Effect of vibrational excitation on the molecular beam reactions of Ca and Sr with HF and DF

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The reactions of Ca and Sr with HF and DF are studied using a beam–gas configuration as a function of reagent and product vibration to obtain state-to-state reaction rates. A beam of alkaline earth metal atoms enters a scattering chamber containing hydrogen fluoride. The HF and DF reagents are pumped from $v = 0$ to $v = 1$ by a pulsed HF or DF laser; the alkaline earth monofluoride products are detected by a pulsed tunable probe laser. The product internal state distribution is determined from the laser excitation spectrum. While no products could be detected for reactions with DF($v = 1$) or DF($v = 0$), the rate constant for the Ca and Sr reactions with HF($v = 1$) are both at least four orders of magnitude larger than the reactions with HF($v = 0$). The implications of these results on bond energies and the fate of the excess energy of reaction are discussed.

I. INTRODUCTION

Lasers are having a profound impact on the study of chemical reaction processes because the intense monochromatic output of a laser can be used to prepare reactants, to alter chemical transformations, and to probe reaction products. In particular, these developments are opening to investigation state-to-state chemistry[1] in which one examines how some specified set of quantum states of the reactants evolve into quantum states of the products following a single-collision event. To obtain this type of information it is often advantageous to use molecular beam methods in order to avoid the occurrence of secondary collisions between the times of reactant preparation and product analysis.

Thus far, only one such laser-prepared, laser-probed beam reaction has been carried out: Ba + HF ($v = 0, 1$) → BaF (v') + H.[2] We report here an extension of this technique to Ca and Sr. For the latter reagents, unlike Ba, the reaction with HF ($v = 0$) is endothermic, while the reaction with HF ($v = 1$) is exothermic. This has the advantage that the reaction rate for HF ($v = 1$) is more than four orders of magnitude larger than for HF ($v = 0$). It is interesting to compare this reaction rate enhancement with the only other molecular beam study of the effect of reagent vibration excitation on an endothermic process. Odiorne, Brooks, and Kasper[3] report for $K + HCl \rightarrow KCl + H$ that vibrationally excited HCl reacts approximately 100 times more rapidly than HCl in the ground vibrational state. These dramatic increases in reaction rate with vibrational excitation support the theoretical concept that reagent vibration is necessary to promote endothermic reactions.[4] While the present investigation only permits a crude population analysis of the internal product states, nonetheless, this suffices to make some generalizations about the fate of the energy in excess of the activation barrier. Moreover, the rapid acceleration of reaction rate with reagent vibrational excitation also encourage speculation as to the possible use of laser-controlled chemistry in bulk processing.

II. EXPERIMENTAL

Figure 1 presents a schematic drawing of the apparatus. The experimental setup is similar to that described previously.[2] A beam of Ca or Sr atoms traverses a scattering chamber filled with HF or DF gas (beam–gas configuration). The output of a pulsed HF or DF laser operating on the $P_1(2)$ transition excites the HF or DF molecules to the $v = 1$, $J = 1$ level. This pump laser is directed either along or perpendicular to the metal beam. The CaF or SrF reaction products are detected by their characteristic excitation spectrum using a tunable pulsed dye laser as a probe laser. The probe beam is directed perpendicular to the metal beam. The pressure of hydrogen fluoride in the scattering chamber is maintained sufficiently low that newly formed alkaline earth monofluoride molecules usually suffer no collisions in the region of the probe laser beam viewed by the photomultiplier.

A. The molecular beam apparatus

This apparatus consists of an oven chamber and a scattering chamber that are separated from each other by a bulkhead flange having a 0.2×2 cm rectangular slit. Each chamber is individually evacuated by a 6 in. diffusion pump.

