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NONADIABATIC INTERACTIONS AND THE DYNAMICS OF CHEMICAL REACTIONS

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Vladimir Z. Kresin and William A. Lester, Jr.

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NONADIABATIC INTERACTIONS AND THE DYNAMICS OF CHEMICAL REACTIONS\*

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\*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098 and by the National Science Foundation.

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## NONADIABATIC INTERACTIONS AND THE DYNAMICS OF CHEMICAL REACTIONS\*

Vladimir Z. Kresin and William A. Lester, Jr.<sup>†</sup>Materials and Molecular Research Division  
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We present a new approach to the dynamics of chemical reactions. Central to the theory is the concept of a chemical reaction as a transition from reactants to products caused by a nonadiabatic interaction. The bound and continuous state of the system is evaluated by analogy with our theory of photodissociation. As an illustration of the approach, we apply it to a model collinear reaction.

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## Introduction

The computation of cross sections for chemical reactions can be formulated on the basis of the formal theory of scattering. The problem of evaluating the T matrix for most systems, however, presents serious computational difficulties (see, e.g., [1-3]). For this reason, the majority of studies have involved the classical trajectory (CT) method (see, e.g., [4]). Because of the inability of the CT method to describe reliably state-to-state properties, as well as tunneling, threshold, resonance, and superposition effects, the search for methods that avoid these limitations remains of interest.

The present paper presents an alternative approach to the study of chemical reactions. It is a generalization of an adiabatic method developed by the authors for polyatomic photodissociation [5]. The approach enables one to use perturbation theory to obtain product energy distributions for chemical reactions.

### Nonadiabatic Operators. Rearrangement as a Nonadiabatic Transition

Consider a bimolecular reaction



where  $\alpha$ ,  $\beta$  are reactants and  $\gamma$ ,  $\delta$  are products and represent, in the general case, polyatomic molecules. According to the Born-Oppenheimer (BO) approximation, the total wavefunction for a specific electronic state can be written in the form

$$\Psi_{BO}(\vec{r}, \vec{R}) = \psi_{el}(\vec{r}, \vec{R}) \phi(\vec{R}) \quad (2)$$

where  $\psi_{e\ell}$  is a solution of the electronic Schrödinger equation,  $\{\vec{r}\}$  are the electronic coordinates and  $\{\vec{R}\}$  are the nuclear coordinates. The wavefunction  $\phi(\vec{R})$  is a solution of the nuclear Schrödinger equation

$$\hat{H}^N \phi(\vec{R}) = E \phi(\vec{R}) \quad (3)$$

Here

$$\hat{H}^N = \hat{T}_{\vec{R}} + V(\vec{R}) \quad (4)$$

where

$$\hat{T}_{\vec{R}} = - \sum_i \frac{1}{2M_i} \frac{\partial^2}{\partial R_i^2} \quad (5)$$

is the kinetic energy operator and  $V(\vec{R})$  is the potential energy for nuclear motion (in units of  $\hbar = 1$  which will be used throughout this paper).

As is well known, the wavefunction (2) is not the exact solution of the Schrödinger equation for the total system. Corrections to the BO zeroth-order approximation (2) are described by nonadiabatic operators  $\hat{H}'$ . One of the more important for polyatomic molecules is the nuclear kinetic energy operator, which can be defined by how it operates on a BO wavefunction [5,6]:

$$\hat{H}'_{kin} \psi_{BO}(\vec{r}, \vec{R}) \equiv \hat{T}_{\vec{R}} \psi_{BO}(\vec{r}, \vec{R}) - \psi_{e\ell}(\vec{r}, \vec{R}) \hat{T}_{\vec{R}} \phi(\vec{R}) \quad (6)$$

The spin-orbit interaction provides another example. The interaction of a molecular system with an external electromagnetic field can also be considered an  $\hat{H}'$ .

Let us consider the initial state (I) of a reactive system. The

nuclear wavefunction  $\phi^I(\vec{R})$  for this state is a solution of Eq. (3) and describes both the internal and relative motion of the reactants.

