Classical Trajectory Study of the HFCO → HF + CO Reaction

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Classical trajectories have been calculated for the unimolecular dissociation reaction HFCO → HF + CO over a modified form of the potential energy surface of Wei and Wyatt (*J. Phys. Chem.* **1993**, *97*, 13580). To ensure the proper asymptotic state of the reaction products and to avoid unphysical areas in the potential energy function, HF and CO two-body potentials, an elaborate range function, and switching functions were introduced into the original analytic function. The initial rotational energy was set to zero. The total vibrational energy was between 68.7 and 73.4 kcal/mol. Clear evidence of mode specificity was found in that the excitation of the six different modes (with approximately equal total energy) gave significantly different rates of decay: CH stretch > CH bend > CF stretch ≫ CO stretch > out-of-plane bend > OCF bend.

I. Introduction

The study of unimolecular dissociation and its precursor intramolecular vibrational energy redistribution (IVR) has long been a topic of both experimental and theoretical molecular dynamics. Of particular recent interest is the possibility of mode-specific chemistry, where the excitation of a particular vibrational mode leads to an enhanced rate of reaction.[1] Recent experimental studies would seem to indicate that HFCO would be a good candidate for vibrationally enhanced, mode-specific unimolecular dissociation.

Moore's group at Berkeley has carried out a series of stimulated emission pumping (SEP) experiments studying the dissociation of vibrationally excited HFCO on the ground S_0 surface.[2−5] They found that for energies between 13 000 and 23 000 cm^{-1} above the dissociation threshold, as energy is increased in the out-of-plane bending mode (ν_6), the ν_6 vibration becomes more and more decoupled from the other vibrational degrees of freedom.[3]

Measurements were also made of the unimolecular dissociation rates of HFCO for well-characterized initial rovibrational states.[4] In the threshold region, the decay rate is very sensitive to the rotational state. At higher energies, clear evidence of mode specificity is found. States with approximately the same total energy dissociated more slowly if the energy was in the ν_6, out-of-plane bending mode. This is, of course, not surprising given the relative isolation of the ν_6 state. Moore's group has also characterized the energy distributions of the CO dissociation products.[5] The product CO is found to have relatively low vibrational energy, with 90% of the product in the $v' = 0$ state and 10% in the $v' = 1$ state. Over 50% of the available energy is released as product translation.

A number of ab initio calculations have been carried out to determine the ground-state potential energy surface.[6−10] There is fairly good agreement among the various studies on the geometry of the transition state (see Table 2 of ref 10). However the exact height of the potential barrier has been more difficult to pin down. Goddard and Schaefer[6] found a barrier height of approximately 47 kcal/mol. The results of Kamia and Morokuma[8] are similar, with a value of 46.9 kcal/mol. Francisco and Zhao[9] found a dissociation energy of −9.0 kcal/mol and a barrier height of 43.2 kcal/mol for the dissociation of HFCO. Wei and Wyatt[10] calculated the ground-state potential surface at 3855 geometries and fit the data to a "global" analytic function, giving a heat of reaction of −5.6 kcal/mol and a barrier height of 48 kcal/mol.

In a very recent work, Yamamoto and Kato[17] reported a new ground-state surface for the title reaction. A total of 3621 ab initio points were calculated and fit to a function of the internal coordinates of the molecule. The barrier was calculated to be 47.8 kcal/mol and the dissociation energy to be −3.5 kcal/mol. The points used to fit the analytical surface ranged from the HFCO potential minimum to 20 kcal/mol above the transition-state energy. Two types of classical trajectory studies were carried out using the surface. First, power spectra were calculated at energies −25, −5, and +15 kcal/mol relative to the dissociation barrier. Second, HF and CO product state distributions were calculated with trajectories initiating near the transition state at energies 12 kcal/mol above the transition-state energy.

In this paper we report the calculation of classical trajectories over a modified form of the potential energy surface of Wei and Wyatt.[10] The purpose is to investigate the rates of unimolecular dissociation resulting from the excitation of specified vibrational modes.