The oven chamber contains the metal atom source. Two types of ovens are used. One is a cylindrical stainless steel tube 4 in. long and 0.5 in. in diameter, having a 0.001 in. wall thickness. It is housed in a water-cooled copper tube. The oven orifice is a 1 mm diam. hole. An ac current passing through this stainless steel tube gradually heats it to a temperature of about 1100 K for Ca or Sr, as measured by an optical pyrometer. The other type of oven is a stainless steel crucible, surrounded by a tantalum heat shield, housed inside a water-cooled copper tube. Here, the ac current passes through the heat shield, indirectly heating the crucible by radiation. This latter design proved to be superior in that it gave the more stable beam.

The bulkhead flange is located 4 cm from the metal atom source and 6 cm from the probe zone. This isolation of the source chamber from the scattering chamber is required to prevent oven reactions.

The HF gas is admitted directly into the scattering chamber through a stainless steel needle valve from a lecture bottle (Matheson, > 99.9% stated purity). The

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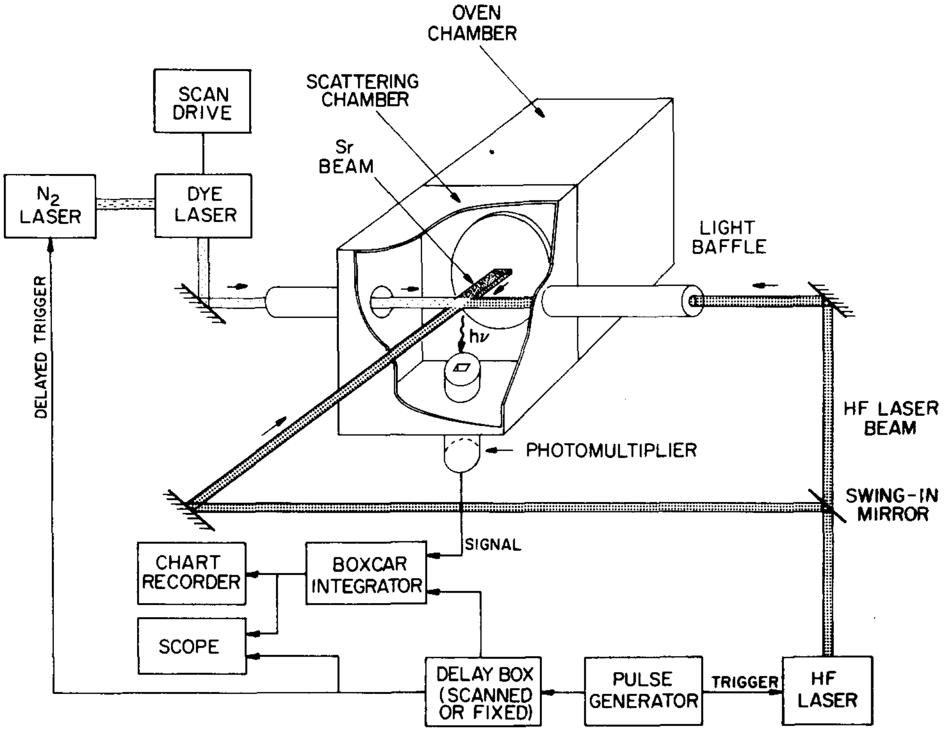

FIG. 1. Cutaway drawing of the experimental setup. A swing-in mirror permits excitation of the HF molecules in the scattering chamber by two different light paths, one antiparallel the other perpendicular to the probe laser beam.

latter is immersed in a dry ice acetone slush so that an HF pressure of 1×10^{-4} to 2×10^{-5} torr can be maintained during an experimental run. For some runs HF was replaced by DF (Merck, Sharp, and Dohme Canada, Ltd., 98 at% D).

The dye laser probe beam enters and exits the scattering chamber through baffle arms (1 m long). In addition, a 3 m focal length lens located in the entrance baffle arm helps to reduce the scattered laser light.

