

BeC₂H₄ complexes are found to have ¹A₁ ground states, while the MgC₂H₂ and MgC₂H₄ complexes have ³B₂ ground states. The minima in the ¹A₁ potential energy surfaces are due to an avoided crossing and concomitant change in electronic configuration at intermediate metal-hydrocarbon distances.

The potential energy surfaces derived from the interaction of Be(¹P) and Mg(¹P) with ethylene and acetylene were not examined in this study. However, in analogy to the Be(¹P) + H₂ and Mg(¹P) + H₂ systems,²⁵ we expect the ¹B₂ surfaces to be very attractive for the interaction of Be(¹P) or Mg(¹P) with C₂H₂ or C₂H₄ and that there are likely to be crossings between the ¹B₂ and ¹A₁ potential energy surfaces, near the potential barriers of the latter. Such crossings could play an important role in the quenching dynamics of the ¹P metal atoms by the hydrocarbons.²⁸

(28) Breckenridge, W. H.; Umemoto, H. *Adv. Chem. Phys.* **1982**, 50, 325.

Several of the properties considered here such as the relative energies of the singlet and triplet states of the complexes could be strongly altered if the metal atoms were replaced by small metal clusters. Theoretical studies of the interaction of C₂H₂ and C₂H₄ with two or more Be or Mg atoms are currently under way in our laboratory.

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Registry No. Be, 7440-41-7; Mg, 7439-95-4; C₂H₂, 74-86-2; C₂H₄, 74-85-1; BeC₂H₂, 92219-99-3; MgC₂H₂, 112816-30-5; BeC₂H₄, 112816-28-1; MgC₂H₄, 112816-29-2.

Unimolecular Reaction Rate Theory for Highly Flexible Transition States. Use of Conventional Coordinates

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An alternative method for implementing RRKM theory for unimolecular reactions with highly flexible transition states is described using conventional coordinates. The number of available states for motion in the transition state N_{EJ} is determined via an appropriate average over the absolute space orientations and body-fixed momenta of the two fragments. The results of calculations of N_{EJ} for the C₂H₆ → 2CH₃ reaction (or alternatively for the corresponding recombination reaction) obtained from the present expression are shown to be equivalent numerically to those obtained previously by Wardlaw and Marcus.

I. Introduction

In recent years there has been an increase in the degree of molecular state selection available in experimental studies of unimolecular reactions.¹ Concurrent with this increase in state resolution has been an increased need for the theoretical determination of energy and angular momentum resolved unimolecular dissociation or isomerization rate constants k_{EJ} for realistic potential energy surfaces. Previous calculations of k_{EJ} have included those involving fully classical methods (both trajectory calculations and variationally implemented RRKM theory),² the statistical adiabatic channel model,³ and a partially quantum partially classical variationally implemented RRKM theory.⁴ The present paper focuses on an alternative method for implementing the latter.

In RRKM theory the specific rate constant, k_{EJ} , for the dissociation or isomerization at a given energy E and total angular momentum quantum number J is given by⁵

$$k_{EJ} = \frac{N_{EJ}}{h\rho_{EJ}} \quad (1)$$

where ρ_{EJ} is the density of states for the reactant at the given E and J . The quantity N_{EJ} is the number of available states for motion in the transition state, which is to be determined variationally, i.e., by finding a potential hypersurface for which N_{EJ} is minimized. In most practical applications the full hypersurface is not varied but rather some coordinate R , which describes the progress of the reaction. The value of R that gives a minimum in N_{EJ} , labeled $R^\ddagger$, is a function of E and J .

In a recent series of articles,⁴ Wardlaw and Marcus have shown how Monte Carlo integration techniques may be used to facilitate the calculation of N_{EJ} 's. The basis of this method is the introduction of an approximate separation of variables into the conserved modes, i.e., modes which do not change their nature in the

transition from reactant to products, and the transitional modes, i.e., modes which do have a considerable such change. The

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conserved modes are typically vibrations and were treated quantum mechanically. In a unimolecular dissociation the transitional modes are typically the fragment-fragment hindered rotations (or bending modes) and the overall rotations and were treated classically. [A quantum correction for the latter for the high-pressure (i.e., canonically averaged) k_{EJ} 's was recently given.^{6]}

