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ATOM TRANSFER REACTIONS IN POLYATOMIC MOLECULES

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## REACTION PATHS AND SURFACES FOR HYDROGEN ATOM TRANSFER REACTIONS IN POLYATOMIC MOLECULES

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**ABSTRACT.** The reaction path/surface Hamiltonian model for polyatomic reaction dynamics is reviewed. Applications to formaldehyde decomposition ( $\text{H}_2\text{CO} + \text{H}_2 + \text{CO}$ ), vinylidene isomerization ( $\text{H}_2\text{C}=\text{C} + \text{HC}=\text{CH}$ ), and intramolecular H-atom transfer in malonaldehyde show that tunneling effects play an important role in these processes.

### 1. INTRODUCTION

Over the last 5-6 years my co-workers and I have developed a series of theoretical methodologies for describing reaction dynamics in polyatomic molecular systems from first principles, namely reaction path and reaction surface Hamiltonian models. This paper reviews these approaches very briefly and discusses their application to several hydrogen atom transfer processes. The effect of tunneling is very significant in these examples and is, in fact, the most interesting feature of them.

### 2. REACTION PATH/SURFACE HAMILTONIAN AND TUNNELING MODELS

The reaction path Hamiltonian for a general polyatomic reaction, and various applications of it, has been reviewed several times recently,<sup>1h,1k</sup> and the reader should see these for a more detailed presentation. The basic idea<sup>2,3</sup> is that one describes the reaction as motion along the steepest descent path (in mass-weighted cartesian coordinates) that passes through the transition state from reactants to products, plus local harmonic motion away from this reaction path.

It is possible to apply such an approach in an ab initio framework since quantum chemists have developed efficient algorithms for computing the gradients of the Born-Oppenheimer potential surface  $V(\underline{x})$  ( $\underline{x}$  = all  $3N$  mass-weighted cartesian coordinates). The reaction path  $\underline{x}_0(s)$ , as a parametric function of the reaction coordinate  $s$  (the cartesian distance along the reaction path), is then determined by the gradient-following prescription

$$\frac{d}{ds} \underline{x}(s) = - \frac{\partial V(\underline{x})}{\partial \underline{x}} / \left| \frac{\partial V}{\partial \underline{x}} \right| \cdot \underline{x}_0(s) . \quad (1)$$

One also needs the force constant matrix along the reaction path  $\underline{K}(s)$ ,

$$\underline{K}(s) = \left( \frac{\partial^2 V}{\partial \underline{x} \partial \underline{x}} \right)_{\underline{x}=\underline{x}_0(s)} , \quad (2)$$

which is diagonalized (for each value of  $s$ ) to determine the eigenvectors  $\{\underline{L}_k(s)\}$  and frequencies  $\{\omega_k(s)\}$  for local harmonic motion orthogonal to the reaction path. The reaction path coordinates  $s, \{Q_k\}$ ,  $k=1, \dots, F-1$  ( $F=3N-6$  since we consider only total angular momentum  $J=0$  in this simplified presentation) are then the reaction coordinate  $s$  and the normal coordinates  $\{Q_k\}$  for vibrational motion perpendicular to the reaction path. The "old" cartesian coordinates  $\underline{x}$  are related to these "new" coordinates by

$$\underline{x} = \underline{x}_0(s) + \sum_k Q_k \underline{L}_k(s) . \quad (3)$$

The Hamiltonian for the molecular system in terms of these new coordinates, and their conjugate momenta, is (for  $J=0$ ),

$$H(p_s, s, \underline{P}, \underline{Q}) = H_0 + H_1 + H_2 + \dots \quad (4)$$

where

$$H_0 = \frac{1}{2} p_s^2 + V_0(s) + \sum_{k=1}^{F-1} \left( \frac{1}{2} P_k^2 + \frac{1}{2} \omega_k(s)^2 Q_k^2 \right) \quad (5a)$$

$$H_1 = - \sum_{k=1}^{F-1} Q_k B_{k,F}(s) p_s^2 , \quad (5b)$$

etc.  $V_0(s)$  is the potential energy along the reaction path, and the functions  $\{B_{k,F}(s)\}$ ,  $k=1, \dots, F-1$  describe coupling of the vibrational modes to the reaction coordinate  $s$ . These coupling functions are related to the curvature of the reaction path. The total curvature  $\kappa(s)$  of the reaction path in the  $F$ -dimensional space at distance  $s$  along it is

$$\kappa(s) = \left[ \sum_{k=1}^{F-1} B_{k,F}(s)^2 \right]^{1/2}; \quad (6)$$

the individual coupling functions  $B_{k,F}(s)$  are a measure of how the total curvature of the reaction path projects locally onto the various modes  $k$  orthogonal to it. It is this curvature of the reaction path which causes the coupling. Synonymous with the effect of non-separability of the reaction coordinate on tunneling, therefore, is the effect of reaction path curvature on tunneling.