B. The HF laser

A pulsed HF laser has been constructed which is similar to one described previously.[5] The HF is excited by a transverse discharge using pin electrodes. The laser tube is 1 m long and has five rows of stainless steel pins, each spaced 5 mm apart from one another. A $CuSO_4$ solution serves as a ballast resistor. Figure 2 shows a cross section of the laser tube. The distance between the pin electrodes and the aluminum ground electrode is 15 mm. A 30 kV, 0.04 μF capacitor (Maxwell) is charged to 15–20 kV, then discharged by a thyratron (ITT model F-43) switch. The laser tube is terminated by 2 in. CaF_2 Brewster windows; the laser cavity is formed by a grating (PTR) blazed at 3.5 μ and an output mirror. The latter is either an uncoated sapphire flat or a Ge flat (30% transmission).

A gas mixture consisting of 100 torr SF_6, 50 torr He, and 5 torr H_2 enters the laser tube at both ends and exits from the center. For operation as a DF laser the H_2 is replaced by D_2. The output beam is 1.5 cm^2 at a distance of 2 m from the output mirror. The repetition rate of the $P_1(2)$ transition is up to 10 Hz. The power per pulse is about 5 mJ.

C. The detection system

A pulsed nitrogen laser (Molectron, 400 kW) pumps a tunable dye laser (Molectron model DL300) to produce the probe beam that is used to detect the CaF and SrF products by their characteristic fluorescence. For CaF the dye laser tunes over the $A\,^2\Pi_{1/2,3/2}$–$X\,^2\Sigma^+$ band system (≈6050 Å) using rhodamine B; for SrF the dye laser tunes over the $A\,^2\Pi_{3/2}$–$X\,^2\Sigma^+$ band system (≈6520 Å) using a dye mixture of rhodamine 6G and cresyl violet perchlorate in ethanol. In the latter case the SrF $A\,^2\Pi_{1/2}$–$X\,^2\Sigma^+$ band system is too far to the red (≈6620 Å) to be observed with this dye. The fine structure assignments are taken from Steimle, Domaille, and Harris.[6] The pulse-to-pulse stability of the dye lase is typically 5% and the repetition rate (determined by the HF laser) is 10 Hz or less.

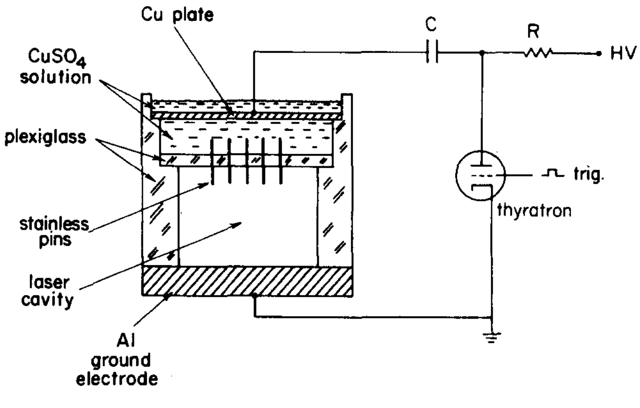

FIG. 2. Cross section of the HF laser.

A photomultiplier tube (RCA 7265, 2 in. diam., S-20 photocathode) observes the molecular fluorescence at right angles to the metal beam and the laser probe beam; it is located 4 cm from the fluorescence zone. A 5 cm focal length metal mirror, placed opposite to the photomultiplier tube, increases the amount of collected fluorescence.

A boxcar integrator (PAR model 162) with two 164 plug-in units averages the photomultiplier signal. A pulse generator (Systron Donner model 100 A) triggers both the boxcar and the nitrogen laser. The pulse generator is triggered, itself, by a pulse originating from the thyratron that fires the HF laser or from a pulse coming from an InAs infrared detector (Judson J12) that observes part of the HF laser output.

After the HF laser fires, the probe laser pulse and the opening of the boxcar gate is delayed from 1–70 μs. The gate width of the boxcar is chosen to be between 5–50 ns, which is up to twice the radiative lifetimes.[7] The dye laser scans wavelength typically at 2.5 Å/min and the time constant of the boxcar is set at 2 s.