Similarly, the final state (F) of the system is described by a nuclear wavefunction  $\phi^F(\vec{R})$  for the products which is also an eigenfunction of the operator  $\hat{H}^N$ . Chemical reaction can be viewed as a quantum transition  $I \rightarrow F$  governed by the matrix element

$$H'_{F \leftarrow I} = \int \Psi^{F*}(\vec{r}, \vec{R}) \hat{H}' \Psi^I(\vec{r}, \vec{R}) d\vec{r} d\vec{R} \quad (7)$$

where

$$\Psi^F(\vec{r}, \vec{R}) = \psi_e^F(\vec{r}, \vec{R}) \phi^F(\vec{R}); \quad (8)$$

$$\Psi^I(\vec{r}, \vec{R}) = \psi_e^I(\vec{r}, \vec{R}) \phi^I(\vec{R}) \quad (9)$$

The nonadiabatic operator  $\hat{H}'$  causes transitions among the eigenstates of the zeroth-order Hamiltonian, i.e., among the BO states  $\Psi(\vec{r}, \vec{R})$  and therefore is the main mechanism for rearrangement.

The major contribution to the integral (7) comes from the region of overlap of the nuclear wavefunctions  $\phi^I$  and  $\phi^F$ , a region corresponding to short distances between reactants (products). Note, that invoking the Condon approximation allows one to approximate the electronic factors as constants (see Eqs. (24) below). The accuracy of this approximation is of the order  $\kappa = (m/M)^{1/4}$ , where  $m$  and  $M$  are the electron and nuclear masses.

Note that we do not follow the common approach of using separate Hamiltonians for reactants and products, i.e.,



$$\hat{H} \equiv \hat{H}_R = \hat{H}_R^{\text{int}} + V_R \quad (10)$$

and

$$\hat{H} \equiv \hat{H}_P = \hat{H}_P^{\text{int}} + V_P \quad (11)$$

where  $\hat{H}_{R(P)}^{\text{int}}$  is the internal Hamiltonian and  $V_{R(P)}$  is the intermolecular potential for reactants (products). This procedure presents difficulties in quantum mechanical theories of chemical reactions because of the need to match reactant and product solutions at a dividing surface to obtain scattering information. In addition, such a formulation cannot be used in a perturbative approach because the potentials  $V_R$  and  $V_P$  are large at short distances. In the present treatment the interaction between reactants (products) is included in the zeroth-order approximation.

### The Probability of Chemical Reaction

Let us turn to the problem of evaluating Eq. (7). The specification of  $\hat{H}'$  was discussed in the previous section. The nuclear wavefunctions  $\phi^I$  and  $\phi^F$  are eigenfunctions of  $\hat{H}^N$  and have both a bound and a continuous part. By this we mean  $\phi^{I(F)}$  describes the internal (bound) motion of the reactants (products) and their relative (continuous) motion. Because intermolecular interactions are strong at small distances, the variables in (3) cannot be separated so that the problem of determining  $\phi^{I(F)}$  is nontrivial, see discussion in refs. [5].

The evaluation of the nuclear wavefunction for a state that has bound and continuous parts has been considered in our theory of photodissociation [5]. Polyatomic photodissociation is a transition from

a bound to a bound-continuous state, while a chemical reaction is a transition from a bound-continuous state of reactants to a bound-continuous state of products. As was proven in refs. 5, a bound-continuous nuclear wavefunction  $\phi$  can be written

$$\phi^\alpha = \phi_{\text{vib}}^\alpha(Q_i^\alpha, \rho^\alpha) \phi_{\text{tr}}^\alpha(\rho^\alpha); \quad \alpha \equiv I, F \quad (12)$$

Here  $\rho^\alpha$  is the distance between the centers of mass in the initial (I) or final (F) arrangement, and  $\phi_{\text{vib}}$  and  $\phi_{\text{tr}}$  are the vibrational and translational parts of the wavefunction. In the harmonic approximation,  $\phi_{\text{vib}}(\theta_i^\alpha, \rho^\alpha)$  is a product of harmonic oscillator wavefunctions and  $\theta_i^\alpha$  is the set of normal mode wavefunctions. For present purposes we need not treat the rotational part of  $\phi$  explicitly. We emphasize, that the normal mode frequencies  $\Omega_i^\alpha$  and the equilibrium positions  $q_{\text{eq}}^\alpha$  depend on  $\rho$ . Exact expressions for  $\Omega^\alpha(\rho^\alpha)$  and  $q_{\text{eq}}^\alpha(\rho^\alpha)$  are determined by the relative magnitudes of the internal energy and the translational energy. For example, if the vibrational motion of the products is accompanied by slow translational motion

$$\Omega_i^F(\rho) = \omega_i^F(\rho) = 1/2 (\partial^2 U(\rho^F, Q_i^F) / \partial Q_i^F{}^2)_{\text{eq}}. \quad \text{In the opposite case,}$$