II. Calculations

Potential Energy Surface. We have used the potential surface of Wei and Wyatt,[10] kindly supplied by the authors. The potential is a four-body polynomial function of the six internuclear coordinates, expressed in terms of Simon−Parr−Finlan coordinates. The functional form of the surface and constants of the polynomial are all given in refs 10 and 11. Figure 1 shows a contour plot of the potential surface supplied by Prof. Wyatt. In the figure the H atom is allowed to move in a Cartesian space, while the positions of the other three atoms are fixed at the transition-state values. Two minima are clearly seen. In the first, at the lower left side of the figure, the H atom lies in a position very close to its position in the HFCO molecule. At the second minimum, close to the product configuration, the H atom has migrated to the vicinity of the F atom. If the C−F distance is gradually increased, the HFCO minimum at the lower left of Figure 1 will gradually fill in and

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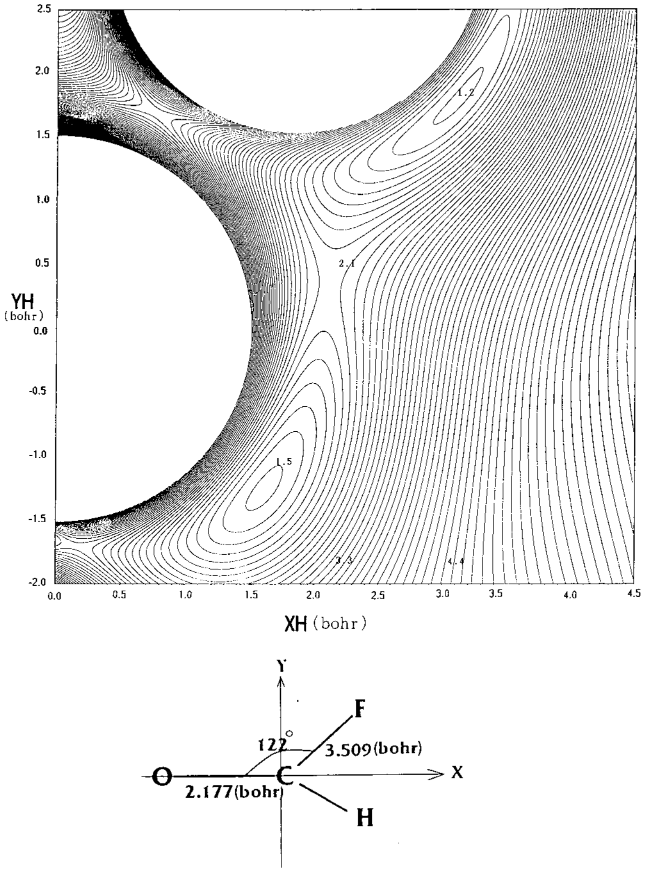

Figure 1. Contour plot of the HFCO → HF + CO potential energy surface, with all atoms constrained to move on a plane. Plotted is the H atom's position, specified by coordinates XH and YH. The positions of the other atoms are fixed. Energy spacing between contours is 0.1 eV. The bond lengths are $D_{CF} = 3.509$ bohr and $D_{CO} = 2.177$ bohr; OCF angle = 122.0°.

the minimum at the upper right corresponding to product HF + CO will gradually deepen.

The surface of Wei and Wyatt consists only of the four-body potential term and does not reduce to the correct asymptotic CO and FH functions after dissociation. Furthermore, the range of the original function is quite restricted, and when running trial trajectories on the fitted surface, we found regions where the potential became unrealistically low, leading to correspondingly high kinetic energies. To remedy these deficiencies, two-body HF and CO functions, as well as a rather elaborate range function, were added to the surface. Hyperbolic tangent switching functions were used to switch between the various regions.

At short internuclear energies, the original surface tended to oscillate. To remedy this switching, functions consisting of hyperbolic tangent functions and Born−Mayer repulsive terms were added. The form of the expanded function, including the repulsive terms, is given by V_1 as shown below.

$$V_1(R_{HF},R_{HC},R_{HO},R_{FC},R_{FO},R_{CO}) = \prod_{i=1}^{6}(1/2)\{1 + \tanh b_i[R(i) - R_i]\}V_0 + \prod_{i=1}^{6}A_i \exp\{-a_i[R(i) - r_i]\} \quad (1)$$

where V_0 is the original function of Wei and Wyatt, $R(i)$ are the interatomic distances, and b_i, R_i and r_i are adjustable parameters. The parameters for the repulsive terms and the switching terms were chosen so as to minimize any influence on the original function. Terms had to be found that not only gave the correct behavior when extending or compressing a single bond but also gave the correct behavior when used together. It should be stressed that these added terms are really quite ad hoc in nature, introduced to allow trajectories to run in a physically meaningful way over the potential surface.

