-3$).

In a recent article,¹⁴ Skodje and coworkers have offered an explanation for the distinctions between product rotational state distributions obtained experimentally for the $D + p\text{-H}_2(j = 0)$ or $D + o\text{-H}_2(j = 1)$ reactions at backward scattering angles. Their explanation was based on the variation of reactivity thresholds with the helicity quantum number; on the possibility of distinguishing $p\text{-H}_2(j = 0)$ from $o\text{-H}_2(j = 1)$ through their helicities (the first can only be found in the $k = 0$ state, the second can be found in $k = 0$ and $k = \pm 1$ states with probabilities of $1/3$ and $2/3$); and on the assumption that the reaction path for backward-scattering $D + H_2$ reactions is essentially collinear. Their conclusion was that the experimental observations can be attributed to differing degrees of participation of two quantum bottleneck states, associated with helicity quantum numbers $k = 0$ or $k = \pm 1$, in the reaction dynamics. Their reasoning was as follows. If the reaction path is essentially collinear, the transition state can be characterized by three quantum numbers (v_{ss} , v_{bend}^Q). For scattering angles close to the backward direction, the helicity quantum number, k , correlates to the vibrational angular momentum quantum number (Ω) of the linear $DHH(v_{ss}, v_{bend}^Q)$ quantum bottleneck state: $k \approx \Omega \approx k'$. This implies that the $p\text{-H}_2(j = 0)$ reaction proceeds only *via* the $[0, 0^0]$ bottleneck state, whereas the $o\text{-H}_2(j = 1)$ reaction proceeds also through the $[0, 1^{\pm}]$ bottleneck state. The higher threshold obtained for

Fig. 5 Quantum (top) and quasiclassical (bottom) CRPs of the $D + H_2$ reaction at $J = 0-3$ and $k = 0-3$. Note that each plot includes four curves for $k = 0$, three curves for $k = 1$ and two curves for $k = 2$. The curves in each of these groups are nearly indistinguishable.

$k = 1$ reactions as compared to $k = 0$ ones was attributed to the higher internal energy of the DHH($0, 1^{1\pm}$) bottleneck state. In later theoretical work,^{15,16} Skodje *et al.* have used quantum calculations to extend their reasoning to higher k values and to stress the relationship between the shift of the reaction threshold with increasing k and increasing quantum bottleneck energies.

Because of its reliance on the reagents helicity, this explanation involves stereodynamical arguments. In the $j = 1$ case, the $k = 0$ value implies “cartwheel” and “helicopter” H_2 rotation and a head-on geometry for the D- H_2 collision; in contrast, $k = \pm 1$ values imply “propeller” H_2 rotation and a side-on geometry for the D- H_2 collision. In addition, due to the collinear geometry of its transition state, one would expect the reaction to be favored by head-on collisions rather than by side-on collisions.

These latter observations, along with the good agreement between quantum and quasiclassical CRPs and DRSs, lead us to suggest that the emphasis should be placed on the reaction stereodynamics rather than on quantum bottleneck states. An important argument here is that the “fingerprint” of the quantum bottleneck states—the shift of the reaction threshold with the reagent helicity quantum number—is also seen in quasiclassical calculations, which do not involve quantized transition states.

As shown in previous work,^{22,23} the agreement between the quantum and quasiclassical descriptions of the stereodynamics of the H_3 family of reactions is excellent, and the two descriptions can be rationalized in much the same way. The potential energy surface of the H_3 system favors collinear triatomic arrangements, specially at energies immediately above the reaction threshold. As the energy increases, stereodynamical constraints are loosened and non-collinear arrangements start to contribute to the reactivity. Note that the smaller the $|k|$ value, the closer to collinear is the collision geometry. This implies (i) that, among all the helicity-dependent CRPs, the one corresponding to $k = 0$ must have the lowest threshold, and (ii) that the higher the $|k|$ value, the further away from collinear is the alignment of the internuclear axis of the reagent diatomic, and consequently the higher the reaction threshold is.