$\Omega_i^F(\rho) = \omega_{i,\text{as}}^F$ , where  $\omega_{i,\text{as}}^F$  are the frequencies of the products in the asymptotic region. A detailed analysis is given in Ref. [5]. The function  $\phi_{\text{tr}}^\alpha(\rho^\alpha)$  which describes the relative motion of the reactants (products), is a solution of

$$\left[ -\frac{1}{2\mu^\alpha} \frac{\partial^2}{\partial \rho^{\alpha 2}} + V_{\text{eff}}^\alpha(\rho^\alpha) \right] \phi_{\text{tr}}^\alpha(\rho^\alpha) = E \phi_{\text{tr}}^\alpha(\rho^\alpha) \quad (13)$$

Here,

$$V_{\text{eff}}^{\alpha}(\rho^{\alpha}) = V[\rho^{\alpha}, q_{\text{eq}}^{\alpha}(\rho^{\alpha})] + E_{\text{vib}}^{\alpha}(\rho^{\alpha}) \quad (14)$$

$$E_{\text{vib}}^{\alpha}(\rho^{\alpha}) = \sum_i (v_i^{\alpha} + 1/2) \Omega_i^{\alpha}(\rho^{\alpha}), \quad (15)$$

and  $\mu^{\alpha}$  is the reduced mass. Equation (13) can be solved readily in the usual semiclassical approximation (far from classical turning points). The general solution, including the turning point region, can also be obtained.

The interfragment interactions  $V_R$  and  $V_p$ , Eqs. (11) and (12), are taken into account in two ways. First, the vibrational frequencies and the equilibrium geometry depend on the distance  $\rho^{\alpha}$ , and second, the effective potential energy  $V_{\text{eff}}^{\alpha}$ , describing the relative motion, contains the vibrational energy  $E_{\text{vib}}^{\alpha}(\rho^{\alpha})$ .

Using Eqs. (8), (9), (12)-(15), one can evaluate the matrix element (7) where, as was mentioned above, the electron factors can be approximated as constant. Then from perturbation theory one can calculate the probability of the  $I \rightarrow F$  transition. For example, if the reaction takes place without interaction with radiation, one obtains

$$dw_{F \leftarrow I} = 2\pi |H'_{F \leftarrow I}|^2 \delta(E_F - E_I) dv_F \quad (16)$$

where  $v_F$  is the set of the quantities that describes the F state. It is of course, necessary to take into account the degeneracy of the I and F states; see, e.g., Ref. 7. Equation (16) enables one to calculate the energy and angular distributions of the products.

### Collinear Reaction

To illustrate our method, consider a collinear reaction  $AB + C \rightarrow A + BC$ . The general case of three-dimensions and polyatomic molecules is straightforward and will be treated elsewhere. The matrix element  $H'_{F \leftarrow I}$ , Eq. (7), becomes

$$H'_{F \leftarrow I} = \int \psi^{F*}(\vec{r}, \rho_2, \ell_2) \phi^{F*}(\rho_2, \ell_2) \hat{H}'_{\text{kin}} \psi^I(\vec{r}, \rho_1, \ell_1) \phi^I(\rho_1, \ell_1) J d\ell_1 d\ell_2 \quad (17)$$

where  $\ell_1$  is the AB internuclear distance and  $\ell_2$  is the BC internuclear distance,  $\rho_1$  is the distance from atom C to the center of mass of AB, and  $\rho_2$  is the distance from atom A to the center of mass of BC. The function  $\phi^\alpha$  is defined by Eq. (12), i.e.,

$$\phi^\alpha = \phi_{\text{vib}}^\alpha(\tau_\alpha, \rho_\alpha) \phi_{\text{tr}}^\alpha(\rho_\alpha) \quad (18)$$