TABLE 1: Bond Distances and Energies of the Minimum Energy Configuration of the HFCO Molecule As Represented by the Original and Expanded Versions of the Potential Energy Surface of Wei and Wyatt[10]

Internuclear Distances (Å)

	HF	HC	HO	FC	FO	CO
original surface	1.999	1.095	2.057	1.375	2.237	1.189
expanded surface	1.999	1.097	2.061	1.358	2.238	1.189

Energies (kcal/mol)

	HFCO minimum	HF and CO at infinite separation[a]
original surface	5.4	−∞
expanded surface	6.3	0.0

[a] r_{HF} and r_{CO} at equilibrium values.

The asymptotic diatomic functions were modeled using extended Rydberg functions,[12]

$$V_{diatomic} = -D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho) \quad (2)$$

where the a_i are constants and $r = R - R_e$, where R is the diatomic bond length and R_e the equilibrium bond length. The constants for the Rydberg functions were taken from ref 13 (HF data, p 66; CO data, p 168). Hyperbolic tangent functions were again used to switch to the two-body potentials. The new expanded potential, V_{exp}, is now given by

$$V_{exp}(R_{HF},R_{HC},R_{HO},R_{FC},R_{FO},R_{CO}) = \{V_1 - V_{TWO}\}\prod_{i=1}^{6}(1/2)\{1 - \tanh d_i[R(i) - R^*_i]\} + V_{TWO} \quad (3)$$

where V_1 is given by eq 1, $V_{TWO} = V_{HF}^{(2)} + V_{CO}^{(2)} + D_e(HF) + D_e(CO)$, the sum of the extended Rydberg functions of eq 2 for HF and CO adjusted to $V = 0$ at equilibrium, and d_i and R^*_i are adjustable parameters. The constants for the diatomic molecules, the Born−Mayer potential parameters, and the parameters for the switching functions are given in ref 11 and are available from the authors upon request.

Table 1 gives the minimum energy configurations and the energies of the reactant and product equilibrium configurations for the original surface of Wei and Wyatt and the expanded surface described by eq 3. The molecular configurations for the two surfaces are essentially the same. The addition of the repulsive terms raised the energy of the HFCO molecule slightly.

Figures 2 and 3 show the potential energy surfaces for the original surface and the expanded surface. The most obvious difference is the bound HF potential in the product valley for the expanded surface. The two surfaces are essentially identical around the HFCO minimum.

We calculated the normal mode vibrations of the HFCO molecule for the two surfaces. The results are shown in Table 2. Also shown are the published results of Wyatt, two ab initio results, and the experimental values. The agreement between the results for the expanded and original surfaces is very good.

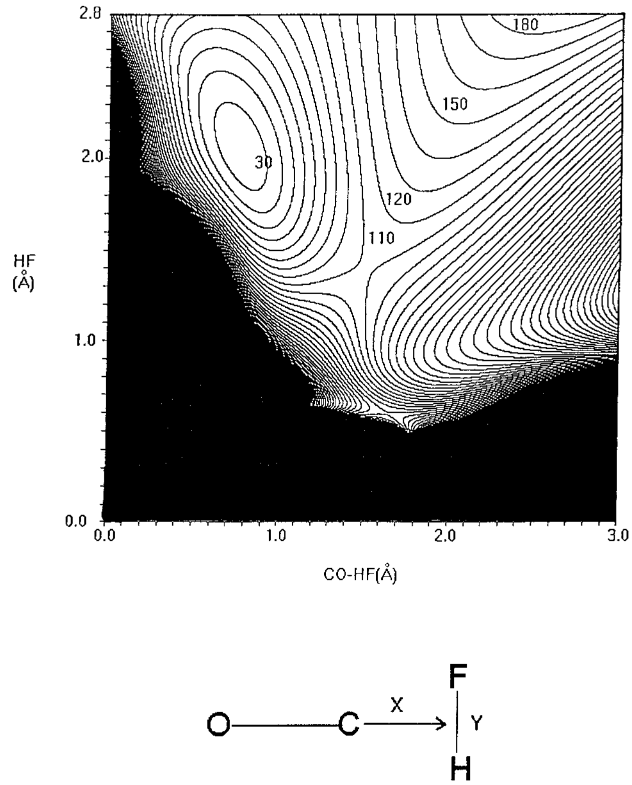

Figure 2. Contour plot of the "original" HFCO potential surface in a "T"configuration with the FH axis perpendicular to the OC axis. The vertical axis of the figure is the FH bond distance and the horizontal axis is the distance from the C atom to the midpoint of the HF bond. Contour intervals are 10 kcal/mol. The CO bond length is 1.1889 Å.

