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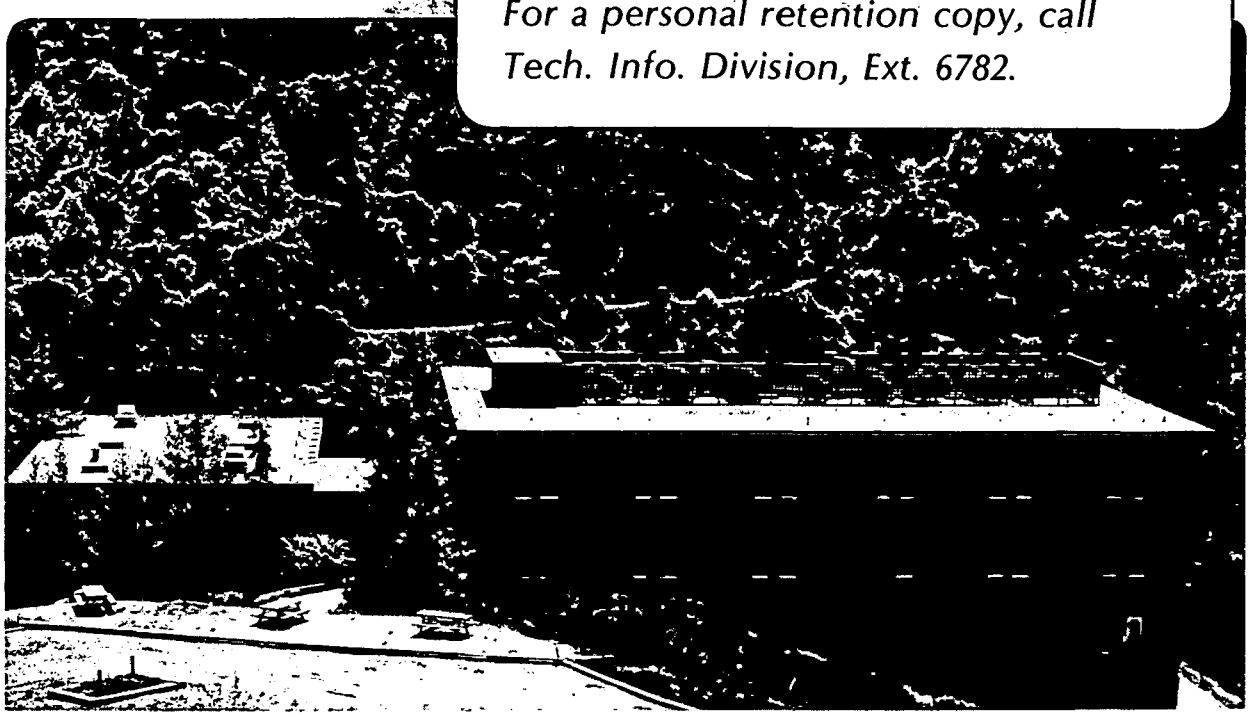

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Mode Specificity in the Unimolecular Dissociation of Formaldehyde ($H_2CO \rightarrow H_2 + CO$), a Two-Mode Model

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Abstract

The reaction path (the minimum energy path in mass-weighted cartesian coordinates), and all the coupling functions which fully characterize the reaction path Hamiltonian of Miller, Handy, and Adams [J. Chem. Phys. 72, 99 (1980)], have been calculated for the unimolecular dissociation of formaldehyde ($H_2CO \rightarrow H_2 + CO$) in its ground electronic state. The reaction coordinate and the four other in-plane vibrational modes are strongly coupled to each other, but the out-of-plane vibration is coupled directly only to the reaction coordinate. Calculations of the type of Waite and Miller [J. Chem. Phys. 73, 3713 (1980); 74, 3910 (1981)] for the state-specific unimolecular rate constants are carried out for a two-mode model consisting of the reaction coordinate and the out-of-plane vibration, and one observes a significant degree of mode-specificity; i.e., the unimolecular rate constant for a given metastable state is not a smooth function of the energy of the state. It is suggested that this mode-specificity may persist in the complete six-mode system.

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I. Introduction

We have recently carried out several theoretical investigations concerning mode-specificity in unimolecular reactions. In one set of studies[1] two of us have calculated the energies and lifetimes of the "eigenmetastable states" for a series of model problems consisting of two coupled oscillators, one of which can dissociate. By mode-specific, or conversely, statistical character in the dynamics we mean simply whether or not the unimolecular rate constant (the inverse of the lifetime) of a given state is a function only of the energy of the state. Not surprisingly, we have found that the degree of mode-specificity depends very much on the potential energy surface that defines the system: other things being equal, the stronger the coupling between the two degrees of freedom the less mode-specificity there is in the state-specific unimolecular rate constants.

Independent of the coupling strength, we have also found that if the reaction path for the process possesses a geometrical symmetry, then this can induce mode-specificity in the rate constants.[1b] For the unimolecular dissociation of formaldehyde,

$$H_2CO \rightarrow H_2 + CO \quad , \qquad (1.1)$$

for example, the reaction path (the minimum energy path in mass-weighted cartesian coordinates) on the ground state potential energy surface is planar[2] (C_s symmetry), and one of us has recently discussed[3] how this leads to mode-specificity in this reaction; i.e., even if the dynamics is as strongly coupled (and statistical) as it can be, there is nevertheless no interaction between A' and A" (the two irreducible

representations of C_s) states and thus a separate rate constant for A' and A" states. A statistical (i.e., microcanonical transition state theory) calculation[3] separately for the A' and the A" rate constants showed this symmetry-induced mode-specificity to be substantial (a factor of $\sim$ 20 difference between the rate constants at the same total energy) in the tunneling region relevant for reaction (1.1).

The formaldehyde dissociation (1.1), which has assumed somewhat the role of a benchmark[4] both experimentally and theoretically in polyatomic reaction dynamics, is also the subject of the present paper. As noted above, planar symmetry of the reaction path implies mode-specificity between A' and A" states, but here we wish to investigate the degree of mode-specificity <u>within</u> the A' and A" manifolds of states themselves, and this requires the kind of detailed state-specific calculation of energies and lifetimes of the type mentioned above.[1] Formaldehyde, however, has <u>six</u> vibrational degrees of freedom, so this is not feasible without simplifying assumptions. In this paper we consider a model of formaldehyde that consists of only two modes, the reaction coordinate and the out-of-plane bend. Since the out-of-plane mode is the one most weakly coupled to the reaction coordinate and also since it is the degree of freedom which leads to the symmetry-induced mode-specificity between A' and A" states, it seems to be the most likely candidate for displaying mode-specificity in the unimolecular rate constants.

Section II first summarizes the reaction path Hamiltonian[5] for the complete description of the formaldehyde system (i.e., all six vibrational degrees of freedom for J=0). The functions which couple

the various modes to the reaction coordinate and to each other are displayed, and one sees explicitly that the five in-plane degrees of freedom and indeed strongly coupled. This also suggests that the out-of-plane mode is the best prospect for showing mode-specific behavior. The state-specific unimolecular rate constants calculated for the two-mode model are presented and discussed in Section III, and one sees that there is indeed a significant degree of mode-specificity present within the A' and A" manifolds themselves. Section IV concludes by discussing several aspects of how these energies and lifetimes for unimolecular decay on the ground state potential energy surface, i.e., electronic state S_0, are related to the experimental measurements[4a,b] of collisionless lifetimes of specific rovibrational states in the electronically excited state S_1.