We assume the harmonic approximation for  $\phi_{\text{vib}}^\alpha$ , i.e.,

$$\phi_{\text{vib}}^\alpha = (K_\alpha/\pi)^{1/4} (2^{\nu_\alpha} \nu_\alpha!)^{-1/2} \exp(-K_\alpha \tau_\alpha^2/2) H_{\nu_\alpha}(\tau_\alpha \sqrt{K_\alpha}) \quad (19)$$

and a semiclassical expression for  $\phi_{\text{tr}}^\alpha$ , in particular,

$$\phi_{\text{tr}}^\alpha = (2\mu'_\alpha/\pi p^\alpha) \cos[\sigma(\rho_\alpha) + \delta] \quad (20)$$

In Eqs. (17)-(20),

$$K_\alpha = \mu_\alpha \Omega^\alpha(\rho_\alpha); \quad \mu_I \equiv \mu_R = M_A M_B / (M_A + M_B); \quad \mu_F \equiv \mu_P = M_B M_C / (M_B + M_C), \quad (21)$$

$$\mu_I' = (M_A + M_B)M_C/M, \quad \mu_F' = (M_B + M_C)M_A/M, \quad M = M_A + M_B + M_C,$$

$$\tau_{\alpha} = \ell^{\alpha} - \ell_{\text{eq}}^{\alpha}(\rho_{\alpha}), \quad \sigma(\rho_{\alpha}) = \int_{a_t^{\alpha}}^{\rho_{\alpha}} p^{\alpha}(x) dx; \quad (22)$$

where  $a_t^{\alpha}$  is the classical turning point, and

$$p^{\alpha}(x) = (2\mu[E - V_{\text{eff}}^{\alpha}(x)])^{1/2}, \quad \rho_1 \equiv \rho_I, \quad \ell_1 \equiv \ell_I; \quad \rho_2 \equiv \rho_F, \quad \ell_2 \equiv \ell_F.$$

We choose  $\ell_1, \ell_2$  as independent variables, and  $J$  is the Jacobian of the transformation. The coordinates  $\rho_1$  and  $\rho_2$  can then be expressed in terms of  $\ell_1$  and  $\ell_2$ :

$$\rho_1 = \alpha_{11}\ell_1 + \alpha_{12}\ell_2; \quad \rho_2 = \alpha_{21}\ell_1 + \alpha_{22}\ell_2 \quad (23)$$

$$\alpha_{11} = M_A/(M_A + M_B); \quad \alpha_{22} = M_C/(M_C + M_B); \quad \alpha_{12} = \alpha_{21} = 1$$

Introducing the Condon approximation reduces the electronic factors

$$L' = \int \Psi_{e\ell}^{F*} (\partial \Psi_{e\ell}^I / \partial \ell_1) d\vec{r}; \quad L'' = \int \Psi_{e\ell}^{F*} (\partial \Psi_{e\ell}^I / \partial \rho_1) d\vec{r}, \quad (24)$$

and  $\Omega^{\alpha}(\rho_{\alpha})$  and  $\Omega_{\text{eq}}^{\alpha}(\rho_{\alpha})$  to constants. Their numerical values then become those of the overlap region of the wavefunctions.

Based on Eqs. (18)-(24), one can carry out the analytical evaluation of the matrix element (17). For simplicity, we assume that the reactant AB is in the ground vibrational state  $v_I = 0$ . After some manipulations, we arrive at the result

$$\hat{H}_F \leftarrow I = L' I_1 + L'' I_2 \quad (25)$$

where  $L'$  and  $L''$  are defined by Eq. (24),  $I_i = I_i^+ + I_i^-$ , and

$$I_1^+ = (2^v v!)^{-1/2} (v^+)^{1/2} e^{-1/2(v^+ + \zeta^+)} H_v(\zeta^+) K^+ \quad (26)$$

$$K^+ = \begin{cases} \sin \sigma^+ & \text{even } v \\ (-1)^{(v-1)/2} \cos \sigma^+ & \text{odd } v \end{cases} \quad (27)$$

$$v^\pm = (\gamma^\pm)^2 / \mu_I \omega_1; \quad \zeta^\pm = (\beta^\pm)^2 / \mu_F \omega_2; \quad (28)$$

$$\gamma^\pm = \alpha_{11} \tilde{p}_1 \pm \alpha_{21} \tilde{p}_2; \quad \beta^\pm = \alpha_{21} \tilde{p}_1 \pm \alpha_{22} \tilde{p}_2; \quad \tilde{p}_1 \equiv \tilde{p}_1(\rho_{1,eq});$$

$$\tilde{p}_2 \equiv p_2(\rho_{2,eq}); \quad \omega_1 = \Omega^I(\rho_{eq}^I); \quad \omega_2 = \Omega^F(\rho_{eq}^F), \quad p_1 \equiv p^I, \quad p_2 \equiv p^F \quad (29)$$

$$\tilde{\sigma}^\pm = \tilde{\sigma}_{01} + \tilde{\sigma}_{02}; \quad \tilde{\sigma}_{0\alpha} = \sigma_{0\alpha} + \delta; \quad \sigma_{0\alpha} = \sigma_{eq}^\alpha; \quad v = v_F \quad (30)$$