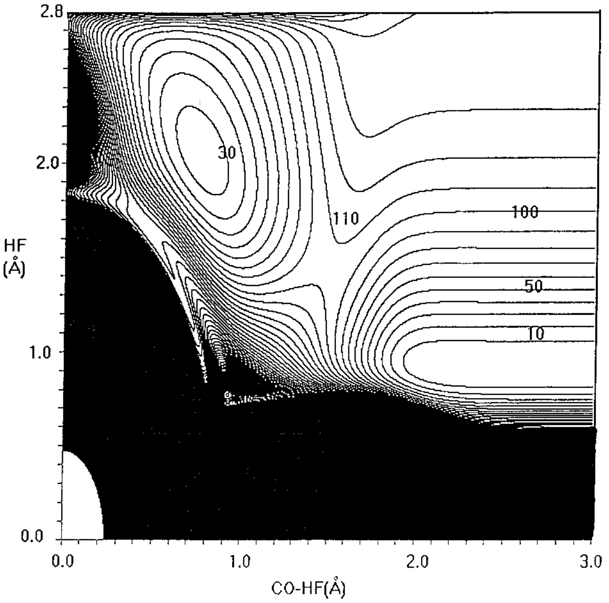

Figure 3. Same as Figure 2 except the plot is for the expanded HFCO potential energy function. The added HF vibrational function is clearly seen on the lower right-hand side of the figure.

TABLE 2: Normal Mode Frequencies Calculated for the HFCO Molecule[a]

surface	CH stretch	CO stretch	CH bend	CF stretch	FCO bend	out-of-plane bend
original[b]	3031	1811	1395	1038	631	978
expanded[c]	3035	1810	1407	1035	640	979
Wyatt[d]	3025	1809	1392	1034	626	977
ab initio I[e]	3160	1845	1377	1043	651	1027
ab initio II[f]	3250	1974	1443	1163	691	1082
experiment[g]	2981	1837	1325	1065	663	1011

[a] Units: cm^{-1}. [b] Calculation using the surface supplied by Prof. Wyatt. [c] Calculation using the expanded surface as described in text. [d] Normal-mode frequencies given in ref 10. [e] Ab initio results, ref 7. [f] Ab initio results, ref 6. [g] ν_1 through ν_5 are from ref 16. ν_6 is from ref 3 (reproduced from ref 10).

TABLE 3: Dissociation Lifetimes for HFCO after Normal Mode Excitation[a]

	CH stretch	CO stretch	CH bend	CF stretch	FCO bend	out-of-plane bend
quantum no.[b]	7	11	14	19	31	20
total energy[c]	73.4	69.6	69.0	68.9	69.4	68.7
reactive trajectories	153	10	82	72	2	5
discarded trajectories[d]	128	1	75	35	32	59
dissociation lifetime (ps)[e]	2.3	26.0	3.4	5.9	84.5	42.2

[a] One thousand trajectories were run for each normal mode. [b] Quantum number of the given normal mode of the reactant HFCO, presuming harmonic normal frequencies. [c] Total energy including excited normal mode and the zero point energy of all all other modes. Units: kcal/mol. [d] Number of trajectories, of the total 1000 run, that wandered into physically unmeaningful regions and were discarded. [e] The dissociation lifetime is defined by eq 4. Units: ps.

This is not unexpected. The added repulsive terms and asymptotic two-body terms are a good distance away from the minimum where the normal modes are calculated.