III. RESULTS

Table I summarizes the heats of reaction of Ca or Sr with HF or DF based on the best presently available thermochemical data. From this table it is clear that all reactions with vibrationally unexcited HF or DF are endothermic, while reactions with HF excited to the $v=1$ vibrational level (11.3 kcal/mole additional energy) are exothermic for Sr and may be exothermic for Ca. The reactions with DF ($v=1$) with an additional energy of 8.3 kcal/mole appear to be thermoneutral but the heats of reaction have a large uncertainty.

TABLE I. Heats of reaction[a] for Ca or Sr with HF or DF in the ground or first vibrationally excited state.

Reaction process	ΔH (kcal/mole)
$Ca + HF(v=0) \rightarrow CaF + H$	$+8.7 \pm 2.8$
$Sr + HF(v=0) \rightarrow SrF + H$	$+6.4 \pm 1.9$
$Ca + HF(v=1) \rightarrow CaF + H$	-2.6 ± 2.8
$Sr + HF(v=1) \rightarrow SrF + H$	-4.9 ± 1.9
$Ca + DF(v=0) \rightarrow CaF + D$	$+10.3 \pm 2.8$
$Sr + DF(v=0) \rightarrow SrF + D$	$+8.0 \pm 1.9$
$Ca + DF(v=1) \rightarrow CaF + D$	$+2.0 \pm 2.8$
$Sr + DF(v=1) \rightarrow SrF + D$	-0.3 ± 1.9

[a] This based on the dissociation energies $D_0^0(HF) = 135.1 \pm 0.3$ kcal/mole, taken from B. de B. Darwent, "Bond Dissociation Energies in Simple Molecules," Natl. Stand. Ref. Data Ser. Natl. Bur. Stand. (1970); $D_0^0(CaF) = 126.4 \pm 2.5$ and $D_0^0(SrF) = 128.7 \pm 1.6$ kcal/mole, taken from P. D. Kleinschmidt and D. L. Hildenbrand, Ref. 11. The error estimate for the CaF bond energy is from J. W. Hastie and J. L. Margrave, J. Chem. Eng. Data 13, 428 (1968); and for SrF from D. L. Hildenbrand, J. Chem. Phys. 48, 3657 (1968).

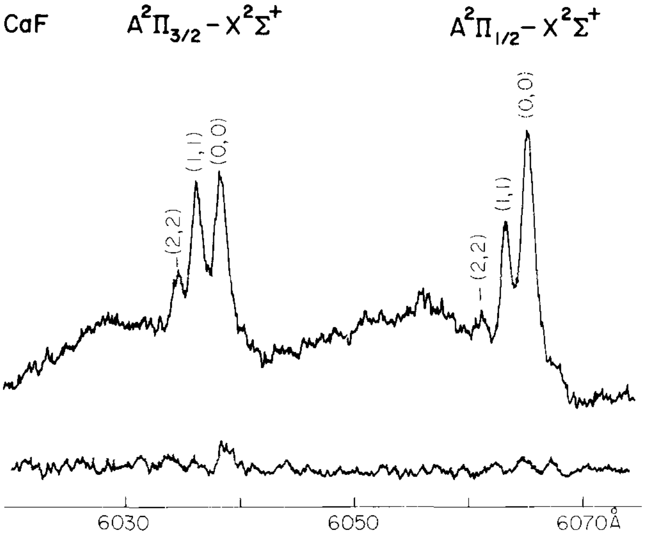

FIG. 3. Excitation spectra of the CaF products resulting from the Ca + HF ($v=1$) reaction (top trace) and the Ca + HF ($v=0$) reaction (bottom trace).

Figure 3 shows the excitation spectrum of CaF obtained from the reaction of Ca with HF ($v=0$) and HF ($v=1$). We are unable to detect any CaF product when Ca atoms collide with vibrationally unexcited HF molecules. However, for Ca + HF ($v=1$) the CaF product appears with high yield. We estimate[2] that no more than a few percent of the HF molecules in the scattering chamber are pumped by the HF laser to $v=1$; consequently, the overall rate constant, proportional to the area under the excitation spectrum, increases by more than four orders of magnitude for Ca + HF ($v=1$) compared to Ca + HF ($v=0$). In the former reaction the CaF products are formed with a vibrational distribution that extends to $v'=2$.