The number of states N_{EJ} is then given by the convolution⁴

$$N_{EJ} = \int_0^E N_V(E - \epsilon) \rho_J(\epsilon) d\epsilon \quad (2)$$

where $N_V(E)$ is the number of quantum states for the conserved modes with an energy less than or equal to E , and $\rho_J(\epsilon)$ is the density of states for the transitional modes at the given energy ϵ and total angular momentum quantum number J for the given R . Upon introducing various canonical transformations using action-angle variables, Wardlaw and Marcus obtained $\rho_J(\epsilon)$ as a reduced phase space average of the product of triangle inequalities and a delta function in $\epsilon - H$, where H is the classical Hamiltonian for the relevant modes. In this reduced phase space average the total angular momentum was fixed, and the z component of the total angular momentum and the two coordinates conjugate to these two momenta had been eliminated via an analytical integration. The problem was thereby reduced to a Monte Carlo integration of a given analytical expression over typically (for the case of two polyatomic fragments) six coordinates and six momenta.

In the present article a simple alternative method for evaluating N_{EJ} is presented, in which the transformation of variables to action-angle coordinates is avoided. For the conditions we have explored it is also shown how an alternative method for handling the integration limits can be used. The resulting overall method is very easily programmed and executed. In section II a series of transformations are introduced which serve to reduce the dimensionality of the phase space integral, without making any transformations in the remaining variables. The resulting phase space integral is then evaluated as a free-rotation canonical average in section III. Results for N_{EJ} from calculations using this method are discussed and compared with previous results of Wardlaw and Marcus in section IV.

II. Determination of N_{EJ} Using Absolute Space Orientations and Conjugate Momenta

Since the rapid determination of accurate $N_V(E)$'s for eq 2 is usually possible through direct count algorithms,⁷ the evaluation of N_{EJ} mainly involves finding a rapid method for determining $\rho_J(\epsilon)$. The first step in evaluating the latter involves the choice of an appropriate coordinate system. In the present article the coordinates chosen are the conventional Euler angles⁸ (θ_i, ϕ_i, ψ_i) for the absolute orientation in space of fragment i , denoted by

Ω_i , and the two angles θ_{12} and ϕ_{12} which describe the spatial orientation of the line of centers of the two fragments. The conjugate momenta for these coordinates are then denoted by $p_{\theta_i}, p_{\phi_i}, p_{\psi_i}, p_{\theta_{12}},$ and $p_{\phi_{12}}$, respectively. The first three of these momenta are denoted later by $\mathbf{P}_i$.

In terms of these coordinates $\rho_J(\epsilon)$ can be written as

$$\rho_J(\epsilon) = \frac{1}{\sigma h^8} \int \delta[\epsilon - H(\tau)] \hbar \delta[J\hbar - J_T(\tau)] d\tau \quad (3)$$

where τ denotes the above-described coordinates and their conjugate momenta. J_T is the magnitude of the total angular momentum as a function of the coordinates and momenta, and now a delta function in $J\hbar - J_T$ is present, unlike in the treatment of Wardlaw and Marcus, who used a fixed J_T as one of their action-angle coordinates. We have introduced the $\hbar$ in eq 3 with the following reasoning: Without it the right-hand side of eq 3 would be the classical number of quantum states per unit energy per unit angular momentum J_T . By multiplying by $\hbar$, we have obtained the semiclassical equivalent of the number of states per unit energy for a given value of the angular momentum quantum number J .

The integral over ϵ in eq 2 can now be performed to yield

$$N_{EJ} = \frac{\hbar}{\sigma h^8} \int N_V[E - H(\tau)] \delta[J\hbar - J_T(\tau)] d\tau \quad (4)$$

The above choice of conventional coordinates is convenient in that it allows for a simple evaluation of the Hamiltonian. However, the dimensionality of the phase-space integral should still be reduced by four, to obtain the dimensionality of integration used previously by Wardlaw and Marcus.⁷ To this end, several transformations of the coordinates and momenta describing the line of centers orientation and momenta are now introduced. These transformations, in conjunction with several observations about the dependence of the integral on certain variables, permit the desired reduction in dimensionality of the integral.