Trajectory Calculations. The classical trajectory method for molecules of four or more atoms is now well established.[14] Classical trajectories were run using the program VENUS, supplied by the authors.[15] The program calculates classical trajectories for many-atom systems using a space-fixed Cartesian coordinate system. A single step size of 0.005×10^{-14} s was used for the numerical integration of all trajectories. This gave energy conservation to better than 1.0×10^{-7} kcal/mol. For all trajectories, set amounts of energy were placed in each of the normal modes and then distributed randomly within that mode. In all cases, the rotational energy was set to zero. Dissociation was defined to occur when the HC distance exceeded 3.5 Å. Because of computer time limitations, trajectories were discontinued after 0.4 ps.

With the addition of the repulsive terms and the asymptotic diatomic potentials, the calculation of trajectories became quite time-consuming. We calculated 6 batches of 1000 trajectories. For each batch, five of the mode quantum numbers were set to zero and the remaining mode was excited such that the total energy of the system was between 68.7 and 73.4 kcal/mol. The excitation energies are given in Table 3. Despite the terms included in the expanded potential function, about 5.5% of the trajectories wandered into physically unrealistic regions and had to be discarded.

III. Results and Discussion

For each batch of trajectories, the dissociation times of the trajectories were least-squares fit to an exponential decay curve,

$$N = N_0 \exp(-t/\tau) \tag{4}$$

where N is the number of unreacted trajectories at time t and N_0 is the total number of trajectories in the batch, in this case 1000. τ is then the decay constant, the time required for the number of unreacted molecules to drop to $(1/e)$ of the original number.

TABLE 4: Product Energy Distributions after Normal Mode Excitation

	CH stretch	CO stretch	CH bend	CF stretch	FCO bend	out-of-plane bend
total energy of excitation[a]	73.4	69.6	69.0	68.9	69.4	68.7
	Average Product Energy Disposal (% of total product energy given in parentheses)[b]					
translation	45.0	46.0	45.9	44.1	33.3	39.3
	(56.0)	(60.8)	(61.0)	(59.2)	(46.7)	(53.0)
	Hydrogen Fluoride, HF					
vibration	18.1	14.8	14.6	15.8	8.4	20.1
	(22.5)	(19.6)	(19.4)	(21.2)	(11.5)	(27.1)
rotation	2.7	3.9	2.5	3.3	2.1	5.9
	(3.4)	(5.1)	(3.4)	(4.4)	(2.8)	(8.0)
	Carbon Monoxide, CO					
vibration	6.8	7.3	5.4	6.5	7.1	6.4
	(8.5)	(9.7)	(7.2)	(8.7)	(9.7)	(8.7)
rotation	7.8	3.6	6.8	4.8	22.1	2.4
	(9.7)	(4.8)	(9.0)	(6.4)	(30.3)	(3.3)

[a] The energy to be disposed of is the total energy of excitation plus the heat of reaction (6.3 kcal/mol). The actual sum of the product energies is slightly higher, presumably due to terminating trajectories at less than infinite separation. [b] Average product energies, with initial mode excitation as indicated. Units: kcal/mol.

Several caveats are in order with respect to the fitting to the exponential decay curve. For the excitation of the CO stretch and especially the out-of-plane and the OCF bending modes, the number of reactive trajectories was so small that the fit is simply a convenient way to obtain a rough, qualitative estimate of the decay time. For the CH stretch, the CH bend, and the CF stretch, there were a sufficient number of trajectories to give a good fit. With the exception of a possible delay on the order of 0.1 ps before the onset of decay (found by fitting the logarithm of eq 4 to a straight line without forcing the curve to pass through zero), there is no evidence of short-term transients. Finally, because unreactive trajectories were discontinued after only 0.4 ps, the data only effectively sample the upper part of the decay curve, and thus nonexponential long-term effects cannot be ruled out.

Table 3 gives the number of reactive trajectories, the number of discarded trajectories, and the decay times for each of the six excited modes. Because of the low number of reactive trajectories, especially the CO stretch and the two bending modes, it is very difficult to assign an uncertainty to the decay times. Perhaps the results are best considered as qualitative estimates.

But despite these problems, the basic trend is clear. With the total energies for each of the mode excitations approximately the same, the excitation of different reaction modes clearly leads to enhanced reaction rates. The level of enhancement is CH stretch > CH bend > CF stretch ≫ CO stretch > out-of-plane bend > OCF bend. There is a clear qualitative difference, both in the number of reactive trajectories and the decay time, for exciting the CH stretch, CH bend, and CF stretch as compared to exciting the other three modes. Or, in other words, the CO stretch, out-of-plane bend, and OCF bend remain rather aloof from the reaction.

