Comparison of reagent translation and vibration on the dynamics of the endothermic reaction Sr+HF

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The endothermic reaction $Sr + HF(v = 0) \rightarrow SrF + H$ has been studied as a function of collision energy (4–14 kcal/mole) using a crossed beam geometry in which a seeded HF beam intersects a thermal Sr beam. At the same total energy this reaction is compared to the $Sr + HF(v = 1, J = 1)$ reaction carried out under beam-gas conditions with a pulsed HF laser as the excitation source. In both cases the SrF products are detected by laser induced fluorescence. Using the $Ba + HF \rightarrow BaF + H$ reaction as an internal reference, the cross section of the $Sr + HF(v = 1)$ reaction is found to be 1–10 times greater than for the $Sr + HF(v = 0)$ reaction when the same total energy is supplied as reagent translation. Product internal energy distribution and total relative cross sections as a function of collision energy are also measured. Phase space calculations are able to reproduce most of these results. This agreement and other arguments suggest that the $Sr + HF$ reaction often proceeds via multiple encounters which scramble the reagent energy modes during the course of a reactive collision.

I. INTRODUCTION

Ever since the work of Arrhenius[1] it has been realized that the exponential increase of thermal bimolecular rate constants with temperature implies the existence of an energy barrier to reaction. Nevertheless, very little is known about what form of reagent excitation (translation, rotation, vibration) is most effective in overcoming the barrier encountered in going from reactants to products. This information is unavailable from thermal kinetic studies because all reagent modes are in equilibrium. Thus one must devise nonequilibrium experiments in which the reagents modes can be energized independently. Prominent among such experiments is the use of lasers to prepare the reagents in known internal states, and the use of molecular beam techniques to define their collision energy.

For endothermic reactions it has been postulated that reagent vibration is much more effective than reagent translation in overcoming the barrier to reaction.[2–5] In general, the barrier to an endothermic reaction is thought to be "late," i.e., to occur as the products separate.[4] Trajectory calculations on direct reactions have shown that reagent vibration is much more effective than translation in crossing a late barrier.[3,6] The reverse is thought to apply to exothermic reactions.[3,7]

Numerous examples are known where vibration is indeed effective in promoting substantially endothermic reactions.[8] However, only the study of Brooks and co-workers[9–11] on the approximately thermoneutral reaction[12]

$$K + HCl \rightarrow KCl + H , \quad \Delta H_0^\circ = 0 \pm 2 \text{ kcal/mole}$$

has compared directly the relative efficacy of vibration and translation. They found that when HCl is excited to its first vibrational level (8.25 kcal/mole) the reaction cross section is roughly ten times greater than when the same total energy is supplied as collision energy. By applying the principle of microscopic reversibility to

exothermic reaction data, Polanyi, Bernstein, and co-workers[13] have found that vibration may be two to three orders of magnitude more effective than translation in promoting a number of substantially endothermic reactions at a constant total energy only slightly above the barrier.

We report here a comparison of the effectiveness of vibrational and translational excitation on the endothermic[14] reaction

$$Sr + HF \rightarrow SrF + H , \quad \Delta H_0^\circ = 6.4 \pm 1.6 \text{ kcal/mole}.$$
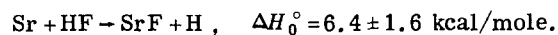
Previously, it has been shown that excitation of the hydrogen fluoride to its first vibrational level increases the rate of reaction with Sr by at least four orders of magnitude over the thermal rate.[14] Since this reaction is more endothermic than K + HCl, one might expect that the energy requirements for Sr + HF would be more selective. Reagent translation is controlled as in the preceding paper[15] by accelerating HF in a seeded nozzle expansion. Reagent vibration is provided by a pulsed HF laser.[14,16] By operating with a mixed beam of Ba and Sr and using the Ba + HF reaction[15] as an internal reference, we find that vibration is only one to ten times more effective than translation in promoting the Sr + HF reaction. We also report SrF internal energy distributions and we compare our results to phase space theory calculations. Factors are discussed which may contribute to the efficacy of reagent translation versus reagent vibration in promoting this endothermic reaction.