The first observation is that the integrand in eq 4 is independent of the direction of the total angular momentum vector $\mathbf{J}_T$ and, hence, of the value of J_{Tz} , the z component of $\mathbf{J}_T$. Thus, the integral will be unchanged if $\mathbf{J}_T$ is restricted to lie along the z axis by introducing a delta function in $J_T - J_{Tz}$, which singles out a particular J_{Tz} , multiplying again by $\hbar$ for reasons analogous to those described for eq 3, and then multiplying by the actual number of J_{Tz} quantum states (semiclassically speaking), for the given J_T , namely, $2J + 1$. Thereby

$$N_{EJ} = \frac{(2J + 1)\hbar^2}{\sigma h^8} \int N_V[E - H(\tau)] \delta[J\hbar - J_T(\tau)] \delta[J_{Tz}(\tau) - J_{Tz}(\tau)] d\tau \quad (5)$$

The dimensionality of the integral in eq 5 can be reduced by two by performing an analytical integration over the arguments of the delta functions. To this end, a transformation of variables is needed to new variables which include J_T and J_{Tz} or their equivalents. For simplicity, the required transformation is divided into two steps with the first transformation being from $\theta_{12}, p_{\theta_{12}},$ and $p_{\phi_{12}}$ to the Cartesian components of the orbital angular momentum $l_x, l_y,$ and l_z ⁹

$$\begin{aligned} l_x &= -p_{\theta_{12}} \sin \phi_{12} - p_{\phi_{12}} \cos \phi_{12} \cot \theta_{12} \\ l_y &= p_{\theta_{12}} \cos \phi_{12} - p_{\phi_{12}} \sin \phi_{12} \cot \theta_{12}, \quad l_z = p_{\phi_{12}} \end{aligned} \quad (6)$$

the Jacobian of the transformation being $|\partial(\theta_{12} p_{\theta_{12}} p_{\phi_{12}}) / \partial(l_x l_y l_z)| = |\sin^2 \theta_{12} / p_{\phi_{12}}|$. The latter equals $|l_z| / [(\cos \phi_{12} l_x + \sin \phi_{12} l_y)^2 + l_z^2]$, thereby yielding

$$N_{EJ} = \frac{(2J + 1)\hbar^2}{\sigma h^8} \int N_V[E - H(\tau')] \times \frac{\delta[J\hbar - J_T(\tau')] \delta[J_{Tz}(\tau') - J_{Tz}(\tau')] |l_z|}{(\cos \phi_{12} l_x + \sin \phi_{12} l_y)^2 + l_z^2} d\tau' \quad (7)$$

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(6) Klippenstein, S. J.; Marcus, R. A. *J. Chem. Phys.* **1987**, *87*, 3410.

(7) When the energies of interest are so large as to make a direct count algorithm inside a Monte Carlo routine too time-consuming, one may instead calculate and store an array of $N_V(E)$ values for all the energies of interest. E.g., see Appendix F of ref 4b.

(8) Goldstein, H. *Classical Mechanics*, 2nd ed.; Addison-Wesley: Reading, MA, 1980. The y convention in this text (Appendix B) is used. It contains a typo in the last row of the matrix $\mathbf{A}$ there: the ψ 's should be replaced by ϕ 's.

where τ' denotes $\Omega_i, \mathbf{P}_i, \phi_{12}, l_x, l_y, l_z$ and $d\tau'$ is the corresponding volume element.

The second transformation is from l_x, l_y , and l_z to J_T, θ , and ϕ , where the θ and ϕ are the polar coordinates of $\mathbf{J}_T$:

$$l_x + k_x = J_T \sin \theta \cos \phi, \quad l_y + k_y = J_T \sin \theta \sin \phi \\ l_z + k_z = J_T \cos \theta \quad (8)$$

Here, k_x, k_y , and k_z are the Cartesian components of the sum of the space-fixed rotational angular momenta of the individual fragments j_i , which in turn are given in terms of the $\mathbf{P}_i$ by⁹

$$j_{x_i} = -[(\cos \theta p_{\phi_i} - p_{\psi_i}) \cos \phi_i / \sin \theta_i + \sin \phi_i p_{\theta_i}] \\ j_{y_i} = -[(\cos \theta p_{\phi_i} - p_{\psi_i}) \sin \phi_i / \sin \theta_i - \cos \phi_i p_{\theta_i}], \quad j_{z_i} = p_{\phi_i} \quad (9)$$

The Jacobian of the transformation is given in this case by $|\partial(l_x, l_y, l_z) / \partial(J_T, \theta, \phi)| = J_T^2 \sin \theta$, yielding

$$N_{EJ} = \frac{(2J+1)\hbar^2}{\sigma h^8} \int N_V [E - H(\tau'')] \delta(J\hbar - J_T) \delta(J_T - J_T \cos \theta) \{ (J_T \cos \theta - k_z J_T^2 \sin \theta) / \\ ([\cos \phi_{12} (J_T \sin \theta \cos \phi - k_x) + \sin \phi_{12} (J_T \sin \theta \sin \phi - k_y)]^2 + (J_T \cos \theta - k_z)^2) \} d\tau'' \quad (10)$$

where τ'' denotes the variables $\Omega_i, \mathbf{P}_i, \phi_{12}, J_T, \theta, \phi$.