The aloofness of the out-of-plane bend was seen clearly in the experiments of Moore and colleagues.[3,4] In their 1992 paper, Moore's group listed dissociation rates for vibrationally excited HFCO. If the zero-point energy is subtracted out of our out-of-plane result, the total υ_6 energy would be 19 586 cm^{-1}, with zero rotational energy. This more or less corresponds with Moore's value of 19 761 cm^{-1} with a decay constant of 30.2 ps. This is in good qualitative agreement with our value of 42.2 ps.

Table 4 gives the number of reactive trajectories and the distribution of energy in the reaction products after excitation of the six modes. For essentially all reactive products, the product translational energy is above 50% of the available energy. This is in good agreement with Moore's result, estimated from the Doppler widths of CO dissociation fragments.[5] Our results indicated that product vibration tends to concentrate in the HF rather than the CO product. The percent of available product energy in CO vibration was always under 10%, also in agreement with Moore's results.[5] In general, the product vibration distributions (not shown) are very broad and featureless. Moore's group found rotationally hot CO products, peaking at $J = 45$. Our results indicate a much cooler CO rotation, with the average rotational energy corresponding to $J = 20$ for the dissociation product of the out-of-plane bend excitation. Moore's group found[5] that although "the CO rotational distributions are quite different for different levels, the ratios of the CO rotational energy to the total available energy are almost the same, ≈20%." Thus, while a further study of the effect of rotation on product energy disposal would be an interesting topic for future research, our presumption of zero reactant rotational energy does not seem to explain the discrepancy.

With one exception, we see the same qualitative trends in the product energy distributions as reported by Yamamoto and Kato.[17] They find the largest percentage of product energy (43.9%) to be in relative translation, consistent with our finding. They also find product HF to be vibrationally excited and product CO to be vibrationally cool, in agreement with our results. The one exception is again the CO rotational distribution. In agreement with experiment,[5] they find a rotationally hot distribution, peaking at $J = 45$. As noted above, our results indicate a much cooler CO rotational distribution. The transition-state bond lengths of the Yamamoto–Kato surface[17] are very similar to those of the Wei–Wyatt surface,[10] but the bond angles differ considerably. The FCH angle is much more compressed in the Yamamoto–Kato surface, only 48.8°, while 68.0° in the Wei–Wyatt surface. (The more compressed FCH transition-state FCH bond angle is also a feature of the surface of Kamiya and Morokuma.[8]) It is possible to speculate that this difference in the surfaces accounts for the cooler CO rotation and slightly warmer CO vibration found in our calculations.

It is not possible to go beyond a qualitative comparison of our product energy distributions with those of Yamamoto and Kato.[17] While the reaction energies are of the same order of magnitude, the methods of initiating the trajectories were quite

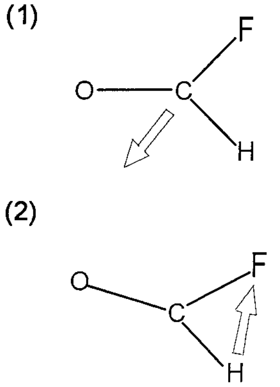

Figure 4. Postulated two-step sequence of reaction. In step (1) the carbon atom moves away from the fluorine, followed by (2) the rapid movement of the H atom toward the fluorine.

different. In our work, we began with the equilibrium configuration of HFCO, placing the zero-point energies in each of the normal modes and then highly exciting a single normal mode. The trajectories of Yamamoto and Kato were, on the other hand, all initiated near the transition state, adopting a procedure used earlier by Chang and co-workers.[18] Zero-point energies were placed with random phases in each of the five bound transition-state normal modes, with the remaining energy placed in the reaction coordinate. Because of this, they were able to calculate many more trajectories, giving much more detailed product distributions. Our purpose was to consider the results of exciting single normal modes; Yamamoto and Kato considered a more averaged state of affairs.

Inspection of the potential energy surface (see Figure 1) and of sample trajectories[11] indicates a general mechanism for the reaction. (a) The carbon moves away from the fluorine, followed by (b) a rapid move of the hydrogen toward the fluorine. This mechanism is illustrated in Figure 4. This model is consistent with our results that excitation of the CH bend and the CF stretch tends to promote the reaction. It is less clear why excitation of the CH stretch is so effective.