II. The Reaction Path Hamiltonian

The reaction path Hamiltonian[5] for a polyatomic reactive system models the potential energy surface as a harmonic valley (in many dimensions) about the minimum energy path (in mass-weighted cartesian coordinates) from the saddle point (i.e., transition state) on the potential energy surface down to products and back to reactants; it is essentially a polyatomic generalization of Hofacker[6] and Marcus'[7] natural collision coordinates.[8] If s and p_s are the reaction coordinate (the distance along the reaction path) and its conjugate momentum, and (Q_k, P_k), k=1,..., F-1 the coordinates and momenta for the vibrational modes orthogonal to the reaction path (F = 3N-6 = the total number of vibrational modes in the system, N = number of atoms), then the classical Hamiltonian for the system in terms of these variables is given by Miller, Handy and Adams[5] (for total angular momentum J=0) as

$$H(p_s, s, \{P_k, Q_k\}, k=1,\ldots,F-1) = \sum_{k=1}^{F-1} \frac{1}{2} P_k^{\,2} + \frac{1}{2}\omega_k(s)^2 Q_k^2$$

$$+ V_0(s) + \frac{1}{2}\Big[p_s - \sum_{\substack{k,k'=1\\ k\neq k'}}^{F-1} Q_k P_{k'} B_{k,k'}(s)\Big]^2 \Big/ \Big[1 + \sum_{k=1}^{F-1} Q_k B_{k,F}(s)\Big]^2 \tag{2.1}$$

where $V_0(s)$ is the potential energy along the reaction path, $\{\omega_k(s)\}$ the frequencies for the transverse vibrational modes (as a function of reaction coordinate), and $\{B_{k,k'}(s)\}$, $k,k' = 1,\ldots,F(k\neq k')$, are the elements which couple the vibrational modes to each other and to

the reaction coordinate (labeled as mode k=F). These coupling elements are given explicity by

$$B_{k,k'}(s) = \frac{\partial \underset{\sim}{L}_k(s)}{\partial s} \cdot \underset{\sim}{L}_{k'}(s) \quad , \tag{2.2}$$

where $\underset{\sim}{L}_k(s)$ is the 3N-dimensional eigenvector of the projected force constant matrix for mode k at distance s along the reaction path. ($\underset{\sim}{L}_F(s)$ is the normalized gradient vector which, by definition, points along the reaction path.) The elements $B_{k,F}(s)$, k=1,...,F-1, depend on how the curvature of the reaction path couples into mode k, and the elements $B_{k,k'}(s)$ (k,k') = 1,...,F-1,k≠k', are coriolis-like coupling elements that arise because the transverse eigenvectors may spiral about the reaction path. A more detailed discussion of the reaction path Hamiltonian, its generalization to non-zero total angular momentum, and its applications are given in previous papers.[2,5,9]

Earlier work of two of us with Yamaguchi and Schaefer[2] determined the reaction path, the frequencies, and the coupling elements which characterize the reaction path Hamiltonian for the formaldehyde reaction in the close vicinity of the transition state, and we have now extended these calculations along the entire reaction path. The results given below are all at the double-zeta self-consistent field (DZ-SCF) level of approximation. A total of 28 steps were taken along the reaction path between H_2CO (s=0) and $H_2CO^{\ddagger}$ (the transition state), and 10 steps from $H_2CO^{\ddagger}$ toward H_2 + CO. The force constant matrix was evaluated at 30 points along the reaction path by taking finite differences of the analytically calculated gradients. Other aspects

of the calculations are essentially the same as before.[2]

Figures 1-5 show the potential profile $V_0(s)$, the transverse frequencies $\{\omega_k(s)\}$, the curvature coupling elements $\{B_{k,F}(s)\}$, and the coriolis coupling element $\{B_{k,k'}(s)\}$, all as a function of the reaction coordinate. The barrier height of 117 kcal/mole at the DZ SCF level (cf. Fig. 1) is rather poor, but it is a simple matter to scale the values to obtain more realistic barrier of 92 kcal/mole given by more accurate CI calculations.[4d] The frequencies $\{\omega_k(s)\}$ have been calculated previously by Yamashita, Yamabe, and Fukui,[10] and there is excellent agreement between their values and ours in Figure 2.

It is worthwhile noting a few qualitative features in these results. As discussed before,[3] the curvature and coriolis coupling elements involving the out-of-plane mode k=5 are all zero by symmetry; this mode is coupled to the reaction coordinate only by virtue of the s-dependence of its frequency, $\omega_5(s)$. The in-plane vibrational modes k=1,...,4 are strongly coupled to each other (cf. Figures 4,5) and to the reaction coordinate (cf. Figure 3). Analogous to potential curves for different electronic states of diatomic molecules, there is a "non-crossing rule" for frequencies $\{\omega_k(s)\}$ (the square roots of the eigenvalues of the projected force constant matrix[5]) of the same symmetry. (The out-of-plane mode k=5 is of A" symmetry, so its frequency is allowed to (and does) cross frequencies of the in-plane (A') modes.) Also analogous to diatomic potential curves, one sees in Figure 2 several examples of "avoided crossings" between in-plane (A') modes, e.g., that between modes 3 and 4 at $s \approx 0.5\ \sqrt{\text{amu}}\ \text{Å}$. Corresponding to this avoided crossing there is a sharp peak in the coupling element $B_{3,4}(s)$ at $s \approx 0.5\ \sqrt{\text{amu}}\ \text{Å}$ (cf. Figure 4). When dealing with avoided crossings

of electronic potential curves it is often useful to switch from an adiabatic electronic representation to a "diabatic" electronic basis;[11] this effectively takes the coupling out of the kinetic energy and puts it into the potential energy, and in many cases this is easier to deal with. An analogous "diabatic" representation of the transverse vibrational modes has been defined by one of us for the reaction path Hamiltonian;[9b] this eliminates the coupling elements $B_{k,k'}(s)$ from the Hamiltonian, but introduces a non-diagonal coupling into the potential energy: the potential energy term

$$\sum_{k=1}^{F-1} \frac{1}{2}\, \omega_k(s)^2\, Q_k^{\,2} \quad , \tag{2.3a}$$

in the Hamiltonian of Eq. (2.1) is replaced by

$$\sum_{k,k'=1}^{F-1} \frac{1}{2}\, Q_k\, \Lambda_{k,k'}(s)\, Q_{k'} \quad . \tag{2.3b}$$

The "diabatic" frequencies, i.e., the diagonal elements $\{\Lambda_{k,k}(s)\}$, may now cross, i.e., go through a local Fermi resonance, and their coupling is determined by the term $\Lambda_{k,k'}(s)\, Q_k Q_{k'}$. We expect that many of the useful approximations (e.g., Landau-Zener) for treating electronic curve crossing problems will also be useful in describing the dynamics of the reaction path Hamiltonian, but this is a topic for future research.

III. The Two-Mode Model

Since the out-of-plane mode (k=5 in the present labeling) is the one most weakly coupled to the reaction coordinate (mode k=6) and its coupling to the other in-plane modes k=1-4 vanishes, it is the most likely candidate to display mode-specificity. How energy in the out-of-plane mode exchanges with that in the reaction coordinate is also extremely relevant to the experimental situation, for non-planarity of the electronically excited state S_1 means that the radiationless transition $S_1 \rightarrow S_0$ should produce S_0 states with a significant amount of excitation initially in the out-of-plane mode. As noted in the Introduction, we have already shown that there is a symmetry-induced mode-specificity for this mode, i.e., even (A') and odd (A") vibrational states of the out-of-plane modes are uncoupled (for J=0), but now we wish to carry out calculations like those of Waite and Miller[1] to see if there is any significant mode-specificity within the A' and the A" manifolds of states themselves.