The integrals over J_T and $\cos \theta$ may now be performed by using the delta functions, whence

$$N_{EJ} = \frac{(2J+1)\hbar^2}{\sigma h^8} \int N_V [E - H(\Omega_i, \mathbf{P}_i, \phi_{12}, J\hbar, \theta=0, \phi)] \times \\ \frac{|J\hbar - k_z J\hbar|}{(\cos \phi_{12} k_x + \sin \phi_{12} k_y)^2 + (J\hbar - k_z)^2} d\phi d\phi_{12} \prod_{i=1}^2 d\Omega_i d\mathbf{P}_i \quad (11)$$

Two final observations permit the analytic evaluation of the ϕ and ϕ_{12} integrations in eq 11 and thus complete the reduction in dimensionality of the integral. Firstly, in the Appendix it is shown that the integrand of eq 11 is independent of ϕ and therefore one may integrate over ϕ yielding a factor of 2π . Next, in the Appendix it is also shown that the dependence of the integrand on the three variables ϕ_1, ϕ_2 , and ϕ_{12} occurs only via $\phi_1 - \phi_{12}$ and $\phi_2 - \phi_{12}$. Therefore, one may choose ϕ_{12} in the integrand to have any constant value, labeled ϕ_{12}^* , and then integrate over ϕ_{12} , yielding a value of 2π .¹⁰ These steps yield

$$N_{EJ} = \frac{(2J+1)}{\sigma h^6} \int N_V [E - H(\Omega_i, \mathbf{P}_i, \phi_{12}^*, J\hbar, \theta=0)] \times \\ \frac{|J\hbar - k_z J\hbar|}{(\cos \phi_{12}^* k_x + \sin \phi_{12}^* k_y)^2 + (J\hbar - k_z)^2} \prod_{i=1}^2 d\Omega_i d\mathbf{P}_i \quad (12)$$

The above expression is seen to involve only conventional coordinates. A Monte Carlo evaluation of this integral requires some treatment of the sampling limits (e.g., assigning some maximum values for the $\mathbf{P}_i$'s). In the next section it is shown how the integral in eq 12 may conveniently be transformed into a form where importance sampling can be used in the Monte Carlo evaluation, thereby eliminating the need for this specific consideration of maximum values.

III. Free-Rotation Canonical Average

The first step in simplifying the Monte Carlo evaluation of N_{EJ} is to remove the dependence of T_i^0 , the kinetic energy of rotation of fragment i about its center of mass, on its orientation θ_i, ϕ_i, ψ_i . This step serves to make the evaluation of weighting factors more efficient in the importance sampling Monte Carlo integration to follow. To remove this orientation dependence of T_i^0 the space-fixed $\mathbf{P}_i$ are first transformed to the three fragment i -fixed components of the angular momenta, $p_{a_i}, p_{b_i}, p_{c_i}$, defined by⁹

$$p_{a_i} = -\cos \psi_i \csc \theta_i p_{\phi_i} + \cos \psi_i \cot \theta_i p_{\psi_i} + \sin \psi_i p_{\theta_i}$$

$$p_{b_i} = \sin \psi_i \csc \theta_i p_{\phi_i} - \sin \psi_i \cot \theta_i p_{\psi_i} + \cos \psi_i p_{\theta_i}, \quad p_{c_i} = p_{\psi_i} \quad (13)$$

In terms of these new momenta T_i^0 is given by

$$T_i^0 = \frac{p_{a_i}^2}{2I_{A_i}^\dagger} + \frac{p_{b_i}^2}{2I_{B_i}^\dagger} + \frac{p_{c_i}^2}{2I_{C_i}^\dagger} \quad (14)$$

where $I_{A_i}^\dagger, I_{B_i}^\dagger$, and $I_{C_i}^\dagger$ are the principal moments of inertia of the rigid-body fragment i for the transition-state structure. The Jacobian of the transformation in eq 13 introduces a factor of $\sin \theta_i \sin \theta_2$ into the integrand of eq 12.