Figure 4 is the corresponding excitation spectrum of SrF with the HF laser on and off. Unlike Ca + HF ($v=0$), the "dark reaction" of Sr + HF ($v=0$) shows a small amount of product formation. We find that the yield of this dark reaction depends strongly on the Sr oven temperature, suggesting that the SrF products arise from the high-temperature tail of the translational energy distribution. For reactions with HF ($v=1$), again the product yield increases enormously, even though only a small fraction of the HF molecules are pumped to $v=1$ by the HF laser. The SrF products are formed up through $v'=3$.

In a separate study the HF was replaced by DF, which was pumped by a DF laser. No reaction of Sr with DF ($v=0$) or DF ($v=1$) could be detected, although Table I suggested that the latter reaction might be slightly exothermic. Because the reaction of Ca with DF is expected to be even more endothermic, its study was not attempted.

In principle, the vibrational and rotational energy distributions can be obtained from the excitation spectrum by computer simulation. However, the high degree of overlap in the present spectra makes this procedure

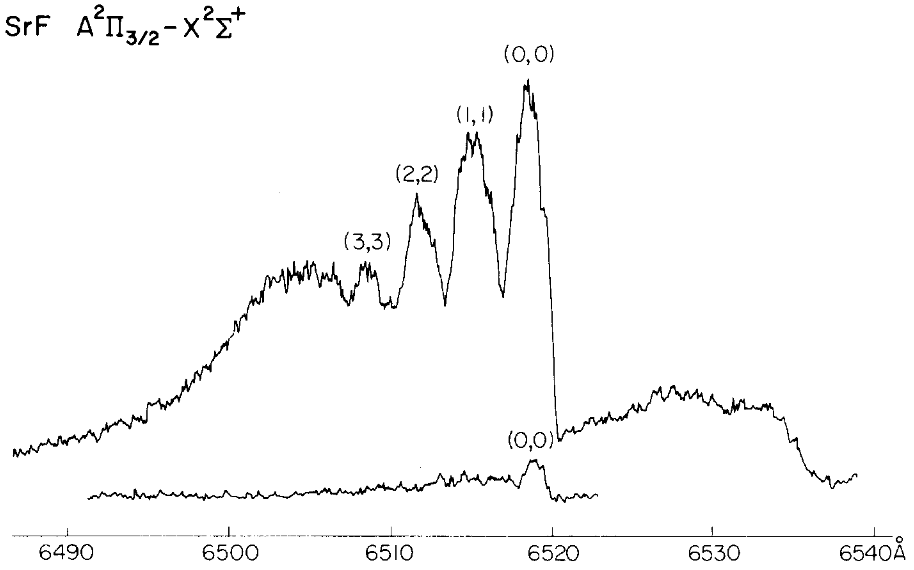

FIG. 4. Excitation spectra of the SrF products resulting from the Sr + HF ($v=1$) reaction (top trace) and the Sr + HF ($v=0$) reaction (bottom trace).

lack uniqueness. Instead, we have assumed that the heights of the $\Delta v=0$ band heads above the envelope of the valleys are proportional to the population of each vibrational level.[8] For the SrF $A-X$ system the Franck–Condon factors $q_{v',v''}$ are assumed to be the same for all the members of the $\Delta v=0$ sequence up to $v'=3$; for the CaF $A-X$ system we use in the $\Delta v=0$ sequence the Franck–Condon factors kindly provided us by Domaille,[9] namely, $q_{0,0}=0.978$, $q_{1,1}=0.936$, and $q_{2,2}=0.896$. Table II lists the relative vibrational populations. This analysis is based on the $A\,^2\Pi_{3/2}-X^2\Sigma^+$ subband. For SrF this is the only information available; for CaF we see from Fig. 3 that the estimated vibrational population distribution is quite crude since the two subbands would yield different distributions, although the trend of decreasing population with increasing v' is not in doubt. Consequently, until the bandwidth of the dye laser can be narrowed sufficiently to permit a deconvolution of the excitation spectra, we must regard the CaF population distribution as only of qualitative significance. The SrF $\Delta v=0$ sequence is better resolved than in CaF, and the population analysis might be expected to be more reliable. Consequently, we list in Table II an extra digit for these relative populations, although we do not believe they are determined to this accuracy.