To make these calculations feasible we consider a system that consists of only the reaction coordinate and the out-of-plane mode itself. The reaction path Hamiltonian for this two-mode system is

$$H(p_s,s,P,Q) = \frac{1}{2} p_s^{\,2} + \frac{1}{2} P^2 + V_0(s) + \frac{1}{2} \omega(s)^2 Q^2 \quad , \qquad (3.1)$$

where the subscript "5" has been dropped from P and Q. The functions $V_0(s)$ and $\omega(s)$ are also approximated by the following polynomials,

$$V_0(s) = a_2 s^2 + a_4 s^4 \qquad (3.2a)$$

$$\omega(s) = \sum_{n=0}^{5} b_{2n} s^{2n} \quad . \tag{3.2b}$$

and Figures 6 and 7 show the comparison of the ab initio results for $V_0(s)$ (scaled to a barrier height of 92 kcal) and $\omega(s)$ and these polynomial approximations. The constants $\{a_n\}$ and $\{b_n\}$ of Eq. (3.2) are given in Table I.

The calculation of the energies and lifetimes of the metastable states for this system using the complex scaling method proceeds as before.[1] One scales the dissociative coordinate $s \to se^{i\alpha}$, and the scaled quantum mechanical Hamiltonian operator is

$$H_\alpha = -\frac{\hbar^2}{2} e^{-2i\alpha} \frac{\partial^2}{\partial s^2} - \frac{\hbar^2}{2} \frac{\partial^2}{\partial Q^2} + V_0(s\, e^{i\alpha})$$

$$+ \frac{1}{2} \omega(s\, e^{i\alpha})^2 Q^2 \quad . \tag{3.3}$$

The complex-symmetric matrix of H_α (using a harmonic oscillator basis for both degrees of freedom) was diagonalized to obtain complex eigenvalues $E_n - i\,\Gamma_n/2$; the energy of the state is E_n and its unimolecular decay rate $\Gamma_n/\hbar$.

The two-dimensional potential surface $V_0(s) + \frac{1}{2}\omega(s)^2 Q^2$ is not only invariant to $Q \to -Q$ (the planar symmetry) but also to $s \to -s$. (A consequence of this latter symmetry is the two equivalent transition states at $s > 0$ and $s < 0$; the decay rate $\Gamma/\hbar$ is the total decay rate for $s \to +\infty$ or $s \to -\infty$.) The complete symmetry of the potential surface is thus C_{2v}, with irreducible representations A_1, B_1, A_2, and B_2,

which are even-even, even-odd, odd-even, and odd-odd on the operations ($Q \rightarrow -Q$) and ($s \rightarrow -s$), respectively. The matrix of H_α is thus block diagonal, and the diagonalization can be carried out separately for each irreducible representation.

Figure 8 shows the results obtained, the unimolecular decay rates of the various metastable states as a function of their energy. Due to precision limiations as well as basis set size, values stable with respect to variation of α and to basis set could be obtained only for energies above $\sim$ 70 kcal/mole, but fortunately this is the region of interest experimentally. The A_1 and B_1 states are shown in Figure 8 by solid squares and circles, respectively, and the A_2 and B_2 states by the open squares and circles. Thus the solid points represent even states in the out-of-planes mode (i.e., with respect to $Q \rightarrow -Q$) and the open points odd states; i.e., for the C_s symmetry that is maintained along the reaction path, A_1 and B_1 are A', A_2 and B_2 are A".

The results in Figure 8 show the symmetry-induced mode specificity discussed earlier--i.e., for a given energy the open points (A" states) fall on the average below the solid points (A' states)--but even more striking is that there is substantial mode specificity even within the A' and A" manifolds of states. For a given total energy the unimolecular rate constant ranges over about two orders of magnitude. By examining the wavefunctions obtained from the matrix diagonalization one can see that the mode-specificity results from a lack of complete mixing of the out-of-plane states; i.e., for a given total energy the fastest decaying states correspond to the lowest quantum number of the out-of-plane mode, and the states decaying more slowly to the highest

quantum number of the out-of-plane mode. As expected, one observes no mode-specificity associated with the even or odd symmetry of the reaction coordinate mode, i.e., between A states and B states.

It is also of interest to note how this degree of mode-specificity in the state-specific unimolecular decay rates correlates with the quasiperiodic or chaotic nature of the classical trajectories of the system. Using the same two-dimensional potential energy surface, Poincare surfaces of section were generated in the usual manner.[12] Chaotic trajectories were observed over the entire energy region shown in Figures 8, i.e., for all energies greater than $\sim$ 75 kcal/mole. By an energy of 92 kcal/mole essentially 100% of the trajectories were chaotic. In spite of this, though, we see that the state-specific unimolecular rate constants show a significant degree of mode-specificity, so it appears that chaotic classical trajectories do not necessarily rule out the possibility of such mode-specificity.

Finally, there is the very pertinent question of how the results for this two-mode model relate to "real" formaldehyde with its six degrees of freedom. As seen in Figures 3-5, the coupling elements which couple the four in-plane modes k=1-4 to each other and to the reaction coordinate (k=F=6) are large and strongly varying functions of s, suggesting that these five in-plane degrees of freedom may behave statistically among themselves. As noted in Section II, the out-of-plane mode (k=5) is coupled directly only to the reaction coordinate, so the question is: does the strong coupling of modes k=1-4 to mode 6 destroy the less-than-complete statisitcal behavior seen in Figure 8 between modes 5 and 6? To get some indiation of the answer we have carried out preliminary calculations for a three-mode system--the

third mode being strongly coupled to the reaction coordinate (k=6) but with no direct coupling to the out-of-plane mode (k=5)--and the rate constants for this system display roughly the same degree of mode-specificity as that in Figure 8. The indication, therefore, is that the mode-specific behavior of the out-of-plane bend may persist in real formaldehyde (at least for J=0).

IV. Concluding Remarks

We conclude with some remarks on how the state-specific unimolecular decay rates of S_0 (the ground electronic state) are related to the experimentally observed[4a,b] decay rates of individual states of S_1 (the first excited singlet electronic state). The situation is the usual picture of a radiationless transition:[13] The initial state in S_1 is prepared by optical excitation from S_0, and then S_1 decays either by spontaneous emission of a photon (i.e., fluorescence) or by making a radiationless transition to a state S_0 that can dissociate. Observation of the fluorescence from S_1 determines the time-dependent population of the initially excited state of S_1, $P(t)$. Standard theory gives this as[13]

$$P(t) = |S(t)|^2 \quad , \tag{4.1a}$$

where

$$S(t) = \langle 0|e^{-iHt/\hbar}|0\rangle$$

$$= (2\pi i)^{-1} \int_C dE\ e^{-iEt/\hbar} \langle 0|(E-H)^{-1}|0\rangle \quad . \tag{4.1b}$$

Here $|0\rangle$ is the initially excited state of S_1, H is the complete Hamiltonian involving S_1, S_0, and their coupling, and the contour C runs from $+\infty + i\varepsilon$ to $-\infty + i\varepsilon$, and encloses the lower half complex E plane.

If $\{E_k,\Gamma_k\}$ are the energies and widths of the states of S_0--the quantities that we have been calculating in Sections II and III--and V_k the non-adiabatic coupling elements of state $|0\rangle$ of S_1 to state k of S_0, then one can readily show that

$$\langle 0|(E-H)^{-1}|0\rangle = [E-E_0 + i\,\frac{\Gamma_0}{2} - \sum_k \frac{V_k^{\,2}}{E-E_k+i\,\frac{\Gamma_k}{2}}]^{-1} \quad , \tag{4.2}$$

where E_0 is the energy of state $|0\rangle$ of S_1 and $\Gamma_0/\hbar$ its radiative decay rate. The most rigorous theoretical calculation would thus take energies and lifetimes of S_0, $\{E_k,\Gamma_k\}$, computed by our method, for example, and the non-adiabatic coupling elements V_k as computed, for example, by van Dijk, et al.,[14] and then use Eqs. (4.1) and (4.2) to determine P(t).