II. EXPERIMENTAL

The effect of reagent translation on the Sr + HF reaction is studied using the crossed molecular beam apparatus described in the preceding paper.[15] The HF is seeded in H_2 or He carrier gas and the relative collision energy is varied between 4 to 14 kcal/mole. The Sr beam effuses from a stainless steel oven at 1050–1100 °K. Unlike the Ba effusive beam, the Sr beam shows erratic fluctuations in intensity, causing a greater scatter in the results. The distribution of collision energies is calculated in the same manner as described in Appendix A of Ref. 15. The strontium metal (Alfa Ven-
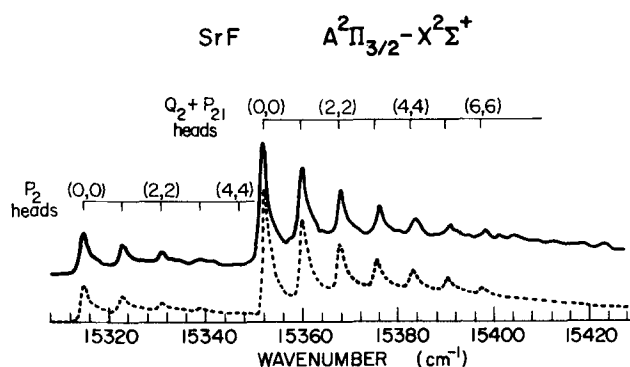
FIG. 1. Excitation spectrum of the SrF product for the reaction Sr + HF with an average collision energy of $\langle E_{trans} \rangle = 12.9$ kcal/mole. The dashed curve is a computer simulation.

tron, 99% purity) is used without further purification. The HF gas (Matheson, 99.9%) was purified before use. The gas cylinder is placed in a dry-ice–acetone slush and pumped on for a few minutes to remove SiF_4 and other volatile contaminants.

The SrF product is detected by laser induced fluorescence. The SrF $A\,^2\Pi_{3/2}-X^2\Sigma^+$ excitation spectrum (649–654 nm) is recorded as a function of laser wavelength using a pulsed dye laser (Molectron DL14P or DL300). The dye is a mixture of rhodamine 6G (2.5×10^{-3} M) and cresyl violet perchlorate (3.3×10^{-3} M) dissolved in ethanol. The typical bandwidth is 0.05 nm (for the DL14P).

The effect of reagent vibration on the Sr + HF reaction is studied using a beam–gas configuration in which a beam of Sr atoms traverses hydrogen fluoride gas at 10^{-4} Torr. Some of the HF molecules are prepared in the first vibrational level ($v = 1$), using a pulsed (5–7 Hz, ~1 μsec pulse width) HF laser. The HF laser, grating tuned to the $P_1(2)$ line, has been described previously.[14,16] The pulse energy is 165 μJ in the interaction region. The HF laser and the dye laser beams are coincident but propagate in opposite directions (see Fig. 1 of Ref. 14). Maximum fluorescence is observed when the dye laser is fired 10 μsec after the HF laser.

A comparison is made of the Sr + HF reaction cross section at the same total energy when this energy is present either as reagent translation or as reagent vibration. For this purpose the strontium beam is replaced by a mixed beam of barium and strontium atoms so that the Ba + HF reaction may serve as an internal reference. Barium and strontium have great mutual solubility and at high temperatures a continuous series of solid solutions exist.[17] Equimolar amounts of barium and strontium are loaded into the same oven, and the relative intensities of the BaF and SrF fluorescence signals are recorded. To promote mixing, the less dense metal (Sr) is placed at the bottom of the crucible and the oven is heated gradually for 1–2 h. Since strontium has a higher vapor pressure than barium, the mole function of Ba in the beam increases with time. Care is taken to compare results only at similar elapsed times from the beginning of the experiment.

III. RESULTS

A. Product internal state distribution

Figure 1 presents an excitation spectrum for the reaction Sr + HF → SrF + H at an average collision energy of 12.9 kcal/mole. In the SrF $A\,^2\Pi_{3/2}-X^2\Sigma^+$ band system,[18] heads are formed in the Q_2 and P_{21} branches at almost the same frequency and value of J,

$$J_{\text{head}}^{Q_2+P_{21}} = (2B'' - B_{\text{eff}}^{(2)})/2(B_{\text{eff}}^{(2)} - B'') , \tag{1}$$

and in the P_2 branch at

$$J_{\text{head}}^{P_2} = (B_{\text{eff}}^{(2)} + 2B'')/2(B_{\text{eff}}^{(2)} - B'') . \tag{2}$$

For the (0, 0) band of the $A\,^2\Pi_{3/2}-X^2\Sigma^+$ transition $J_{\text{head}}^{Q_2+P_{21}} \approx 36$ and $J_{\text{head}}^{P_2} \approx 111$. Thus, the appearance of heads in the P_2 branch implies that high rotational levels are appreciably populated. As is characteristic of all the low-lying electronic states of the alkaline earth monohalides, the Franck–Condon factors of the $\Delta v = 0$ sequence are nearly unity for the lowest vibrational levels.[19]