## 2.1 Tunneling Models

The simplest description of tunneling effects on the rate constant for the reaction is obtained by neglecting the coupling between modes (i.e., using only  $H_0$  for the Hamiltonian Eq. (4)) and then using a statistical approximation - i.e., transition state theory, RRKM theory, etc. - to determine the average rate constant. The unimolecular rate constant, for example, for a molecule with total energy  $E$  and total angular momentum  $J$  is given by<sup>5,6</sup>

$$k(E, J) = [2\pi h \rho(E, J)]^{-1} \sum_{\underline{n}, K} P(E - \epsilon_{\underline{n}JK}^\ddagger), \quad (7a)$$

where  $\{\epsilon_{\underline{n}JK}^\ddagger\}$  are the vibrational and rotational energy levels of the "activated complex" in terms of the  $(F-1)$  vibrational quantum numbers  $\underline{n} = (n_1, n_2, \dots, n_{F-1})$  and angular momentum quantum numbers  $(J, K)$ . ( $J$  is the conserved total angular momentum quantum number and  $K$  is the non-conserved projection of total angular momentum onto a body-fixed axis.)  $P(E_F)$  is the one-dimensional tunneling probability as a function of the energy  $E_F$  along the reactant coordinate at the transition state.  $\rho$  is the density of reactant states per unit energy

$$\rho(E, J) = \sum_{\underline{n}, k} \delta(E - \epsilon_{\underline{n}JK}), \quad (7b)$$

where  $\{\epsilon_{\underline{n}JK}\}$  are the energy levels of the reactant molecule in terms of the  $F$ -vibrational quantum numbers  $\underline{n} = (n_1, \dots, n_F)$  and angular momentum quantum numbers  $(J, K)$ .

Coupling of the reaction coordinate to the transverse vibrational modes - via the curvature coupling in the perturbative  $H_1$ , Eq. (5b) - however, can have a significant effect on tunneling probabilities. A very simple model for describing these effects, which is usually semi-quantitative, is the semiclassical infinite order sudden approximation.<sup>7,10</sup> Here the tunneling probability is

$$P_{\underline{n}}(E) = e^{-2\theta_0} \prod_{k=1}^{F-1} I_0(\theta_k), \quad (8a)$$

where  $\theta_0$  is the usual barrier penetration integral

$$\theta_0 = \int_{s_<}^{s_>} ds \sqrt{2[V_n(s) - E]}, \quad (8b)$$

and  $V_n$  is the vibrationally adiabatic potential,

$$V_n(s) = V_0(s) + \sum_{k=1}^{F-1} M\omega_k(s)(n_k + \frac{1}{2}); \quad (8c)$$

i.e., the factor  $e^{-2\theta_0}$  in Eq. (8a) is the zeroth order tunneling probability. The action integrals  $\{\theta_k\}$  contain the influence of reaction path curvature,

$$\theta_k = \left| \int_s^s ds \sqrt{2[V_n(s) - E]} \left[ \frac{2n_k + 1}{\omega_k(s)} \right]^{\frac{1}{2}} e^{i\theta_k(s)} B_{k,F}(s) \right|; \quad (8d)$$

Since the Bessel function  $I_0$  in Eq. (8a) is an increasing function of its argument (and  $I_0(0) = 1$ ), one sees that reaction path curvature in general increases the tunneling probability.

For the well-studied test case  $H + H_2 \rightarrow H_2 + H$ , this simple model [Eqs. (8a-d)] corrects the tunneling probability from being a factor of 50-100 too small if reaction path curvature is ignored to within a factor of 2 of the correct value.<sup>1c</sup> If the curvature correction of the tunneling probability is smaller than this, then one has some confidence that this model will be able to describe it reasonably well.<sup>8-10</sup> There are other such simple models that do an equally good job.