In the perturbative limit Eq. (4.2) is approximated by[13]

$$\langle 0|(E-H)^{-1}|0\rangle \approx [E-E_0 + i\,\frac{\Gamma_0}{2} - \sum_k \frac{V_k^{\,2}}{E_0-i\,\frac{\Gamma_0}{2} - E_k + i\,\frac{\Gamma_k}{2}}]^{-1} \quad , \tag{4.3}$$

and it is not hard to show that Eq. (4.1) then gives

$$P(t) \sim e^{-t/\tau} \quad . \tag{4.4a}$$

where

$$\hbar/\tau = \Gamma_0 + \sum_k \frac{V_k^{\,2}(\Gamma_k-\Gamma_0)}{(E_k-E_0)^2 + (\frac{\Gamma_k}{2} - \frac{\Gamma_0}{2})^2} \quad . \tag{4.4b}$$

This expression has been used by Weishaar and Moore[4a] to interpret their measurements of the electric field dependence of lifetimes of S_1 states.

Another limit in which Eqs. (4.1) and (4.2) can be evaluated explicitly is if the state $|0\rangle$ interacts significantly with only <u>one</u> state in S_0. One thus approximates Eq. (4.2) by the following

$$\langle 0|(E-H)^{-1}|0\rangle \simeq [E-E_0 + i\,\frac{\Gamma_0}{2} - \frac{V_k^{\,2}}{E-E_k + i\,\frac{\Gamma_k}{2}}]^{-1} \quad . \tag{4.5a}$$

The contour integral in Eq. (4.1b) can then be evaluated (there are now two poles) and one obtains

$$S(t) = e^{-i(E_0+E_k)t/2\hbar}\, e^{-(\Gamma_k+\Gamma_0)t/4\hbar}\, [\cos(Rt) - i\,(\frac{E_0-E_k - i\,\frac{\Gamma_0}{2} + i\,\frac{\Gamma_k}{2}}{2R})\sin(Rt)] \tag{4.5b}$$

where

$$R = \{[\frac{E_0-E_k}{2} - \frac{i}{4}\,(\Gamma_0-\Gamma_k)]^2 + V_k^{\,2}\}^{1/2} \quad .$$

In P(t) this leads to bi-exponential decay with two lifetimes τ_+ and τ_-,

$$\hbar/\tau_\pm = \frac{1}{2}\,(\Gamma_0+\Gamma_k) \pm \sqrt{2}\,[\sqrt{a^2+b^2} - a]^{1/2} \quad , \tag{4.6a}$$

with an oscillatory structure (i.e., quantum beats) of frequency

$$\omega = \sqrt{2}\ [\sqrt{a^2+b^2} + a]^{1/2} \quad , \tag{4.6b}$$

where

$$a = \mathrm{Re}(R^2) = (\frac{E_0-E_k}{2})^2 + V_k^{\ 2} - (\frac{\Gamma_k-\Gamma_0}{4})^2$$

$$b = \mathrm{Im}(R^2) = (\frac{E_0-E_k}{2})(\frac{\Gamma_k-\Gamma_0}{2}) \quad .$$

Equation (4.6a), for example, shows that

$$\hbar/\tau_+ + \hbar/\tau_- = \Gamma_0 + \Gamma_k \quad , \tag{4.7}$$

so that if the radiative rate ($\Gamma_0/\hbar$) is known, then Γ_k, the width of the S_0 level, can be determined. If the two-state approximation (i.e., Eq. (4.5a)) is valid, then determination of the two exponential decay constants and the beat frequency would allow one to use Eq. (4.5b) with Eq. (4.1) to determine the three unknown parameters E_k, Γ_k, and V_k, assuming that E_0 and Γ_0 are known.

To address the question of mode-specificity in S_0 experimentally, however, it would clearly be desirable to excite an individual state k of S_0 directly and observe its unimolecular decay rate $\Gamma_k/\hbar$, without having to go through S_1 with non-adiabatic transitions to perhaps many states in S_0. The recent report by Reisner[15] et al., of selective vibrational excitation in S_0 by stimulated emission pumping may offer a way of doing this.

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14. J. M. F. van Dijk, M. J. H. Kemper, J. H. M. Kerp, and H. M. Buck, J. Chem. Phys. 69, 2462 (1978).

15. D. E. Reisner, P. H. Vaccaro, C. Kittreel, R. W. Field, J. L. Kinsey, and H.-L. Dai, J. Chem. Phys. 77, 573 (1982).

Table I. Coefficients[a] for Polynomial Fits to $V_0(s)$ and $\omega(s)$.

n	a_n [b]	b_n [c]
0		1191
2	93.87755	-511.755
4	-23.94835	-343.317
6		520.867
8		-159.227
10		14.186

[a]Cf. Eq. (3.2). Units for s are $\sqrt{\text{amu}}$ Å.

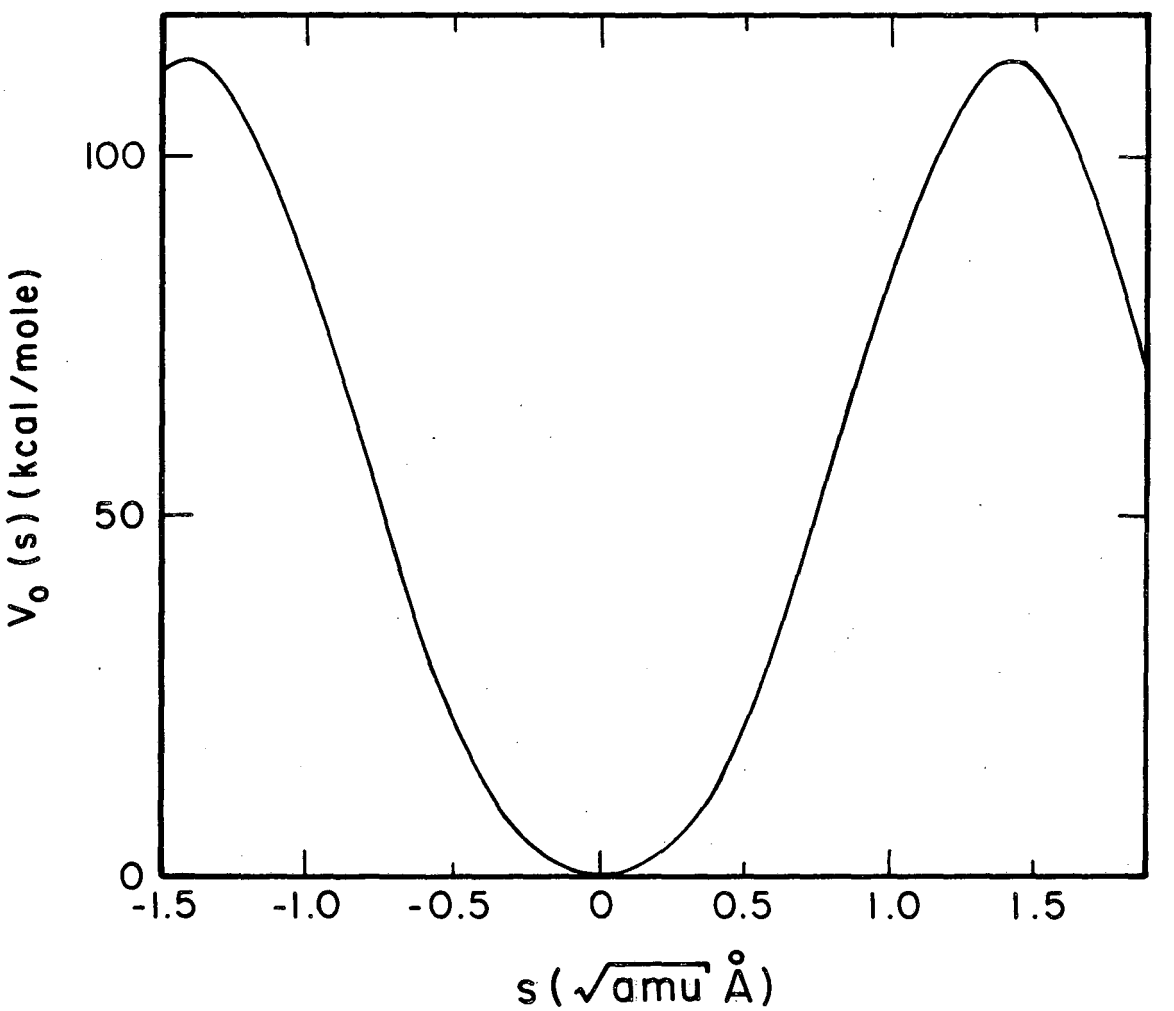
[b]Units for $V_0(s)$ are kcal/mole.