The next step is to select an appropriate weighting function. We recall that in importance sampling¹¹ a weighing function is introduced which has a large weight in the regions where the integrand is large and also for which the integral over the desired coordinates is known. The function $\exp[-\beta(T_1^0 + T_2^0)] \sin \theta_1 \sin \theta_2$ is suitable, since β may be chosen to restrict the momenta coordinates to the region where the mean value of the kinetic part of H is less than E , the region of importance to the integrand given in eq 12. In addition, the integral of this function over $\Omega_i, p_{a_i}, p_{b_i}, p_{c_i}$, for $i = 1, 2$ (i.e., the coordinates which specify the orientation in space of each fragment and the body-fixed momenta of each fragment), is just h^6 times the product of the free-rotation canonical partition functions for the two fragments Q_0 , defined by

$$Q_0 = \frac{1}{h^6} \int \exp[-\beta(T_1^0 + T_2^0)] \prod_{i=1}^2 d\cos \theta_i d\phi_i d\psi_i dp_{a_i} dp_{b_i} dp_{c_i} \\ = 8\pi(k_B T / \hbar^2)^3 \prod_{i=1}^2 (I_{A_i}^\dagger I_{B_i}^\dagger I_{C_i}^\dagger)^{1/2} \quad (15)$$

Making the transformation described in eq 13 and introducing the above weight function into eq 12 by multiplying the integrand by $\exp(\beta \sum_{i=1}^2 T_i^0) \exp(-\beta \sum_{i=1}^2 T_i^0)$, eq 12 for N_{EJ} becomes

$$N_{EJ} = \frac{(2J+1)J\hbar}{\sigma} \langle Q_0 \left[\frac{N_V [E - H(J\hbar - k_z) \exp[\beta(T_1^0 + T_2^0)]]}{(\cos \phi_{12}^* k_x + \sin \phi_{12}^* k_y)^2 + (J\hbar - k_z)^2} \right] \rangle \quad (16)$$

where $\langle \rangle$ denotes an average with respect to the free-rotation weight function

$$\langle f \rangle = \frac{\int f \exp[-\beta(T_1^0 + T_2^0)] \prod_{i=1}^2 d\cos \theta_i d\phi_i d\psi_i dp_{a_i} dp_{b_i} dp_{c_i} / Q_0 h^6}{Q_0} \quad (17)$$

For each sampling point the integrand f is set equal to zero whenever $H > E$.

A Monte Carlo evaluation of eq 16 is now straightforward using crude sampling for the orientational coordinates and importance sampling¹¹ for the momentum coordinates, with $\exp[-\beta(T_1^0 + T_2^0)]$ as the weighting function. This sampling using the free-rotation canonical distribution is most effective in those cases in which the potential energy is not too large in the regions of importance to the original integral. This situation corresponds to large values of $R^\ddagger$, since the interaction potentials are smaller at large $R^\ddagger$. However, in the present calculations it was observed that the free-rotation sampling was reasonably efficient at all E 's and J 's of interest (e.g., see discussion and Table I in the next section.)

IV. Results and Discussion

The formalism described above for evaluating N_{EJ} was applied to the methyl radical recombination reaction (or ethane dissociation), using the same potential energy function as that employed

(10) More precisely, one transforms to variables $\phi_{12}, \bar{\phi}_i = \phi_i - \phi_{12}$ ($i = 1, 2$) and then, after the ϕ_{12} integration, transforms the $\bar{\phi}_i$ back to the ϕ_i with ϕ_{12} set at any preassigned value ϕ_{12}^* .

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TABLE I: Test of N_{EJ} . Calculation for the Reaction $2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$

$E - E_{\text{ZP}}(\infty)^a$ kcal mol ⁻¹	$J, \hbar$	$R^\dagger, \text{\AA}$	N_{EJ}^b	N_{EJ}^c
0.13	25	5.7	1.4	1.7
0.44	25	5.6	1.4 (3)	1.4 (3)
1.18	25	5.6	4.5 (4)	4.4 (4)
	50	4.4	1.1 (4)	1.1 (4)
2.36	25	3.8	4.4 (5)	4.3 (5)
	50	4.0	2.7 (5)	2.8 (5)
4.73	25	3.6	4.3 (6)	4.2 (6)
	50	3.6	4.2 (6)	4.1 (6)
	100	3.7	1.5 (5)	1.4 (5)
9.53	25	3.3	7.5 (7)	7.1 (7)
	50	3.4	9.4 (7)	8.8 (7)
	100	3.4	1.7 (7)	1.7 (7)
19.55	25	3.1	3.1 (9)	3.4 (9)
	50	3.1	5.0 (9)	4.9 (9)
	100	3.1	1.9 (9)	1.8 (9)
	150	3.1	1.1 (8)	1.0 (8)
39.10	25	2.8	3.6 (11)	3.7 (11)
	50	2.8	6.9 (11)	6.7 (11)
	100	2.8	4.1 (11)	4.2 (11)
	150	2.8	6.4 (10)	6.7 (10)
63.52	25	2.6	1.6 (13)	2.0 (13)
	50	2.6	4.3 (13)	3.9 (13)
	100	2.6	3.5 (13)	2.8 (13)
	150	2.6	8.5 (12)	7.9 (12)