Hence only a cursory inspection of Fig. 1 suffices to determine the qualitative disposal of energy among the internal states of the SrF product. We conclude from the presence of the P_2 heads that substantial rotational excitation of the product occurs. In addition the SrF vibrational populations peak at $v = 0$ and decrease monotonically with increasing v. This degree of rotational excitation contrasts with the thermal reaction Sr + HF($v = 1$), where HF vibration is used to overcome the endothermic barrier and no P_2 heads are observed.[14]

Quantitative estimates of the product internal state distributions are made by means of a computer simulation.[15] Table I lists the spectroscopic constants used. The vibrational populations and rotational temperatures of each vibrational level are iteratively adjusted until a best fit is obtained (see the dashed curve in Fig. 1). Rotational temperatures are used rather than rotational

TABLE I. Spectroscopic constants (cm^{-1}) of SrF used for computer simulation.

Constants	$X^2\Sigma^+$	$A\,^2\Pi_{3/2}$
T_e [a]	0.0	1535.20
ω_e [a]	498.0	505.1
$\omega_e x_e$ [a]	2.15	2.18
$\omega_e y_e$ [a]	0.0039	0.0
B_e [b]	0.250533	0.25392
α_e [b]	0.001546	0.00156

[a]M. M. Norikov and L. V. Gurvich, Opt. Spectra 22, 295 (1967).

[b]The X state value is from P. J. Domaille, T. C. Steimle, and D. O. Harris, J. Mol. Spectrosc. 68, 146 (1977); the A state value is derived from the constants of T. C. Steimle, P. J. Domaille, and D. O. Harris, ibid. 73, 441 (1978). For the X state the value of B_e is B_e, but for the $A\,^2\Pi_{3/2}$ state it is $(B_e^{(2)})_{\text{eff}} = B_e(1 + B_e/A)$. The program uses the approximation $(B_v^{(2)})_{\text{eff}} = (B_e^{(2)})_{\text{eff}} - \alpha_e (v + \frac{1}{2})$.
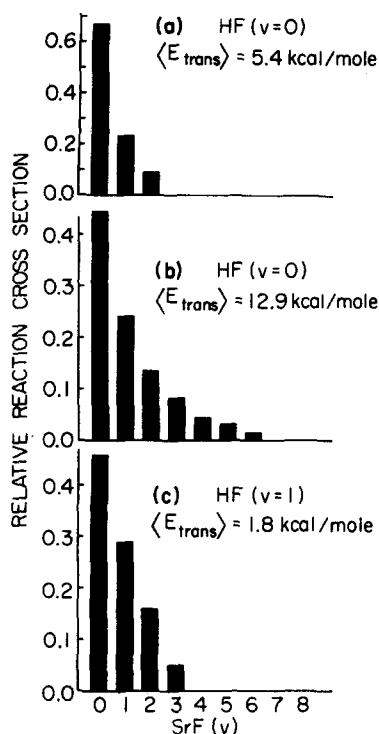
FIG. 2. Relative cross sections $\sigma(v)$ for producing $SrF(v)$ under various reagent conditions.

surprisal parameters, which require a knowledge of the total energy. The endothermicity of the Sr + HF reaction is not known to better than ± 1.6 kcal/mole, and the spread in the collision energy causes a spread in the total energy which is *comparable* to the total energy available to the products. Consequently, the product translational energy cannot be extracted reliably from a knowledge of the product internal energy and triangle plots, like those obtained for the Ba + HF reaction,[15] would have doubtful significance.

The results of the computer simulations are summarized in Figs. 2 and 3. Figures 2(b) and 2(c) are for
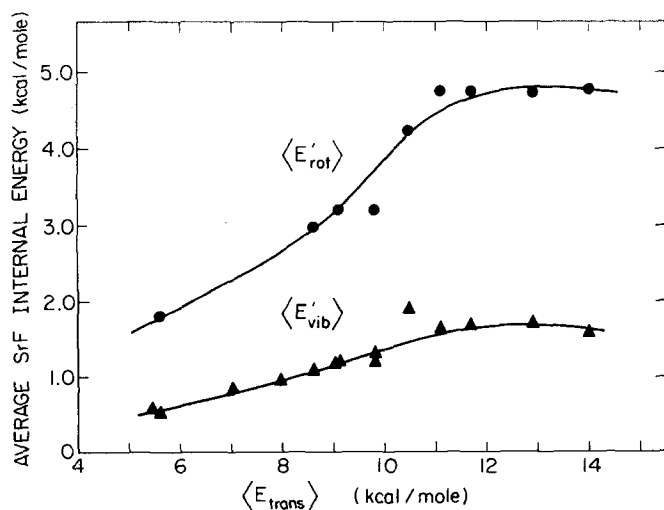