[c]Units for $\omega(s)$ are cm^{-1}.

Figure Captions

1. Potential energy along the reaction path for reaction (1.1), $H_2CO \rightarrow H_2 + CO$, on the ground state potential energy surface.
2. Frequencies for the vibrational modes (labeled by k=1-5) orthogonal to the reaction path, as a function of the reaction coordinate s, for reaction (1.1). s=0 corresponds to H_2CO, and the verticle dashed line indicates the location of the transition state.
3. Curvature coupling elements which couple vibrational mode k to the reaction coordinate (mode k=F); the curves are labeled by k. See Eqs. (2.1) and (2.2) for their definition and the way these coupling elements (and those shown in Figures 4, 5) enter into the reaction path Hamiltonian.
4. Coriolis-like coupling elements which couple vibrational modes k and k'; the curves are labeled by (k,k').
5. Same as Figure 4.
6. Comparison of the <u>ab initio</u> potential along the reaction path (solid curve), scaled to a barrier height of 92 kcal/mole, to the polynomial fit (dashed curve), given by Eq. (3.2a) and Table I.
7. Comparison of the <u>ab initio</u> frequency along the reaction path (solid curve) for the out-of-plane mode (k=5) to the polynomial fit (dashed curve) given by Eq. (3.2b) and Table I.
8. State-specific unimolecular decay rates for the two-mode model of reaction (1.1); see Section III. Each point corresponds to a complex eigenvalue $E_n - i\Gamma_n/2$; the energy of the metastable state is E_n and its unimolecular decay rate $k_n = \Gamma_n/\hbar$. The solid

squares and circles are states of A_1 and B_1 symmetry, respectively, and open squares and circles are A_2 and B_2 states.