This, of course, is precisely what one observes when considering the problem in terms of CRPs, regardless of whether these are determined with quantum or quasiclassical methods. Indeed, the CRP is a quantity that is very well suited to this type of analysis, for it makes the threshold shift immediately obvious, *cf.* Fig. 4 and 5. (A problem that remains, however, is how such theoretical findings can be tested against experimental observation. This problem was addressed by Gustafsson *et al.*,^{15,16} who used a scaling factor to clearly show the effects of the k -dependence of the reaction threshold on rotationally resolved reaction probabilities and differential cross sections.)

The formulation of the CRP in terms of helicity states is also useful for analysis of other aspects of reaction dynamics. A noteworthy one, which has been recently examined by Bonnet *et al.*,²⁴ is the effect of conservation of triatomic parity on observable reaction properties. Those authors have attributed the failure of quasiclassical calculations to reproduce sharp

Fig. 6 Quantum and quasiclassical $I = \pm 1$ parity-dependent CRPs (top) and DRSs (bottom) of the D + H_2 reaction at $J = 3$.

peaks in the differential cross sections of insertion reactions involving H_2 molecules and excited atoms²⁵ to the fact that QCT calculations do not comply with parity conservation (prior to their analysis, this disagreement between quasiclassical and quantum results was attributed to tunnelling).

As shown in section 2, when dealing with CRPs and DRSs one can also use quasiclassical methods to study the dependence of these quantities on parity. Furthermore, quasiclassical parity-dependent CRPs and DRSs can be directly compared to their quantum counterparts. We show one such comparison—for the D + H_2 reaction at $J = 3$ —in Fig. 6.

For this system, the most conspicuous prototype of a direct reaction,²⁶ the agreement between the quantum and quasiclassical CRPs is again excellent. The general agreement between the quantum and quasiclassical DRSs is also good, although the quasiclassical curves are smoother than the quantum ones. This good agreement between the two theoretical methods is not altogether surprising, for (as shown in section 2) the parity-dependent formulation of CRPs and DRSs is equivalent to the helicity-dependent formulation we have discussed throughout the paper.

Although the effects of differing reagent helicities on reactivity (and on the reaction threshold in particular) can be rationalized in terms of the stereodynamical arguments given above, the step-like structure of the quasiclassical CRPs (and the corresponding DRS undulations) deserve additional comments. We have indicated above that in our QCT calculations we only consider discrete states through the usual pseudo-quantization of the initial internal states of the reagents. As a consequence, the appearance of structure in the quasiclassical CRPs and DRSs must be attributed to the gradual incorporation of additional quantum states of reactants to the global reactivity. The opening of new channels associated with excited H_2 states can certainly produce a step-like structure

in the quasiclassical CRPs and DRS, and it can also be responsible for the longer lived trajectories observed by Aoiz *et al.* for certain values of the collision energy (see Fig. 10 of ref. 17). Within this picture one needs not introduce an explicit quantization of the transition state into the dynamics. The initial (pseudo)quantization of reagents is, to a certain extent, preserved as the reaction unfolds. Note, however, this important point: although this “blurred memory” of the initial quantum states can be responsible for the structures and longer collision times observed in the quasiclassical data, it cannot justify the sharp dependence of the reaction threshold on the reagents helicity quantum number.

4. Summary and conclusions

In this article we have presented a quasiclassical trajectory method for the calculation of cumulative reaction probabilities and densities of reactive states by sampling of the helicity quantum number of the reagents. This method and its quantum counterpart have been applied to the $D + H_2$ reaction at various energies and total angular momenta.

We have found a good agreement between quantum and quasiclassical CRPs and DRSs, which might be at first sight surprising, since the step-like structure of the CRPs and the undulatory structure of the DRSs are usually linked to the quantal structure of the transition state, not contemplated in the quasiclassical treatment. Nevertheless, the pseudo-quantization of the reagents' states used in the QCT method can give rise to a classical analogue of a quantized transition state, albeit without sharply defined levels, if the adiabaticity of the internal molecular motions is somehow preserved during the reactive encounter.