FIG. 3. Energy disposal as a function of average collision energy. The solid curves serve only to aid in visualizing the data.
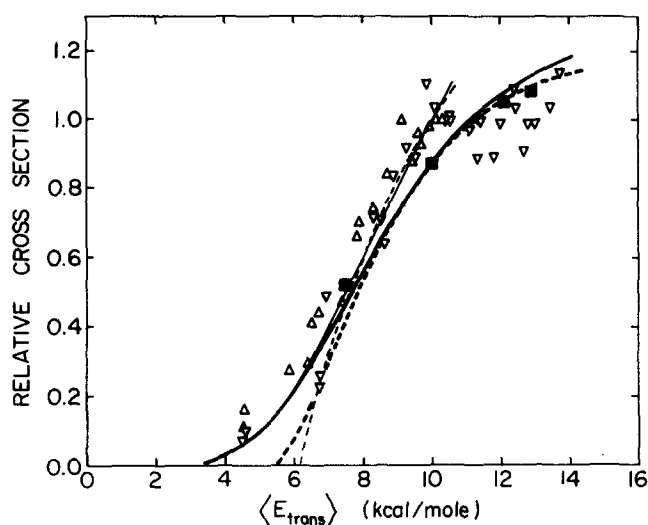

FIG. 4. Relative reaction cross section as a function of average collision energy. The data points with H_2 or He as a seeding gas are denoted by ∇ or Δ, respectively. The solid squares are calculated using phase space theory. The light solid curve is the best fit to the experimental data below 11 kcal/mole using the line of centers model. It is obtained by convolution of the light dashed curve $(E_0 = 6.2$ kcal/mole) with the collision energy distribution at each energy. The heavy solid curve is the best fit to all of the experimental data using Eq. (4). It is obtained by convolution of the heavy dashed curve with the spread in collision energies at each average collision energy.

nearly identical total energies. Comparison shows that the SrF vibrational distributions are quite similar irrespective of whether the reagent energy is in translation [Fig. 2(b)] or in vibration [Fig. 2(c)]. Differences between Figs. 2(b) and 2(c) may reflect both the different spreads in collision energies and the different methods of analysis [Fig. 2(c) is based on peak height analysis]. The importance of the first factor is evident from an examination of Fig. 2(a) where the average collision energy $\langle E_{trans} \rangle = 5.4$ kcal/mole is less than the endothermicity of the reaction.

Figure 3 illustrates the average rotational and vibrational energy appearing in the product for different average collision energies. Note that $\langle E'_{rot} \rangle$ exceeds $\langle E'_{vib} \rangle$ by more than a factor of 2 for all collision energies. Both $\langle E'_{rot} \rangle$ and $\langle E'_{vib} \rangle$ initially increase with collision energy but then level off at collision energies in excess of 10 to 11 kcal/mole. This implies that in the high collision energy regime, increments in E_{trans} are transformed into product translational energy E'_{trans}, which is in agreement with the generalization[20] $\langle \Delta E_{trans} \rangle \rightarrow \langle \Delta E'_{trans} \rangle + \langle \Delta E'_{rot} \rangle$.

B. Dependence of reaction cross section on collisional energy

The relative cross sections for the Sr + HF $(v = 0)$ reaction are determined by measuring the integrated fluorescence intensity, as described in Ref. 15. The cross section increases with collision energy to about 10 kcal/mole and then levels off (Fig. 4). The threshold data $(E_{trans} < 11$ kcal/mole) may be fit to the line of centers model[21]

$$\sigma(E_{\text{trans}}) \propto (E_{\text{trans}} - E_0)/E_{\text{trans}} , \qquad (3)$$

by convoluting Eq. (3) with the distribution of collision energies.[22] As shown in Fig. 4, this model yields a value for the threshold energy of

$$E_0 = 6.2 \text{ kcal/mole},$$

which agrees well with the estimated reaction endothermicity (6.4 ± 1.6 kcal/mole). This result suggests that the reverse reaction H + SrF → Sr + HF has little or no activation energy. The role of HF rotation (~1 kcal/mole) in these experiments is unclear.