XBL 828-11180

Figure 1

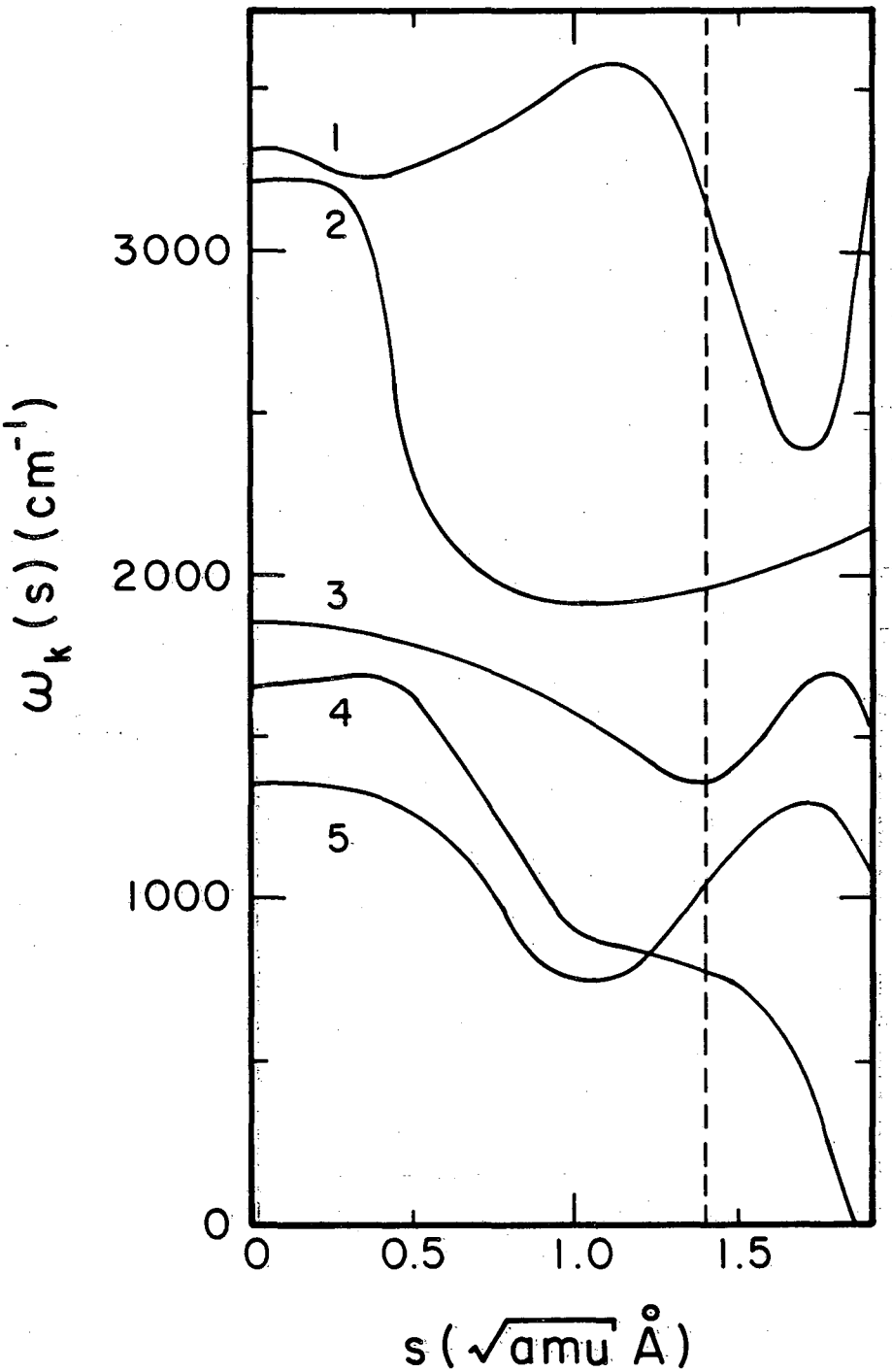


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Figure 2

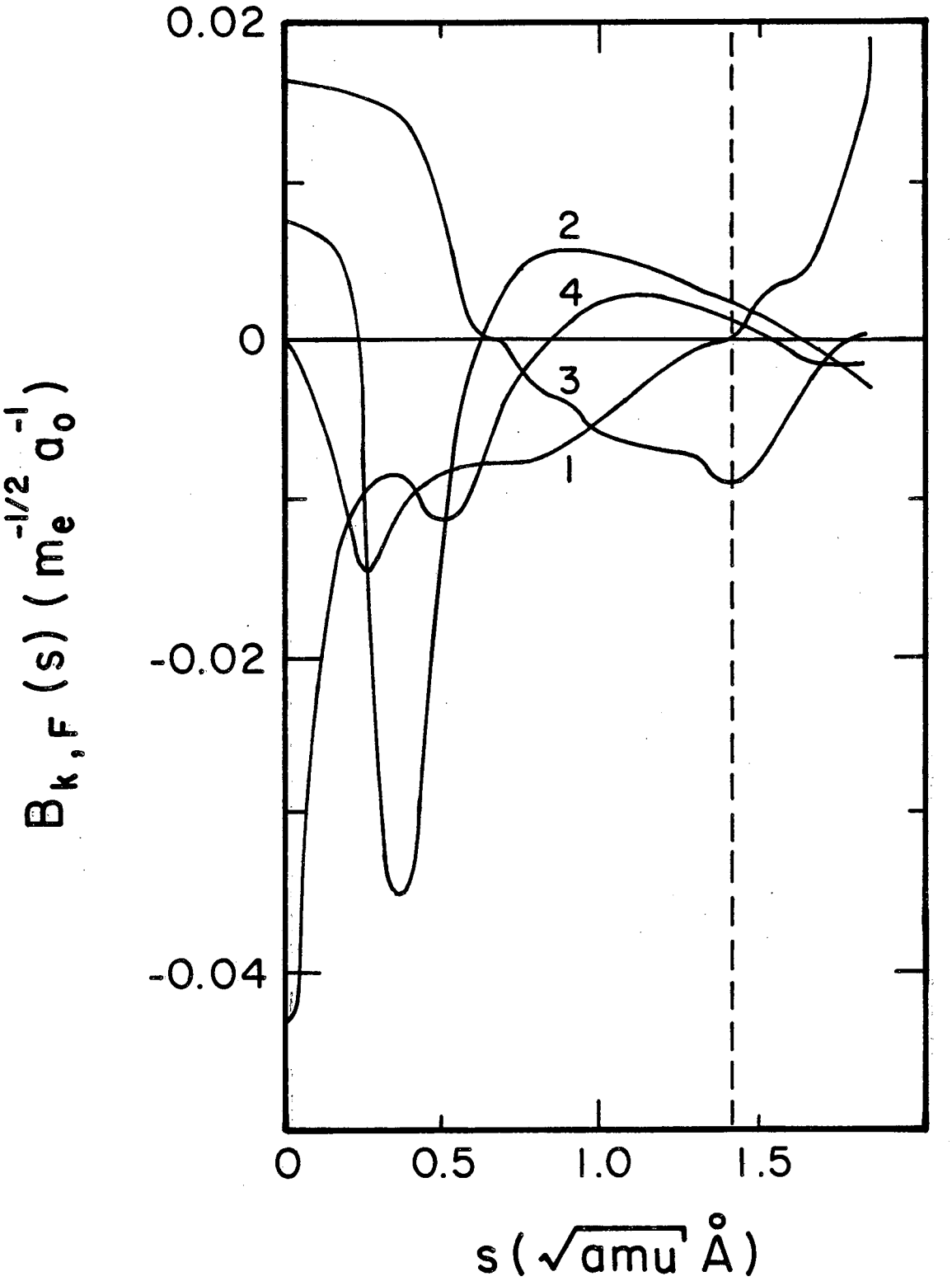

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Figure 3

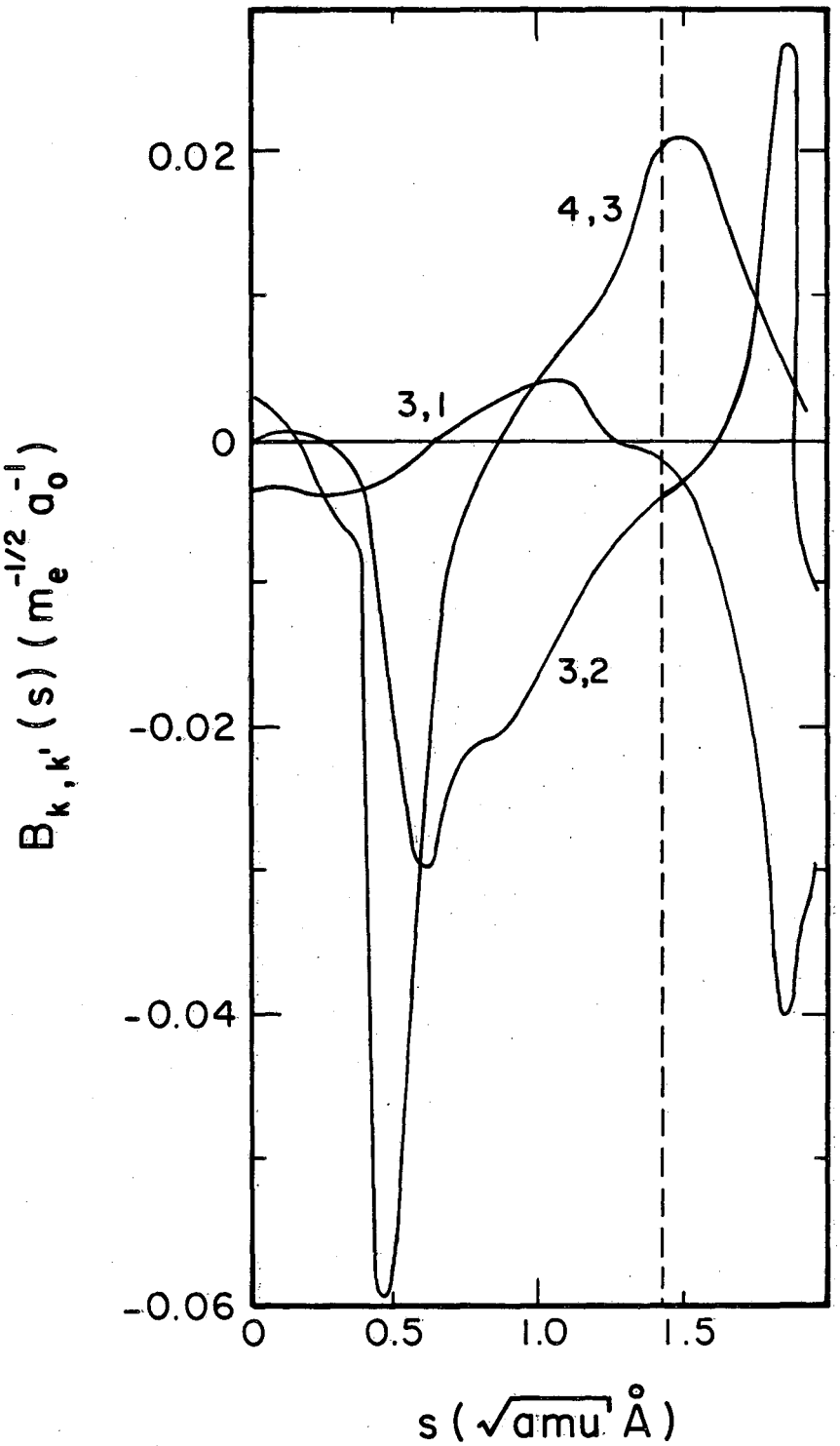