^a $E_{\text{ZP}}(\infty)$ refers to the zero-point energy of the products (i.e., the zero-point energy of two isolated CH_3 fragments). ^bPresent calculations of N_{EJ} . The numbers in parentheses denote the power of 10. Monte Carlo errors are in all cases less than 7%, with the largest error bars arising in the highest energy calculations. ^c N_{EJ} taken from ref 4c.

by Wardlaw and Marcus.^{4b} The structure of the rigid-body fragments for a given $R^\dagger$ was taken to be as in ref 4b, and σ was taken to be 72.

The results for N_{EJ} are given in Table I, together with the previous results of ref 4c, the latter multiplied by $(2J+1)/\sigma$, since the results reported there are actually $N_{EJ}\sigma/(2J+1)$ (cf. footnote in ref 4d). Also, no $J=0$ results are presented here since the transformation given by eq 8 is not valid in this special case. In the calculations 80 000 Monte Carlo points were used and typical computation times were only 10–15 min on a Vax 11/780. The sampling temperature was chosen to keep the maximum kinetic energy sampled 1–2 times the maximum available energy (E minus the minimum $V(R)$ for the given R , minus the zero-point energy difference), since this choice seemed to give the most rapid convergence. At small $R^\dagger$ there is a slower convergence of this particular importance sampling because of the increased importance of the potential energy term, although, as we have noted previously, we did not encounter any difficulty in our current calculations. Had such a difficulty been encountered, we could have used a sampling method analogous to the earlier one.⁴

Inspection of the results given in Table I indicates that both methods give equivalent numerical results.¹² As mentioned previously, the action-angle transformations are now avoided and an alternative method for handling the integration limits has been used. To be sure, the action-angle transformations are straightforward albeit a little tedious. It may also be possible to implement in the method of Wardlaw and Marcus the same idea of avoiding these integration limits although this possibility has not yet been explored. The present calculation is very easily programmed and implemented.

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(12) The minor differences at higher energies corresponding to smaller $R^\dagger$'s are most likely due to the ad hoc "dynamic" barrier restriction in the Monte Carlo sampling procedure which was used in ref 4c (see footnote 15 there) but not here. Also, the Monte Carlo errors in the present calculation are larger at these higher energies.

Appendix: Dependence of the Integrand in Eq 11 on ϕ , ϕ_i , and ϕ_{12}

The Hamiltonian may be written as $H = T^0 + V$, where T^0 is the kinetic energy and V is the potential energy. The kinetic energy may be written as

$$T^0 = T_1^0 + T_2^0 + T_{12}^0 \quad (\text{A1})$$

where T_{12}^0 is the kinetic energy of rotation of the line of centers about the overall center of mass; T_i^0 is as described in the text and is given by the standard expression¹³

$$T_i^0 = \frac{1}{2I_{A_i}^\dagger} \left[p_{\theta_i} \cos \psi_i + (p_{\phi_i} - p_{\psi_i} \cos \theta_i) \frac{\sin \psi_i}{\sin \theta_i} \right]^2 + \frac{1}{2I_{B_i}^\dagger} \left[p_{\theta_i} \sin \psi_i - (p_{\phi_i} - p_{\psi_i} \cos \theta_i) \frac{\cos \psi_i}{\sin \theta_i} \right]^2 + \frac{1}{2I_{C_i}^\dagger} p_{\psi_i}^2 \quad (\text{A2})$$