To evaluate  $I_1^-$  one simply replaces  $v^+$ ,  $\zeta^+$ ,  $\sigma^+$  by  $v^-$ ,  $\zeta^-$ ,  $\sigma^-$  in Eq. (26). The term  $I_2$  is given to

$$I_2 = I_2^+ + I_2^-; \quad I_2^\pm = (\tilde{p}_1^2 / \mu_I \omega_1)^{1/2} (v^\pm)^{-1/2} I_1^\pm \quad (31)$$

If  $\tilde{p}_1^2 / (\mu_I \omega_1) \ll 1$ , one can neglect the second term in (25).

Equations (25)-(31) together with Eq. (16) describe the vibrational and translational distribution of the products. The translational energy of the products and  $v$  can be chosen as the quantities  $v_F$  required in Eq. (16). Generally speaking, one sees that the dependence of the distribution on  $v$  is non-monotonic. We also emphasize the dependence of the matrix element (25) on the linear combination of momenta  $\tilde{p}_1$  and  $\tilde{p}_2$  (see Eq. (28)).

For reactions involving the exchange of atoms of light mass, i.e., for

$$M_C \ll M_B \text{ and } M_A \ll M_B \quad (32)$$

we have  $(\beta^\pm)^2 = \tilde{p}_1^2$ ,  $(\gamma^\pm)^2 = \tilde{p}_2^2$ , and the momenta are separated.

In this case we obtain

$$I_1^+ = (\pi/2)^{1/2} \phi_v(\kappa_1) \phi_1(\kappa_2) K^+ \quad (33)$$

Here  $\phi_n(z)$  is the parabolic cylinder function (see, e.g., [8]), and

$$\kappa_1 = (\tilde{p}_1^2 / \mu_F \omega_2)^{1/2}, \quad \kappa_2 = (\tilde{p}_2^2 / \mu_I \omega_1)^{1/2} \quad (34)$$

A similar equation can be obtained for  $I_1^-$ . We have assumed also that  $s/L \ll 1$  and  $p_2 S \ll 1$ , where  $s = |a_t^F - \rho_{2,eq}|$  and  $L$  is the characteristic distance over which the potential  $V$  varies by an appreciable amount. Then  $\sigma^\pm$  depends primarily on  $p_1$ . If  $v_I = 0$ , then

$$\tilde{p}_1^2 / 2\mu'_I = E - \omega_1/2; \quad E = \tilde{p}_2^2 / 2\mu'_F + (v + 1/2)\omega_2 \quad (35)$$

The quantity  $\kappa_2$  in Eq. (34) can be written in the form  $\kappa_2 = (\tilde{p}_2^2 / 2\mu'_F \omega_2) \lambda$ , where  $\lambda = 2(\omega_2 \mu'_F / \omega_1 \mu_I)$ . For concreteness, we choose the numerical values:  $\lambda = 1.25$  (this value approximates the reaction  $\text{OH} + \text{D} \rightarrow \text{OD} + \text{H}$ );  $E = (4.5)\omega_2 + 0.01\omega_2$ , a total energy slightly above the  $v = 4$  vibrational state. The product energy distributions are presented in Fig. 1. The main feature is an inverse distribution. It would be useful to have measurements of product energy distributions for  $\text{OH} + \text{D} \rightarrow \text{OD} + \text{H}$  to compare with the present predictions. Note that inverted distributions have been obtained previously using other methods. [9]

It is worth noting that product energy distributions for the reactions  $\text{H} + \text{ClBr} \rightarrow \text{HBr} + \text{Cl}$  [10] and  $\text{H} + \text{IBr} \rightarrow \text{HI} + \text{Br}$  [11] are characterized by inversion. Both systems approximately satisfy condition (32). Hence, there is qualitative agreement between experimental data and the collinear model based on the theory outlined in this paper.