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Figure 4

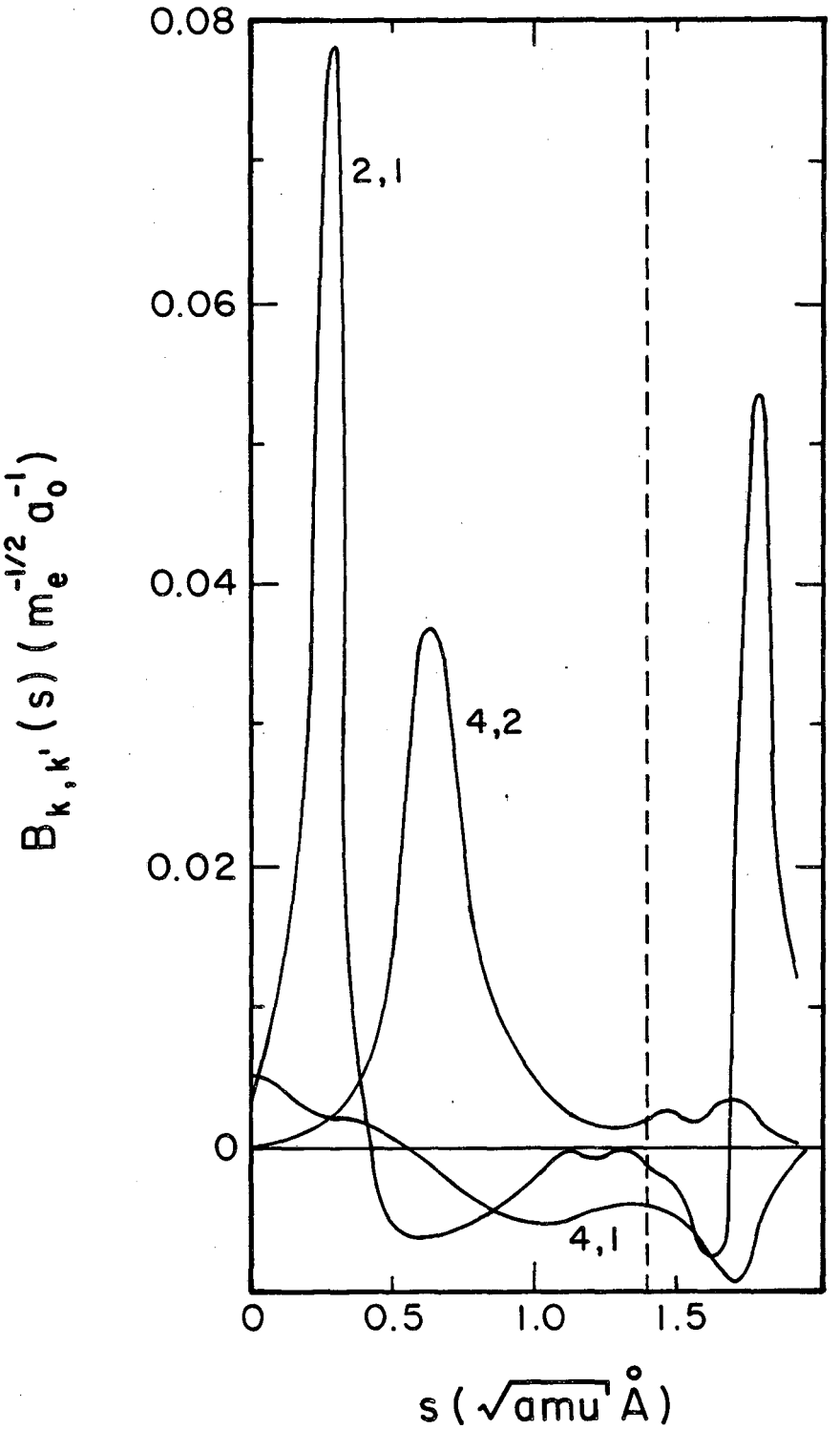

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Figure 5

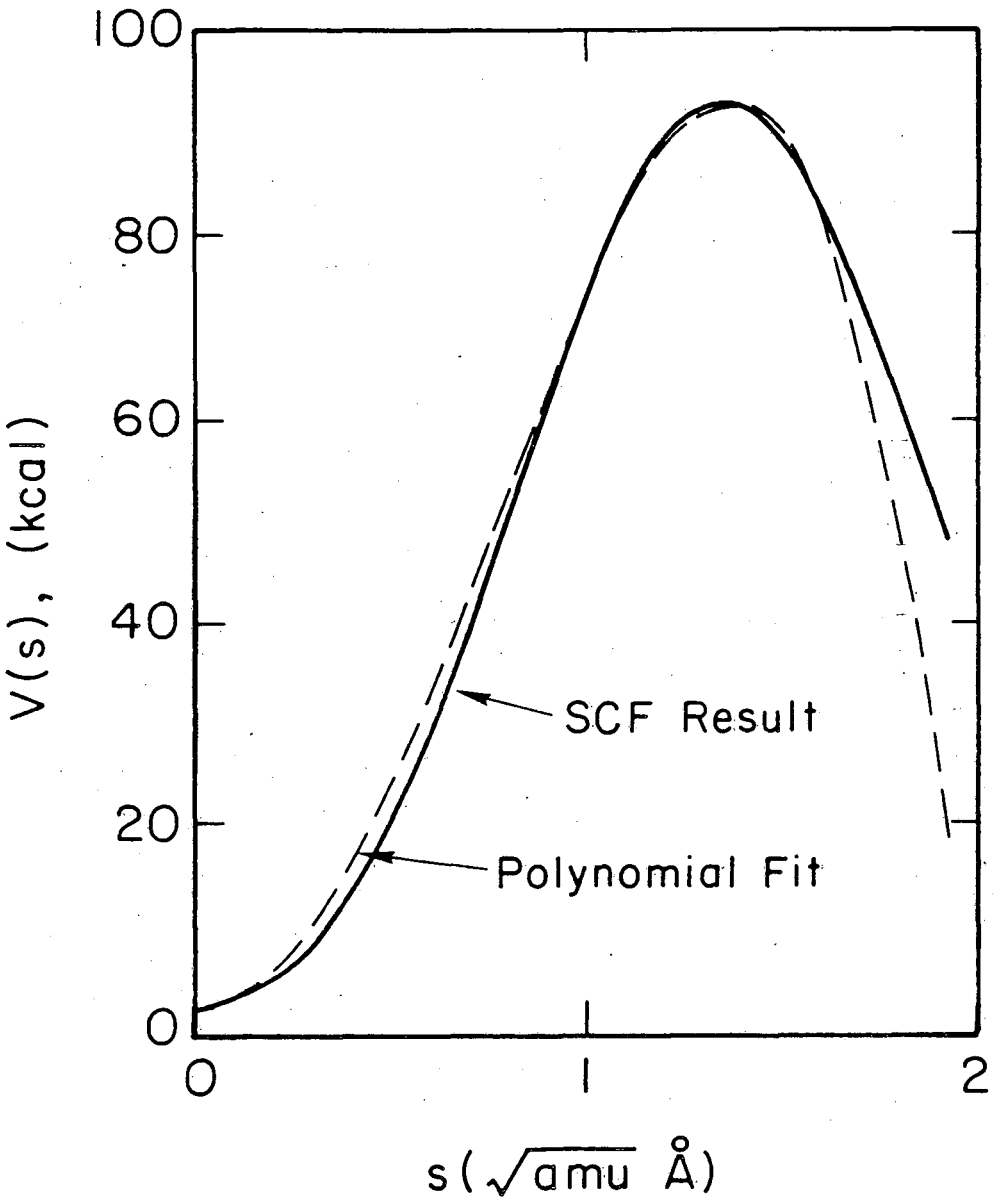

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