T_{12}^0 is given by¹³

$$T_{12}^0 = \frac{1}{2I_{\text{di}}^\dagger} \left(p_{\theta_{12}}^2 + \frac{p_{\phi_{12}}^2}{\sin^2 \theta_{12}} \right) \quad (\text{A3})$$

where $I_{\text{di}}^\dagger$ is the "diatomic" moment of inertia for the centers of mass of the two fragments. Upon transforming to the variables appearing in eq 11 of the text, eq A3 becomes

$$T_{12}^0 = \frac{1}{2I_{\text{di}}^\dagger} (\mathbf{J}_T - \mathbf{k})^2 = \frac{1}{2I_{\text{di}}^\dagger} (J_T^2 + k_x^2 + k_y^2 + k_z^2 - 2J_T k_z) \quad (\text{A4})$$

since $\mathbf{J}_T$ is chosen to have only one nonzero component, J_{T_z} .

We now consider how T^0 depends on the four variables ϕ , ϕ_1 , ϕ_2 , and ϕ_{12} . An inspection of eq A1–A4 shows that $k_x^2 + k_y^2$ is the only quantity in T^0 which depends on the above angles. Referring to eq 9 of the text and focusing on the dependence of k_x and k_y on these above angles, it is seen that k_x and k_y may be written in the form

$$k_x = \sum_{i=1}^2 (f_i \cos \phi_i + g_i \sin \phi_i) \quad (\text{A5a})$$

$$k_y = \sum_{i=1}^2 (f_i \sin \phi_i - g_i \cos \phi_i) \quad (\text{A5b})$$

where f_i and g_i are functions of the remaining variables ($\theta_i, \psi_i, \mathbf{P}_i$). Thereby, after some simplification

$$k_x^2 + k_y^2 = f_1^2 + f_2^2 + g_1^2 + g_2^2 + 2(f_1 f_2 + g_1 g_2) \cos(\phi_1 - \phi_2) + 2(g_1 f_2 - f_1 g_2) \sin(\phi_1 - \phi_2) \quad (\text{A6})$$

We note, too, that $\phi_1 - \phi_2$ can be written as $\bar{\phi}_1 - \bar{\phi}_2$. Thus, the T^0 in eq A1 is independent of ϕ_{12} . Also, eq A1–A4 and A6 show that T^0 is also independent of ϕ .

It remains to be shown that the potential energy $V(\theta_i, \phi_i, \psi_i, \phi_{12}, \theta_{12})$ is independent of ϕ_{12} and ϕ when the $\bar{\phi}_i$ are introduced. This independence can be shown by first considering the dependence of θ_{12} on the variables ϕ_i , ϕ_{12} , and ϕ and then considering the dependence of the interatomic separation distances on these same variables.

We first note that θ_{12} depends on ϕ_{12} via the expression, obtained from a consideration of eq 6 and 8 with $\sin \theta$ set to zero

$$\theta_{12} = \cot^{-1} \left(\frac{k_x \cos \phi_{12} + k_y \sin \phi_{12}}{J_T - k_z} \right) \quad (\text{A7})$$

Use of the definitions of k_x and k_y and use of eq A5 show that an expression occurring in eq A7, as well as in the Jacobian term in eq 11, may be written as

(13) McQuarrie, D. A. *Statistical Mechanics*; Harper and Row: New York, 1976.

$$k_x \cos \phi_{12} + k_y \sin \phi_{12} = \sum_{i=1}^2 (f_i \cos \bar{\phi}_i + g_i \sin \bar{\phi}_i) \quad (\text{A8})$$

Thus, θ_{12} is independent of ϕ and ϕ_{12} when written in terms of the $\bar{\phi}_i$'s.

The space-fixed coordinates $\mathbf{x}_i$ of a specific point in fragment i relative to the space-fixed coordinates of the center of mass of fragment i are given by $\mathbf{A}_i^{-1}\mathbf{x}'_i$, where the $\mathbf{x}'_i$ are the body-fixed coordinates of the point in fragment i and $\mathbf{A}_i^{-1}$ is the inverse rotation matrix⁸ (using the convention in ref 8). The space-fixed coordinates of the center of mass of fragment i relative to a space-fixed origin at the overall center of mass are $\mathbf{A}_{12}^{-1}\mathbf{x}_{12,i}'$, where the $\mathbf{x}_{12,i}'$ are the coordinates describing the initial location (i.e., along the space-fixed z axis) of the center of mass of fragment i and $\mathbf{A}_{12}^{-1}$ is the inverse rotation matrix describing the orientation of the line of centers. Thereby

$$\mathbf{x}_i = \mathbf{A}_i^{-1}\mathbf{x}'_i + \mathbf{A}_{12}^{-1}\mathbf{x}_{12,i}' \quad (\text{A9})$$