The excitation spectrum was taken with variable time delay between the HF laser pump pulse and the dye laser probe pulse. The delay time needed to obtain the excitation spectrum with maximum intensity depended on the configuration used. When the HF laser beam is colinear to the metal beam (see Fig. 1), the maximum fluorescence occurs after a 45 μs delay. This delay time depends neither on the HF pressure nor on the spectral feature observed. Its value is similar to the one obtained for Ba + HF ($v=1$).[2]

When the HF beam is perpendicular to the metal beam but opposite to the probe beam (see Fig. 1), the maximum fluorescence intensity occurs at a delay time of about 12 μs (see Fig. 5), which is again independent of HF pressure and spectral feature. The time evolution of the signal comes about from the build up of the MF (v') product as metal atoms react with vibrationally excited HF as well as from the falloff of the MF (v') product as it moves away from the probe excitation zone. For the colinear geometry many more MF (v') products are produced between the probe excitation zone and the oven, accounting for their later appearance. Because the same excitation spectra are obtained in both configurations, we conclude that vibrational relaxation of the MF (v') product is negligible under our experimental conditions. It is not possible to relate the risetimes of the two curves of growth to the absolute reaction cross section without additional information on the absolute product flux. Nevertheless, the total reactive cross sections for Sr + HF ($v=1$) and Ca + HF ($v=1$) must be rather large since the laser-induced fluorescence signals are comparable to the signal for Ba + HF ($v=0$), although we excite only 1%–2% of the HF present.

IV. DISCUSSION

Although we have only obtained approximate state-to-state reaction rates in the present study, this information enables us to calculate the bond energies of CaF and SrF, and to determine the disposal of the excess

TABLE II. Relative vibrational distribution of the reaction products for Ca + HF ($v=1$) and Sr + HF ($v=1$).

Reaction product		Relative population
CaF	$v'=0$	1.0
	$v'=1$	0.7
	$v'=2$	0.4
SrF	$v'=0$	1.0_0
	$v'=1$	0.6_3
	$v'=2$	0.3_5
	$v'=3$	0.1_8

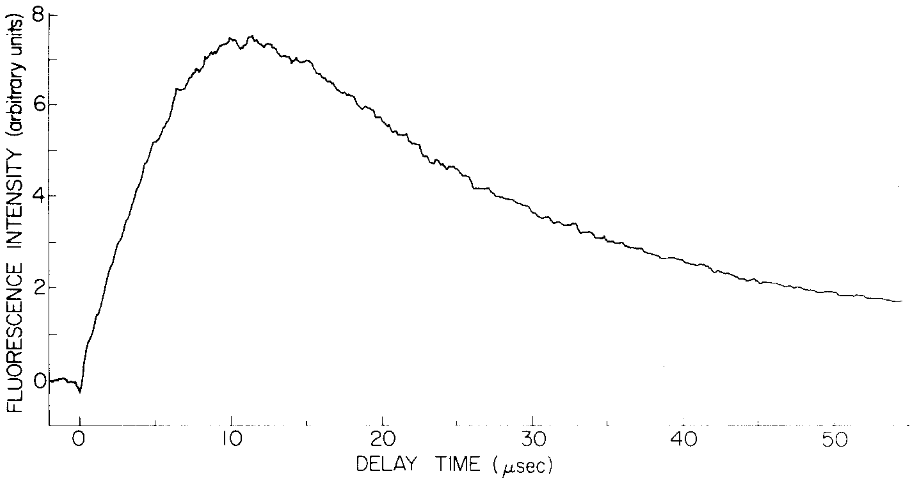

FIG. 5. The laser-induced fluorescence signal (SrF) as a function of the delay time between the HF laser pump pulse and the dye laser probe pulse when the pump laser beam is opposed to the probe laser beam.