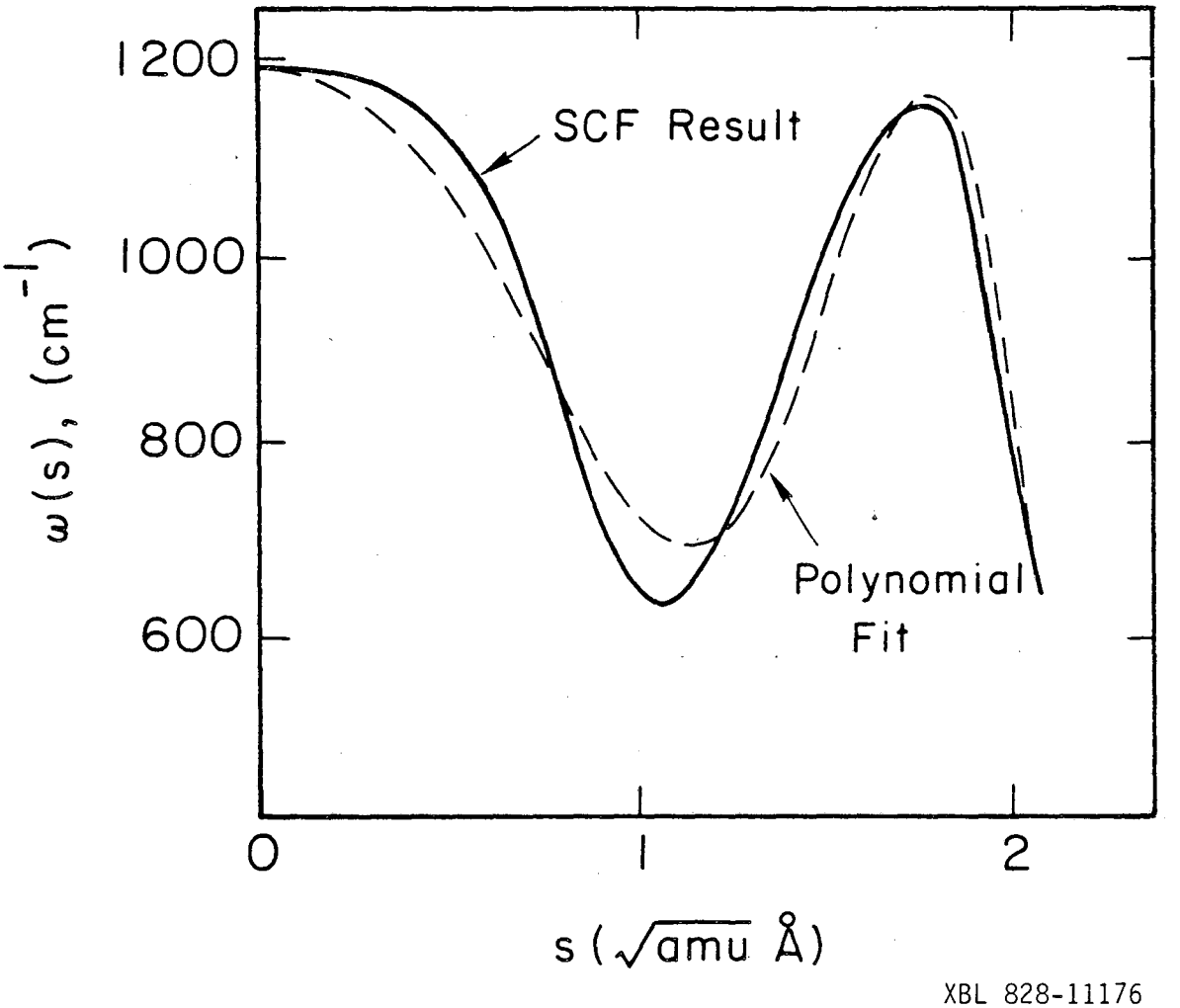
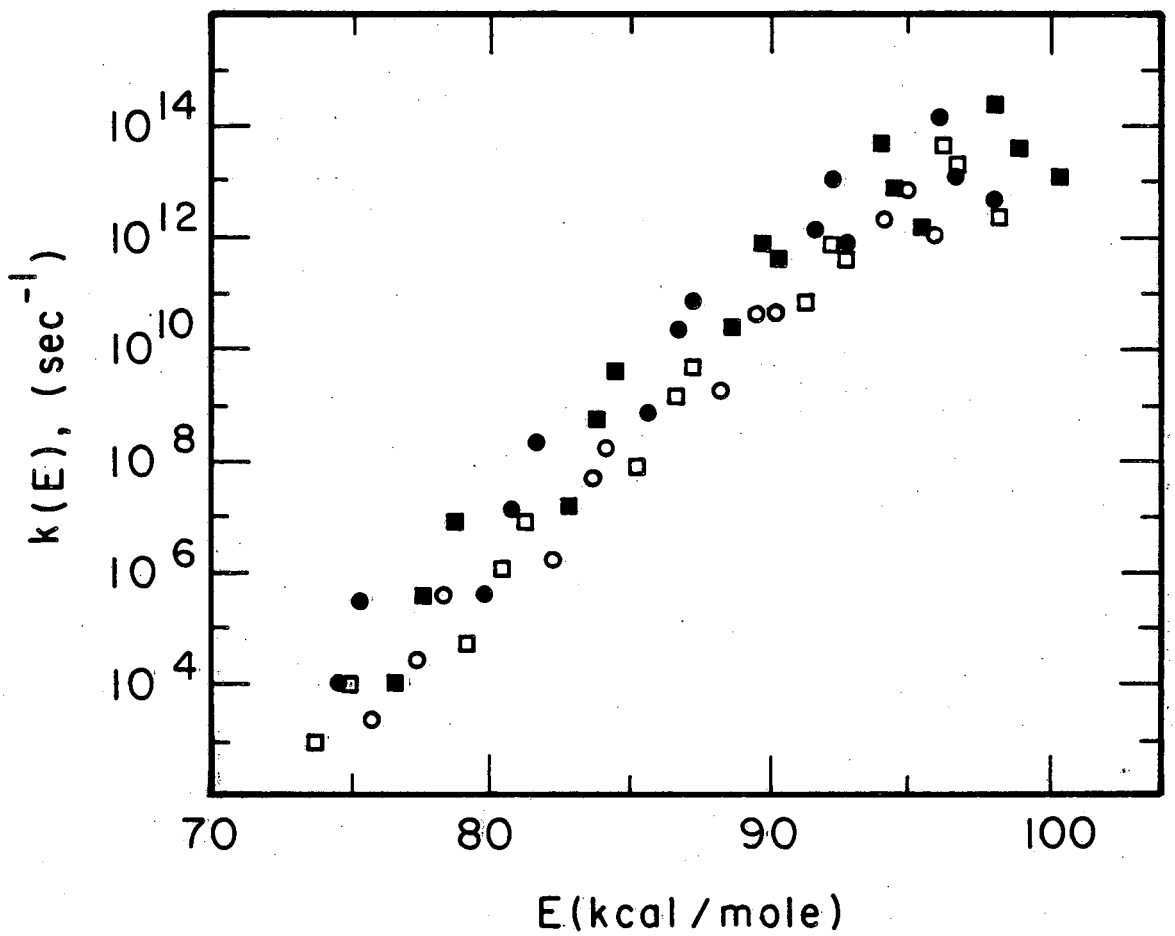
Figure 6



XBL 828-11176

Figure 7



XBL 828-11179

Figure 8

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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