## 2.2 Reaction Surface Hamiltonian

When the curvature coupling elements become too large, the reaction path description of the dynamics becomes poor. Often, though, it is only one of the coupling elements  $\{B_{k,F}(s)\}$  that becomes large - i.e., only one mode  $k$  is strongly coupled to the reaction coordinate motion. In such cases it is therefore useful to allow two degrees of freedom to undergo arbitrarily large amplitude motion, by introducing two reaction-like coordinates, with all other degrees of freedom described as local harmonic motion away from this two-dimensional "reaction surface". Since two degrees of freedom are allowed arbitrarily large amplitude motion, all dynamics that involves strong coupling between only two degrees of freedom can be described exactly via this approach. Since two degrees of freedom is dynamically equivalent to a collinear atom-diatom system, all dynamical phenomena that appear in collinear  $A+BC$  reactions can be described accurately by this reaction surface model. The present case of H-atom transfer typically involves only two degrees of freedom in an intimate way and should thus be described well.

The same method used to derive the reaction path Hamiltonian<sup>1a</sup> can be generalized to construct the reaction surface Hamiltonian.<sup>1j,1k</sup> It has the same general structure as Eqs. (4) and (5); e.g.,  $H_0$  is

$$H_0 = \frac{1}{2} \underline{P}_r \cdot \underline{S}(r_1, r_2)^{-1} \cdot \underline{P}_r + V_0(\underline{r}) + \sum_{k=1}^{F-2} \frac{1}{2} P_k^2 + \frac{1}{2} \omega_k(\underline{r})^2 Q_k^2, \quad (9)$$

where  $\underline{r} = (r_1, r_2)$  and  $\underline{P}_r = (P_{r_1}, P_{r_2})$  are the two coordinates and momenta for motion on the reaction surface, and  $\underline{S}^{-1}$  is the  $2 \times 2$  Wilson G-matrix for these two degrees of freedom.  $\{Q_k\}$  are the local normal coordinates for harmonic vibrational motion away from the reaction surface.  $H_1$  for the reaction surface Hamiltonian involves a generalization of the curvature couplings of Eq. (5b) - i.e., if the two-dimensional surface were a plane, these couplings would vanish - and couples motion on the reaction surface, i.e., coordinates  $(r_1, r_2)$ , to motion away from it, i.e., coordinates  $\{Q_k\}$ . At the level of  $H_0$ , therefore, one solves accurately for dynamics on the two-dimensional reaction surface - a very manageable problem - and then coupling of this motion to the vibrational modes  $k$  is treated perturbatively.

### 3. APPLICATIONS TO HYDROGEN ATOM TRANSFER

#### 3.1 Unimolecular Decomposition of Formaldehyde

The photodissociation of formaldehyde has been studied in

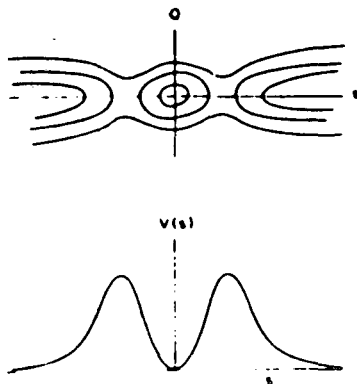
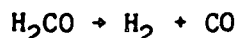


FIGURE 1. Sketch of the potential energy surface for the formaldehyde dissociation  $H_2CO \rightarrow H_2 + CO$ . The upper figure is a contour plot of the potential as a function of the reaction coordinate  $s$  and the out-of-plane bend coordinate  $Q$ . The lower figure is the potential along the reaction path, i.e., along the line  $Q=0$  of the upper figure. The barrier height for this reaction is  $-80$ - $90$  kcal/mole.



considerable detail experimentally, and there have also been very elaborate quantum chemical calculations for the potential energy surface.<sup>11</sup> Fig. 1 shows a sketch of the ground electronic state potential energy surface.

The rate constant  $k(E, J)$  [from Eq. (7)] for the unimolecular decomposition



is shown in Fig. 2 for  $J=0$ , as a function of energy relative to the classical threshold. The dashed line is the classical RRKM result that neglects tunneling. Since the radiative decay rate of excited formaldehyde is  $\sim 10^5 \text{ sec}^{-1}$ , unimolecular decomposition will be the major decay pathway if this rate is greater than  $10^5 \text{ sec}^{-1}$ . From Fig. 2 one sees that this will be the case for energies as much as 10 kcal/mole below the classical threshold. Tunneling thus plays a large role in the unimolecular dissociation of formaldehyde into molecular products  $\text{H}_2 + \text{CO}$ .