The accordance between the classical and quantal CRPs is particularly good with respect to the shift of the reaction threshold with reagents helicity. Given the absence of sharply defined transition state threshold levels in the classical treatment, the best way to reconcile the results from the two theoretical approaches is to lay the emphasis on the stereodynamical constraints, which are present in quasiclassical as well as in quantum mechanical calculations.

Appendix A. Sampling of initial conditions at a given J

In the absence of electronic and spin angular momenta, the reagents helicity quantum number (k) is the quantum number associated with the projection of the total (J) and rotational angular momenta (j) of the reagents on R_{cm} , the vector from the reagent atom (A) to the center of mass of the reagent diatomic (BC). Since our trajectories are referred to a space-fixed frame whose Z axis lies along the initial relative atom-diatom velocity vector (v_{rel}), in practice, the trajectories are initiated by sampling of $M_J = m_j$ (M_J and m_j are the projections of J and j onto v_{rel}). The procedure is entirely similar to that presented in ref. 17 and 19, except that quantization of the orbital angular momentum is replaced by quantization of the helicity.

With this sampling the reaction probability summed over product states but resolved with regard to reagent state is given by eqn (9).

The sampling method is therefore as follows. For each trajectory with a given J value, the total energy is sampled randomly and uniformly within the $[E_1, E_2]$ interval. Once the energy has been selected, the energetically accessible states are determined and the initial BC rovibrational (v, j) state randomly selected from the set of accessible states. Once the (discrete and integer) J and j values have been determined, the k value is uniformly sampled through integer values in the

$$-\min(J, j) \leq k \leq \min(J, j)$$

range. This enables determination of the polar angles of the J and j vectors (respectively, θ_J and θ_j). As for the azimuthal angles of these vectors in the space-fixed frame (ϕ_J and ϕ_j), they are sampled randomly. Subsequently, the components of the orbital angular momentum (ℓ) are calculated as

$$\ell_X = J_X - j_X, \quad (A1a)$$

$$\ell_Y = J_Y - j_Y, \quad (A1b)$$

$$\ell_Z = J_Z - j_Z = 0. \quad (A1c)$$

Since $\ell = R_{cm} \times P$, the X and Y components of R_{cm} are easily obtained as

$$R_X = -\ell_Y/P, \quad (A2a)$$

$$R_Y = \ell_X/P, \quad (A2b)$$

where P (the modulus of P) equals P_Z , for this is the only nonzero component of P . As for R_Z , it is calculated through

$$R_Z = -(R_{cm}^2 - R_X^2 - R_Y^2)^{1/2} \quad (A3)$$

where the negative sign results from the fact that v_{rel} is chosen to lie along the $+Z$ axis.

The components of the vectors specifying the directions of the BC internuclear axis (r) and the linear momentum perpendicular to it ($p_{\perp}$), are determined after random choice of the third Euler angle (η_j) in the $[0, 2\pi]$ interval. Application of eqn (B8)–(B13) of ref. 19 completes the specification of coordinates and momenta necessary for propagation of the trajectory.

This procedure is in principle general for any value of J, j and k . However, if $J = 0$, ℓ and j are antiparallel, and θ_j is equal to $\pi/2$ with $\phi_j (= \pi + \phi_J)$ randomly selected. Therefore, for the determination of the components of r and $p_{\perp}$ it is sufficient to choose η_j randomly. When j is equal to zero, it is sufficient to sample randomly $\cos \theta_j$, ϕ_j and η_j .

Acknowledgements

This work was financed by the DGES of Spain under grants CTQ2005-08493-C01-01, FTN2003-0828-C03-03 and FIS 2004-00456. The research was performed within the Unidad Asociada “Química Física Molecular” between the Universidad Complutense and CSIC.