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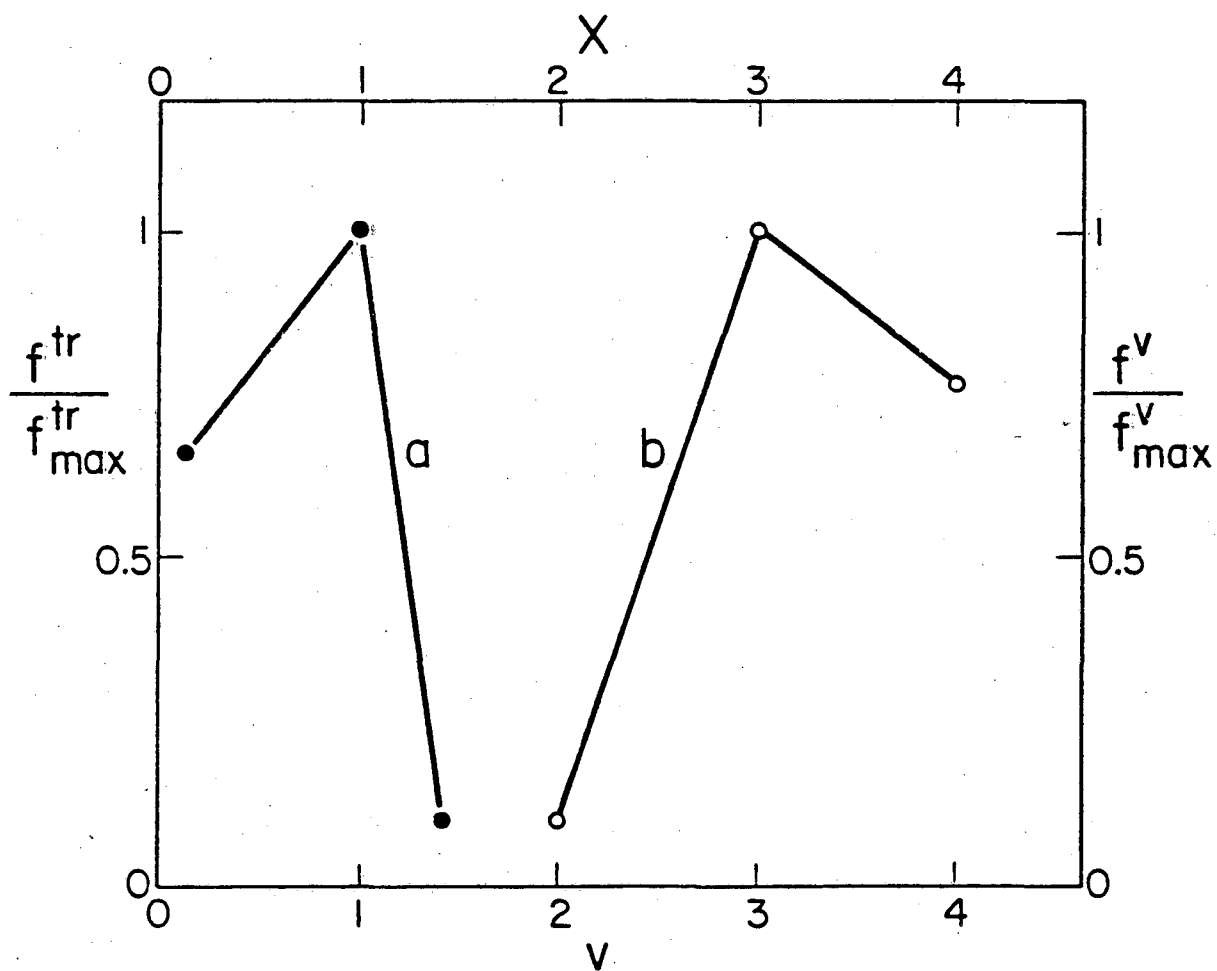
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Fig. 1 Product energy distributions ( $f^\alpha/f_{\max}^\alpha$ ) for a model collinear system with parameters chosen to approximate  $\text{OH} + \text{D} \rightarrow \text{OD} + \text{H}$   
 (a) relative translational distribution;  $x \equiv (p_2^2/2\mu_F\omega_2)^{1/2}$   
 and (b) vibrational distribution of BC.



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