At the transition state, the HC and CO bond lengths are within a few percent of their equilibrium values. However the FC bond length is extended from 1.36 to 1.80 Å and the FCH angle is reduced from 109.2° to 68°. In the product channel, the CO bond is only very slightly shorter than the value at the transition state, while for the HF the transition-state value of 1.74 Å has been shortened to 0.92 Å in the product diatomic. This accounts for the relatively high HF product vibration and the relatively low CO vibration. Also, the presence of an early barrier on an exothermic surface is consistent with the high degree of product translation.

Kamiya and Morokuma[8] carried out a detailed reaction path analysis for their potential energy surface, and a comparison with our results is instructive. Their calculated configuration for equilibrium HFCO is within 1% of the equilibrium configuration calculated by Wei and Wyatt.[10] The bond lengths for the two surfaces at the transition state are identical. The major difference is the FHC angle of the transition state which is reduced to only 48.8° in the Kamiya−Morokuma surface, as compared to 68° in the Wei−Wyatt surface. This would seem to indicate the two surfaces are very similar, with a somewhat later transition state in the Kamiya−Morokuma surface. In Figure 5 of their paper, Kamiya and Morokuma show the HFCO bond lengths and bond angles as a function of the reaction coordinate, clearly indicating the same mechanism as we suggest in the preceding paragraph. In two very instructive figures, Kamiya and Morokuma present the projection of the curvature of the intrinsic reaction coordinate, *k*, onto the normal modes of the molecule as a function of the reaction coordinate (Figure 7) and the coupling between normal modes (Coriolis coupling), also as a function of the reaction coordinate (Figure 8). In line with the suggested mechanism, they find that before the transition state the CF stretch and, somewhat later, the CH bend couple strongly to the reaction coordinate. From this qualitative picture, they suggest that “the CF stretching and CH bending mode of HFCO is considered to promote the molecular dissociation reaction. The CH stretching and the CO stretching are expected to be of minor importance at an early stage of the reaction”.

In many ways, our results are similar to conclusions of Kamiya and Morokuma. We find the CF stretch to be important in promoting reaction, though not as significant as the CH stretch and CH bend. We also find that the CO stretch and the other bending modes are much less effective in promoting reaction.

However, our results differ in one important respect: our finding that excitation of the CH stretch strongly enhances the reaction. We have carried out some initial studies of the intramolecular vibrational energy redistribution (IVR) in the reacting HFCO molecule, plotting the approximate mode energy as a function of time for several sample trajectories (see ref 11). Indications are that there exists a high degree of IVR between the CH stretch and CH bend, allowing both excitations to promote dissociation. Kamiya and Morokuma only see this enhanced coupling at a later stage of the reaction. Our presumption is that our trajectories, run at approximately 22 kcal/mol above the barrier, access configurations more conducive to the vibrational coupling than if they remained strictly on the “reaction coordinate”. The power spectra reported by Yamamoto and Kato[17] are consistent with these results. Not unexpectedly, they find that the peak corresponding to the out-of-plane bend remains quite sharp even at energies 15 kcal/mol above the dissociation energy. On the other hand, the peak at 3000 cm^{-1}, which is presumed to correspond to the CH stretch, is very broad and “grassy”, indicating a high degree of IVR.

In our plots of normal mode energies as functions of time, we also see a reasonably large interchange between the CO stretch and the CF stretch. It is possible that the CO stretch provides a sink for the CF excitation energy, decreasing its efficiency in promoting dissociation. Finally the aloofness of the OCF bending and, especially, the out-of-plane bending is clearly seen.

In our calculations, we limited ourselves to the excitations of a single mode and did not consider other combinations. These initial IVR results would seem to indicate combinations of the CH bend and CH stretch would promote reaction as well as the pure overtones. This, however, remains to be proven.

The preliminary results presented here suggest several avenues of further research. There is an obvious need for a more physically realistic range function that would permit trajectories to move freely over all energetically allowed regions of the potential energy surface. Larger numbers of trajectories over such a surface would allow truly quantitative estimates of decay times and the product energy distributions as well as give a better understanding of IVR within the molecule. There is also a need to consider more carefully the potential surface, especially near the transition state. Such developments would provide interesting challenges to experimentalists.

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