Both the line of centers model and the more general form $(E_{\text{trans}} - E_0)^s / E_{\text{trans}}$ fail to describe the variation of the reaction cross section over the entire range of collision energies. However, a better fit to the present data is obtained (see Fig. 4) using

$$\sigma(E_{\text{trans}}) \propto (E'_{\text{tot}})^s \exp[-\xi (E'_{\text{tot}})^{1/2}] / E_{\text{trans}}^{1/2} , \qquad (4)$$

where $E'_{\text{tot}} = E_{\text{trans}} + E_{\text{rot}} - \Delta H_0^\circ$ is the total energy available to the products. This model was first introduced by Pruett, Grabiner, and Brooks[10] in their study of the K + HCl ($v = 0$) reaction. The factor $(E'_{\text{tot}})^s$ represents the density of product states, $\exp[-\xi (E'_{\text{tot}})^{1/2}]$ is the average state-to-state transition probability, and $E_{\text{trans}}^{1/2}$ is proportional to the relative velocity of the reagents. The free parameters s and ξ are adjusted to give a best least squares fit. For our data we find $s = 2.1$ and $\xi = 1.1$ (kcal/mole)$^{1/2}$, which are similar to values obtained for K + HCl [$s = 2.2$ and $\xi = 1.36$ (kcal/mole)$^{1/2}$]. Whereas the cross section predicted by the line of centers model always increases with collision energy, the cross section based on Eq. (4) exhibits a maximum. In the present case the maximum occurs at 15.5 kcal/mole, which is close to the highest collision energy studied.

C. Comparison of vibration to translation

At the same total energy we determine the cross section ratio for Sr + HF($v = 0$) to Sr + HF($v = 1$). The Sr + HF($v = 0$) reaction is carried out at high collision energy in a crossed molecular beam configuration whereas the Sr + HF($v = 1$) reaction is studied at low collision energy in a beam–gas configuration. These differences prevented a direct comparison.[23] Instead we rely upon an indirect procedure in which each reaction is referenced to the Ba + HF ($v = 0$) reaction under the same conditions by loading the oven with equimolar amounts of Sr and Ba.

In the beam–gas configuration, one measures the intensity of SrF from reaction with HF($v = 1$) at the collision energy $E_{\text{trans}} = 1.8$ kcal/mole, denoted by I[Sr + HF($v = 1$), 1.8]. Under the same conditions one also measures the intensity of BaF from reaction with HF($v = 0$), denoted by I[Ba + HF($v = 0$), 1.6]. The difference in mass between Sr and Ba causes the respective collision energies to differ slightly. Similar measurements of I[Sr + HF($v = 0$), 8.7] and I[Ba + HF($v = 0$), 8.4] are made in the beam–beam configuration. The cross section ratio at the total energy $E_{\text{trans}} + E_{\text{vib}} = 13.1$ kcal/mole is found by evaluating the product of four factors

$$\frac{\sigma[\text{Sr} + \text{HF}(v=1), 1.8]}{\sigma[\text{Sr} + \text{HF}(v=0), 13.1]} = \left(\frac{\sigma[\text{Sr} + \text{HF}(v=1), 1.8]}{\sigma[\text{Ba} + \text{HF}(v=0), 1.6]} \right)$$
$$\times \left(\frac{\sigma[\text{Ba} + \text{HF}(v=0), 1.6]}{\sigma[\text{Ba} + \text{HF}(v=0), 8.4]} \right) \times \left(\frac{\sigma[\text{Ba} + \text{HF}(v=0), 8.4]}{\sigma[\text{Sr} + \text{HF}(v=0), 8.7]} \right)$$
$$\times \left(\frac{\sigma[\text{Sr} + \text{HF}(v=0), 8.7]}{\sigma[\text{Sr} + \text{HF}(v=0), 13.1]} \right) . \qquad (5)$$

The product of the first and third factors may be related to the product of the intensity ratios by

$$\left\{ \frac{\sigma[\text{Sr} + \text{HF}(v=1), 1.8]}{\sigma[\text{Ba} + \text{HF}(v=0), 1.6]} \right\} \times \left\{ \frac{\sigma[\text{Ba} + \text{HF}(v=0), 8.4]}{\sigma[\text{Sr} + \text{HF}(v=0), 8.7]} \right\}$$
$$= \frac{1}{\beta} \left\{ \frac{I[\text{Sr} + \text{HF}(v=1), 1.8]}{I[\text{Ba} + \text{HF}(v=0), 1.6]} \right\} \times \left\{ \frac{I[\text{Ba} + \text{HF}(v=0), 8.4]}{I[\text{Sr} + \text{HF}(v=0), 8.7]} \right\}, \qquad (6)$$

where β is the ratio of the observed SrF intensity from Sr + HF($v = 1$) to that from the same reaction under steady-state conditions in which the number density of HF($v = 1$) is the same as the total HF number density. The equality in Eq. (6) is based on the almost perfect cancellation of a number of factors, such as the different sensitivities of the optical detection system to BaF and SrF fluorescence, the different excitation source conditions to probe BaF and SrF, and the different number densities and velocities of the metal atoms. The second and fourth factors in Eq. (5) are determined from the collision energy dependence of the respective reactions. The product of the intensity ratios in Eq. (6) is experimentally determined to be 0.027 ± 0.006, based on three independent runs. The error limits embrace all measurements.