References

- 1 W. H. Miller, *J. Chem. Phys.*, 1974, **61**, 1823.
- 2 W. H. Miller, *J. Chem. Phys.*, 1975, **62**, 1899.
- 3 S. Chapman, S. M. Hornstein and W. H. Miller, *J. Am. Chem. Soc.*, 1975, **97**, 892.
- 4 W. H. Miller, *J. Chem. Phys.*, 1976, **65**, 2216.
- 5 W. H. Miller, *Acc. Chem. Res.*, 1976, **9**, 306.
- 6 W. H. Miller, *Acc. Chem. Res.*, 1993, **26**, 174.
- 7 D. C. Chatfield, R. S. Friedman, D. G. Truhlar, B. C. Garrett and D. W. Schwenke, *J. Am. Chem. Soc.*, 1991, **113**, 486.
- 8 D. C. Chatfield, R. S. Friedman, D. G. Truhlar and D. W. Schwenke, *Faraday Discuss.*, 1991, **91**, 289.
- 9 D. C. Chatfield, R. S. Friedman, D. W. Schwenke and D. G. Truhlar, *J. Phys. Chem.*, 1992, **96**, 2414.
- 10 D. C. Chatfield, S. L. Mielke, T. C. Allison and D. G. Truhlar, *J. Chem. Phys.*, 2000, **112**, 8387.
- 11 D. Dai, C. C. Wang, S. A. Harich, X. Wang, X. Yang, S. D. Chao and R. Skodje, *Science*, 2003, **300**, 1730.
- 12 R. T. Skodje and X. Yang, *Int. Rev. Phys. Chem.*, 2004, **23**, 253.
- 13 M. Gustafson and R. T. Skodje, *J. Chem. Phys.*, 2006, **124**, 144311.
- 14 J. Zhang, D. Dai, C. C. Wang, S. A. Harich, X. Wang, X. Yang, M. Gustafson and R. T. Skodje, *Phys. Rev. Lett.*, 2006, **96**, 093201.
- 15 M. Gustafsson, R. T. Skodje, J. Zhang, D. Dai, S. A. Harich, X. Wang and X. Yang, *J. Chem. Phys.*, 2006, **124**, 241105.
- 16 M. Gustafsson and R. T. Skodje, *Chem. Phys. Lett.*, 2007, **434**, 20.
- 17 F. J. Aoiz, M. Brouard, C. J. Eyles, J. F. Castillo and V. Sáez Rábanos, *J. Chem. Phys.*, 2006, **125**, 144105.
- 18 In the literature the CRP is commonly denoted as $N^J(E)$. As in ref. 17, we have reserved N and N_r for the total number of trajectories and the number of reactive trajectories at a given total energy E and total angular momentum J . In order to avoid confusion with this notation, we will use $C_r^{Jk}(E)$ and $C_r^J(E)$ for the cumulative reaction probabilities at a given J and k and at a given J , respectively.
- 19 F. J. Aoiz, V. Sáez Rábanos, B. Martínez-Haya and T. González-Lezana, *J. Chem. Phys.*, 2005, **123**, 094101.
- 20 A. I. Boothroyd, W. J. Keogh, P. G. Martin and M. R. Peterson, *J. Chem. Phys.*, 1996, **104**, 7139.
- 21 D. Skouteris, J. F. Castillo and D. E. Manolopoulos, *Comput. Phys. Commun.*, 2000, **133**, 128.
- 22 M. P. de Miranda, D. C. Clary, J. F. Castillo and D. Manolopoulos, *J. Chem. Phys.*, 1998, **108**, 3142.
- 23 M. P. de Miranda, F. J. Aoiz, L. Bañares and V. Sáez Rábanos, *J. Chem. Phys.*, 1999, **111**, 5368.
- 24 L. Bonnet, P. Larregaray, J.-C. Rayez and T. González-Lezana, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3951.
- 25 F. J. Aoiz, L. Bañares and V. J. Herrero, *J. Phys. Chem. A*, 2006, **110**, 12546.
- 26 F. J. Aoiz, L. Bañares and V. J. Herrero, *Int. Rev. Phys. Chem.*, 2005, **24**, 119.