The separation distance r_{12} between a point in fragment 1 and a point in fragment 2 is given by

$$r_{12}^2 = (\mathbf{x}_1 - \mathbf{x}_2) \cdot (\mathbf{x}_1 - \mathbf{x}_2) \quad (\text{A10})$$

Here, the observation is made that any inverse rotation matrix for rotation through $(\theta_i, \phi_i, \psi_i)$ may be written in the form⁸ $\mathbf{A}_i^{-1} = \mathbf{D}_i^{-1}\mathbf{C}_i^{-1}\mathbf{B}_i^{-1}$, where all of the dependence of $\mathbf{A}_i^{-1}$ on ϕ_i is in the matrix $\mathbf{D}_i^{-1}$, which in turn is given by⁸

$$\mathbf{D}_i^{-1} = \begin{pmatrix} -\sin \phi_i & -\cos \phi_i & 0 \\ \cos \phi_i & -\sin \phi_i & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (\text{A11})$$

Also, $\mathbf{A}_{12}^{-1}$ for rotation through (θ_{12}, ϕ_{12}) may be written in the form $\mathbf{A}_{12}^{-1} = \mathbf{D}_{12}^{-1}\mathbf{C}_{12}^{-1}$, where $\mathbf{D}_{12}^{-1}$ contains all the ϕ_{12} dependence and is given by eq A11 with ϕ_i replaced by ϕ_{12} . Upon substituting eq A11 and A9 into eq A10, one finds after some straightforward algebraic manipulations that the separation distance r_{12} depends on the variables $\bar{\phi}_i$ and ϕ_{12} only through the variables $\bar{\phi}_i$ and is independent of ϕ . Thus, all the quantities in eq 11 have now been shown to be independent of ϕ and ϕ_{12} when written in terms of the $\bar{\phi}_i$'s.

Theoretical Study of the Absorption Process during Chemical Reactions: Potential Surface and Classical Trajectory Study on K + NaCl

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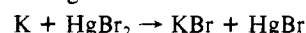
Photon absorption spectra during the reaction between the K atom and the NaCl molecule are investigated theoretically. The potential energy surfaces of the ground ($1^2A'$) and the electronically excited states ($2^2A'$, $3^2A'$, and $1^2A''$) are determined by the MRSD-CI method with effective core potentials. The absorption intensity is assumed to be proportional to the density of KCINa classical trajectories on the ab initio fitted ground-state potential surface and to the square of ab initio transition dipole moments at the respective geometries. It is found that the spectra consist of two broad bands which originate from two types of transitions: $1A' \rightarrow 2A'$ and $1A' \rightarrow 3A'$ (as well as $1A' \rightarrow 1A''$), respectively. Some structures seen in the spectra are further interpreted in terms of potential surfaces characteristics of the ground and the excited electronic states and the ground-state collision dynamics. The breadth of each band has been found to represent the angular distribution of trajectories in the collision. A spectroscopy that would probe bound states on the $2A'$ and $3A'$ excited states of the complex is proposed.

Introduction

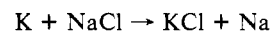
The influence of lasers on chemical reaction processes had long been a topic of only theoretical interest¹ without any reliable experimental data. However, recently experimental studies on the possibility of direct photoexcitation or spectroscopic observation of transition species that are intermediates between reactants and products, the "transition states" or "reaction complexes", have received considerable attention² related to experimental probes of potential energy surfaces in interaction regions as well as laser-catalyzed chemical reactions.

Polanyi and co-workers³ have studied the $F + Na_2$ reaction and observed a broad "wing" emission on either side of the Na D line, which they ascribed to the emission from the FNa_2 transition state.

Brooks and co-workers have reported evidence for absorption from the intermediate configurations in the reactions⁴



and⁵



More recently, laser-assisted reactions have been observed in $Hg/HgBr_2$ gas mixtures⁶ and in the MgH_2 collision system.⁷

Stimulated by these studies, theoretical simulations have been carried out by Polanyi and co-workers⁸ on the transition-state absorption spectra for $H + H_2 \rightarrow H_2 + H$ based on classical trajectory calculations. They studied the effects of increasing relative translational energy and reagent vibrational excitation on the features of the absorption spectrum. It has been found that several peaks present in the spectra reflect characteristic

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