The value of β is much less than unity since only a small fraction of all HF molecules in a 300 °K gas are in resonance with the $P_1(2)$ line of the HF laser. Let α denote the fraction of HF molecules excited by the laser into $v = 1$; it is determined directly by using the apparatus as a low pressure absorption cell. The apparatus is filled with HF to a pressure of 10^{-2} Torr as measured by a capacitance manometer. For a laser power of 165 μJ and a beam diameter of 8 mm, we find $\alpha = 0.009 ± 0.002$. Actually, α represents an upper bound on the value of β. It takes a finite time for the excited HF molecules to react with Sr and consequently the firing of the probe dye laser is delayed from the firing of the HF pump laser. However, during this time some SrF products leave the detection zone, causing β to be less than α. From the time dependence of the SrF signal we are able to estimate that $\beta/\alpha = (0.22 ± 0.06)$ (see Appendix) at the peak of the SrF fluorescence signal, which occurs 10 μsec after the firing of the HF pump laser. Thus we take β as 0.0020 ± 0.0007. This value of β is similar to that estimated by Pruett and Zare[24] for their experimental study of Ba + HF($v = 1$).

The second factor in Eq. (5) is estimated to be 0.33 ± 0.19, and its error represents the largest source of uncertainty in the present determination of the cross section ratio. This factor is evaluated using the line of centers cross section for the Ba + HF($v = 0$) reaction (see Fig. 8 of Ref. 15) taking into account the thermal distribution of velocities that exist in the beam–gas con-

figuration. Its large error reflects the uncertainty in the value of the threshold energy for the Ba +HF(v =0) reaction. The fourth factor in Eq. (5), which may be read from Fig. 4, is 0.75 ± 0.1.

When all of the factors are combined in Eq. (5) we find that the cross section ratio σ[Sr +HF(v =1), 1.8]/ σ[Sr +HF(v =0), 13.1] has the value 3 but according to propagation of error theory may range from 1 to 5. Consideration of possible systematic errors suggests that this ratio is not likely to be much less than unity but might be as much as ten.[25] In any case, the cross section ratio is a small number, implying that vibration is somewhat more effective than translation in promoting the endothermic Sr +HF reaction, but not dramatically so.

IV. DISCUSSION

It may at first appear surprising in the Sr +HF reaction that vibration is only one to ten times more effective than translation in promoting this substantially endothermic reaction. Other studies[4–6,13] on endothermic reactions might have suggested that vibration would be 100– 1000 times more effective, although the reactions are more endothermic than Sr +HF and the reagent energies are only slightly above threshold. We suggest that snarled trajectories in which the reagents make multiple encounters before the products separate may account for this behavior. Several factors may combine to favor such dynamics.

The Sr +HF reaction is an example of the mass combination

$$H + H'L \rightarrow HH' + L ,$$
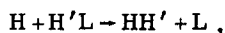
where H, H' are heavy atoms and L is a light atom. Classical trajectory studies have shown that this mass combination minimizes the requirement of vibrational energy in surmounting the endothermic reaction barrier.[6,26] The barrier to reaction is expected to be located well along the product separation coordinate. However, the potential energy surface, when scaled and skewed for this mass combination,[27] has its barrier at the head of a wide exit valley. The entrance valley is very narrow compared to the exit valley. As the reagents approach with high collision energy, a trajectory may fail to cross the barrier on its first encounter. It may also fail to find its way back into the narrow entrance valley, causing a secondary encounter, etc. Because the H atom is so light and its motion so rapid, it may be expected to rebound from and to oscillate about its heavier partners during the approach of Sr and F. Indeed, three-dimensional trajectory calculations on the related system Ba +HCl show just this behavior.[28] Because of the divalent character of Sr, the H–Sr–F species should be stable. Thus, it may be possible for the system to explore this region of phase space, enhancing the likelihood of snarled trajectories. Such snarled trajectories may help to scramble translation and vibration of the reagents, making translational excitation compete on a more equal footing with vibrational excitation in promoting reaction.