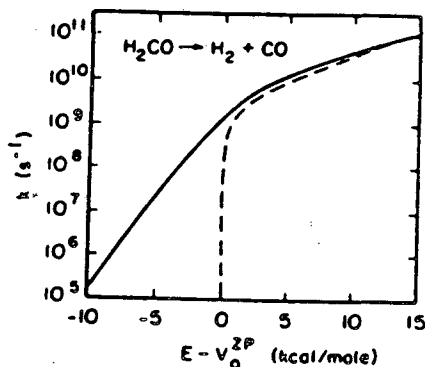


FIGURE 2. The microcanonical unimolecular rate constant for the formaldehyde dissociation ( $J=0$ ) as a function of energy relative to the classical threshold. The solid line includes the effects of tunneling, and the broken line is the classical result that neglects tunneling:

$k(E)$  in Fig. 2 is the average unimolecular rate for this reaction as a function of total energy in the molecular, but it is of considerable interest to determine the state-specific unimolecular rate constants, i.e., the decay rates of individual quantum states of formaldehyde. Experimental results for these quantities are beginning to become available.<sup>12-15</sup> Calculations have been carried out for a two-mode model of formaldehyde,<sup>16</sup> the two modes being the reaction coordinate and the out-of-plane bend mode (this being chosen since it was considered to be the one most weakly coupled to the reaction coordinate are thus most likely to show state-specific effects).

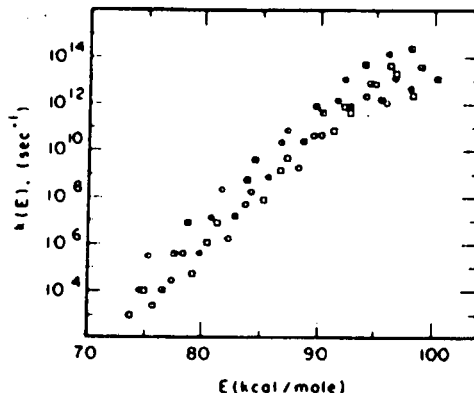
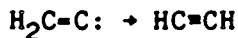


FIGURE 3. State-specific unimolecular rate constants for the two-mode model of the formaldehyde dissociation.

Fig. 3 shows these state-specific rate constants for the two-mode model of the present reaction, and one does indeed see a significant degree of state-specificity. That is, the decay rates for different states with essentially the same total energy can differ by as much as two orders of magnitude. This is approximately the same degree of state-specificity that has been seen experimentally.<sup>14-15</sup>

### 3.2 Isomerization of Vinylidene

Vinylidene ( $\text{H}_2\text{C}=\text{C}:$ ) is a very shallow minimum on the ground electronic state potential energy surface of  $\text{H}_2\text{C}_2$ .<sup>16</sup> Acetylene ( $\text{HC}=\text{CH}$ ), of course, is the much more stable, absolute minimum. Fig. 4 shows the average (microcanonical) rate constant  $k(E)$  (for  $J=0$ ) for isomerization of vinylidene to acetylene,



as a function of the excitation energy of vinylidene above its ground vibrational state. This is shown for two different values of the

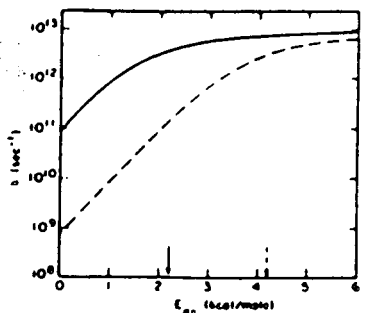


FIGURE 4. Microcanonical rate constant for the vinylidene + acetylene isomerization, as a function of vibrational excitation energy in vinylidene. The solid curve is for a barrier height of 4 kcal/mole and the dashed curve for 6 kcal/mole.

assumed barrier height; if the barrier is scaled down to be only 2 kcal/mole, the ground state ( $E_{\text{ex}}=0$ ) rate increases to  $\approx 3 \times 10^{12} \text{ sec}^{-1}$ .

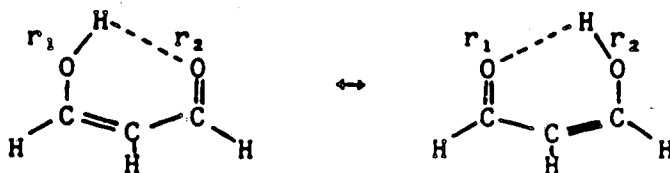
Even with a lifetime  $\tau = k^{-1}_{\text{ex}}$  of less than a picosecond, however, vinylidene lives long enough to have a physically meaningful existence, i.e., it has a well-defined vibrational spectrum. Moreover, this vibrational spectrum has recently been observed in photodetachment experiments by Lineberger's group.<sup>16</sup> The observed vibrational frequencies (and isotopic shifts) are in excellent agreement with the ab initio quantum chemistry values.