Not only is this mass combination favorable for en-

hancing the effects of translational excitation, but the shape of the potential may also bias the energy requirements for reaction. If the approach to the barrier is gradual rather than sudden, then reagent translation will be relatively more effective.[28,29]

To assess the role of snarled trajectories and to make a quantitative estimate of their influence, we have carried out calculations using phase space theory.[30–32] In this model every product state, which is constrained only by the conservation of energy and angular momentum, is equally probable. Such a statistical model generally implies a preference for reagent vibration as against translation, based on the following argument. Suppose that the reaction proceeds through the formation of a complex which may dissociate into products or return to reagents. If the outcome depends only on the total energy and angular momentum, then the relative efficiency of vibration and translation in promoting the reaction is approximately the relative cross sections for complex formation. If the centrifugal barrier is the only barrier to complex formation, then the cross section decreases with collisional energy. Therefore energy present as vibration will be more effective than translation in complex formation and hence in promoting the endothermic reaction. The actual branching ratio into products or reagents depends on many factors in addition to the total energy and angular momentum, such as the mass combination and the nature of the potential energy surface.

Table II lists the results of the phase space theory calculation,[33] which is based on using interaction potentials of the form $C^{(6)} r^{-6}$.[ ] Whereas at high collision energy the experimental and calculated average product rotational energies $\langle E'_{rot} \rangle$ are in reasonable agreement, we find that at low collision energy $\langle E'_{rot} \rangle$ is 30% too low for reactions with HF(v =1). For this mass combination $\langle E'_{rot} \rangle$ is determined by the maximum initial orbital angular momentum L_{max}.[15] Thus, we increase L_{max} until the $\langle E'_{rot} \rangle$ matches with experiment. This adjustment implies a more attractive potential for HF(v =1) than for HF(v =0). Under these conditions we find that phase space theory (Table II) predicts vibration to be 3.2 times more effective than translation, in remarkably good agreement with experiment.

The K +HCl reaction system belongs to the same mass combination as Sr +HF. Statistical and nonstatistical phase space calculations by Truhlar[31] on the K +HCl reaction predicted vibration to be four to six times more effective than translation, which is in reasonable agreement with the experimental findings of Brooks and coworkers.[9,10] These results suggest that snarled trajectories may play an important role for thermoneutral or endothermic reactions with this mass combination.

We have also examined other consequences of the phase space model. The calculated variation of the reaction cross section with collision energy (solid squares in Fig. 4) follows closely the experimental data (open triangles in Fig. 4). Because Sr +HF is an endothermic reaction, only a small fraction of phase space is available to products at energies near threshold. This has the consequence of restricting the size of the cross sec-

TABLE II. Results of phase space calculation.

$\langle E_{trans}\rangle$ (kcal/mole)	1.8	1.8	7.5	10.0	12.1	12.9
$\langle E_{vib}\rangle$ (kcal/mole)	11.3	11.3	0.0	0.0	0.0	0.0
J_i[a] ($\hbar$)	1	3	4	4	4	4
L_{max} ($\hbar$)	70	70	94	104	111	113
σ (Å^2)	24.3	24.5	3.6	6.1	7.4	7.6
$\langle E'_{rot}\rangle$ (kcal/mole)	1.6[b]	1.6[b]	1.0	2.0	3.0	3.3
$\langle E'_{vib}\rangle$ (kcal/mole)	1.6	1.8	0.2	0.6	1.0	1.2
$\langle E'_{rot}\rangle_{expt}$ (kcal/mole)	1.6[c]	1.6[d]	...	...	4.7[e]	4.7[e]
$\langle E'_{vib}\rangle_{expt}$ (kcal/mole)	0.7[e]	1.1[d] 1.0[e]	...	...	1.7[e]	1.7[e]

[a]Rotational level of the reagent molecule (HF) for which calculation has been done. The rotational energy for this level matches approximately with the average rotational energy for the experiment.
[b]This has been forced to match the experimental result by adjusting L_{Max}.
[c]Reference 16.
[d]Reference 14.
[e]This work.

tion and the amount of internal energy in the products. As the collision energy increases, these restrictions are relaxed. However, at still higher collision energies, large impact parameters, corresponding to the population of energetically inaccessible product rotational levels, cannot contribute to reaction, causing the cross section to level off. In addition, as the collision energy increases, the cross section for complex formation decreases, further enhancing the falloff of the cross section at very high collision energies. We have also investigated how the cross section depends on the rotational excitation of the reagent. According to the phase space model (Table II), the cross section hardly changes, increasing by only 1%, when $Sr + HF(v = 1, J = 1)$ is compared to $Sr + HF(v = 1, J = 3)$. While no experimental evidence is presently available for this reaction system, the corresponding study[11] on $K + HCl(v = 1, J)$ shows that the cross section decreases to one-third its value on comparing $K + HCl(v = 1, J = 1)$ to $K + HCl(v = 1, J = 3)$. This last finding cannot be explained on a statistical basis.