Lineberger's<sup>16</sup> experiments show that not only does vinylidene exist, but so do its excited vibrational states. Motivated by this, more detailed quantum mechanical calculations were carried out<sup>11</sup> to determine the energies and isomerization rates for individual states of vinylidene. The results are consistent with all experimental observations to date and show an interesting degree of mode-specificity. For example, the isomerization rate is increased by a factor of 6 if the  $\text{CH}_2$  rock mode (-1.3 kcal/mole of excitation energy) is excited; this is the mode which evolves into the reaction coordinate and is thus expected to be the most efficient in promoting the reaction. Exciting the  $\text{CH}_2$  scissors mode (-3.3 kcal/mole excitation energy) also increases the rate; but only by a factor of -2. Exciting the C-C stretch mode (-4.7 kcal/mole excitation energy) is predicted to decrease the rate by a factor of -2; this is an adiabatic effect due to the C-C bond becoming stiffer in going from vinylidene to acetylene.

These calculations thus provide a rather detailed prediction of mode-specific features in this reaction.

### 3.3 Malonaldehyde

Hydrogen atom transfer in malonaldehyde,



is a classic example of a double-well potential; the potential along the reaction coordinate is shown in Fig. 5. The tunneling splitting in the ground vibrational state has been observed in the microwave spectrum<sup>17</sup> and thus provides a direct measure of tunneling in this polyatomic system.

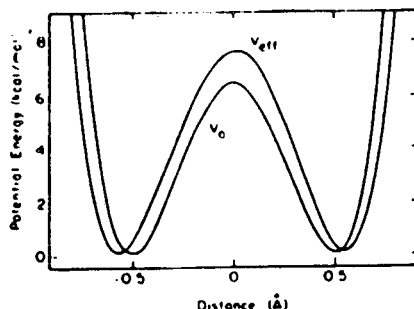


FIGURE 5. Potential energy along the reaction path for intramolecular H-atom transfer in malonaldehyde.  $V_0$  is the "bare" potential and  $V_{eff}$  the vibrationally adiabatic potential, shifted so that the local minima both are at 0.

Because this reaction path is very strongly curved in this case, the reaction surface model noted in Section 2.2 was used for this application.<sup>14</sup> The two reaction surface variables were chosen to be the two OH bond lengths,  $r_1$  and  $r_2$ ; Fig. 6 shows the 2-dimensional surface for this reaction.

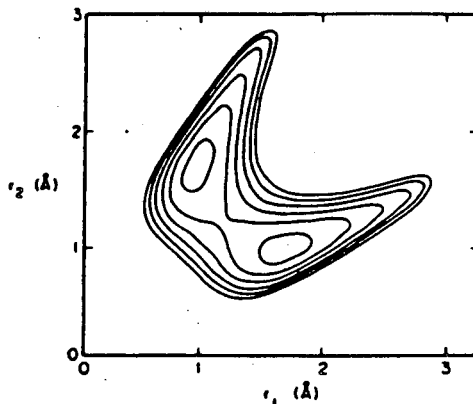


FIGURE 6. Contour plot of the potential energy for malonaldehyde on the 2-dimensional  $(r_1, r_2)$  reaction surface.

Calculations of the tunneling splitting were carried out<sup>14</sup> by diagonalizing the reaction surface Hamiltonian, Eq. (9), in a 2-dimensional basis set and then including all the other degrees of freedom by perturbation theory. It is found that the experimental tunneling splitting ( $21\text{cm}^{-1}$ ) can be obtained if the barrier height is adjusted to be 6 to 7 kcal/mole. Within  $\pm 2$  kcal/mole, this is in agreement with various levels of ab initio quantum chemistry calculations.<sup>18</sup>

## 4. CONCLUDING REMARKS

As is well-recognized nowadays, tunneling can be a significant aspect of chemical dynamics when the motion is primarily that of hydrogen atoms. This paper has reviewed a methodology, and some of its applications, for carrying out ab initio calculations for such processes in polyatomic molecular systems. Further developments in the methodology and continued applications to various chemical processes can be expected.

## ACKNOWLEDGMENTS

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