Table II shows that the phase space calculation for $\langle E'_{vib}\rangle$ differs somewhat from experiment. Part of this difference may be caused by uncertainty in the population of high vibrational levels of the product. In agreement with experiment, the calculated SrF vibrational distributions peak at $v = 0$ and decrease monotonically with increasing v.

The qualitative effect of reagent rotation on the product internal state distribution is experimentally known. Karny et al.[16] found enhanced energy in product vibration on increasing reagent reagent rotation from $HF(v = 1, J = 1)$ to $HF(v = 1, J = 3)$. As shown in the first two columns of Table II, this trend is reproduced by the phase space calculation. It may be regarded simply as a consequence of the greater total energy available to the products for a given initial translational energy.

Karny et al.[16] also found enhanced product vibration

when the $HF(v = 1, J = 1)$ reagent was preferentially oriented perpendicular to the approach direction of the Sr atom. The present phase space calculations are unable to account for this effect because no angular dependence of the potential has been assumed.

In conclusion, we find that phase space theory is successful in qualitatively reproducing almost all the known results for the $Sr + HF$ reaction system. This suggest three possibilities: (a) the reaction proceeds through a sufficiently long-lived complex that the dynamical distributions are statistical; (b) the reaction proceeds by "snarled" trajective causing some observables to be statistical; or (c) the reaction proceeds via a direct mechanism which for this particular mass combination and potential energy surface favors the dynamical distributions we have observed to be statistical. We believe presently that the most likely explanation of our data is (b), i.e., snarled trajectories facilitate the mixing of reagent modes during the formation of products. Further experiments as well as theoretical calculations are under way in order to test this hypothesis.

V. ACKNOWLEDGMENTS

APPENDIX: DETERMINATION OF THE RATIO β/α

By modeling the time dependence of the SrF fluorescence signal as a function of the delay between the pump

and probe lasers, an estimate of β/α is obtained. We suppose that the concentration of HF($v = 1$) in the reaction zone has the functional form $\exp(-t/\tau_1)$, where τ_1 is the time constant for the net removal of HF($v = 1$) from the reaction zone and t is the time. Then the reaction rate at a time t' following the pump laser pulse is $k \exp(-t'/\tau_1)$, where k is a proportionality constant. Of the products formed at time t' the fraction that remains in the detection zone at time t is $\exp[-(t-t')/\tau_2]$, where τ_2 is the time constant for the net removal of SrF from the detection zone. Therefore the total concentration of products in the detection zone at time t is

$$[SrF] = \int_0^t k \exp\left(\frac{-t'}{\tau_1}\right) \exp\left(\frac{-(t-t')}{\tau_2}\right) dt'$$

$$= k \frac{\exp(-t/\tau_1) - \exp(-t/\tau_2)}{\tau_2^{-1} - \tau_1^{-1}} . \qquad (A1)$$

Equation (A1) predicts that the SrF fluorescence signal first rises then falls with increasing time delay. The SrF concentration in the detection zone reaches a maximum value of

$$[SrF]_{max} = k \tau_1 (\tau_1/\tau_2)^{\tau_1/(\tau_2 - \tau_1)} , \qquad (A2)$$

at the time

$$t_{max} = [\tau_2 \tau_1/(\tau_2 - \tau_1)] \ln(\tau_2/\tau_1) . \qquad (A3)$$

To find the ratio β/α, we compare $[SrF]_{max}$ to the concentration of SrF that would have been obtained if the HF($v = 1$) concentration were maintained indefinitely at the level it was immediately after the firing of the HF laser. The latter is evaluated from the first line of Eq. (A1) by setting $\tau_1^{-1} = 0$ and letting t approach infinity. We obtain

$$[SrF]_{ss} = k \tau_2 , \qquad (A4)$$

from which we determine

$$\beta/\alpha = [SrF]_{max}/[SrF]_{ss} = (\tau_1/\tau_2)^{\tau_2/(\tau_2 - \tau_1)} \qquad (A5)$$

Equation (A1) is fit to Fig. 5 of Ref. 14 from which it is found that $\tau_1 = 7$ μsec and $\tau_2 = 16$ μsec. The functional form of Eq. (A1) reproduces the time dependence of [SrF] to within 5% over the time range 0–40 μsec. This result encourages us to believe that Eq. (A1) has validity during this time interval. With the values of τ_1 and τ_2 determined from the fit we estimate [Eq. (A5)] that

$$\beta/\alpha = 0.22 \pm 0.06 . \qquad (A6)$$

The error estimate reflects the variation in the values of τ_1 and τ_2 which give a satisfactory fit.

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