energy of reaction among product translation and internal excitation. According to energy balance, we write

$$D_0^\circ(\mathrm{MF}) = D_0^\circ(\mathrm{HF}) + E_{\mathrm{int}}(\mathrm{MF}) - E_{\mathrm{int}}(\mathrm{HF}) + [E_{\mathrm{trans}}^{f} - E_{\mathrm{trans}}^{i}] \ , \tag{1}$$

where $D_0^\circ(\mathrm{HF})$ is the HF bond energy, $E_{\mathrm{int}}(\mathrm{MF})$ and $E_{\mathrm{int}}(\mathrm{HF})$ are the internal (vibrational-rotational) energies of the MF product and the HF reactant, respectively, and E_{trans}^{i} and E_{trans}^{f} are the relative translational energies of the reactants and products, respectively. We take $D_0^\circ(\mathrm{HF})$ to be 135.1 ± 0.3 kcal/mole.[10] The value of $E_{\mathrm{int}}(\mathrm{MF})$ is the energy of the highest vibrational level of MF populated in the reaction; the value of $E_{\mathrm{int}}(\mathrm{HF})$ is the energy of the $v = 1$ vibrational level. In both cases the energies are measured from the vibrationless ground state. By neglecting the difference between the initial and final relative translational energies, the quantity appearing in brackets in Eq. (1), we make the estimates

$$D_0^\circ(\mathrm{CaF}) = 127.1 \pm 2 \ \mathrm{kcal/mole} \tag{2}$$

and

$$D_0^\circ(\mathrm{SrF}) = 128.0 \pm 2 \ \mathrm{kcal/mole} \ . \tag{3}$$

We are unable to give a precise error limit but we believe that the neglect of the translational energies combined with the neglect of the amount of rotational excitation in the highest v' product level detected and the 0.3 kcal/mole error estimate for the HF bond energy should make these values not uncertain by more than 2 kcal/mole. Our dissociation energies agree well with those determined mass spectrometically,[11] namely, $D_0^\circ(\mathrm{CaF}) = 126.4 \pm 2.5$ and $D_0^\circ(\mathrm{SrF}) = 128.7 \pm 1.6$ kcal/mole. With the bond energies given in Eqs. (2) and (3) we find that the Ca + DF ($v = 1$) reaction is endothermic by 1.3 ± 2 kcal/mole, and the Sr + DF ($v = 1$) reaction is endothermic by 0.4 ± 2 kcal/mole. The fact that we observe no SrF products from Sr + DF ($v = 1$) suggests that either the SrF bond energy is still slightly too high or that there is a small activation energy for this reaction.

Since the first reactive scattering experiments of alkaline earth atoms with hydrogen halide molecules,[12] these systems have shown the puzzling feature that a large fraction of the reaction exoergicity appears in product translational energy, despite the theoretical prediction[13] that in a reaction of a heavy atom H with a heavy–light diatomic molecule H′L to form the products HH′ and L the energy should be partitioned preferentially into HH′ vibrational excitation.

In a previous study of Ba + HF, Pruett and Zare[2] report that the total available energy appearing in product vibration increases from 12% to 33% in going from Ba + HF ($v = 0$) to Ba + HF ($v = 1$). In the present study we find that $\overline{f}_v = 29\%$ for Sr + HF ($v = 1$) and $\overline{f}_v = 40\%$ for Ca + HF ($v = 1$). These results may suggest a trend to increasing vibrational excitation with decreasing mass of the alkaline earth atom. However, even with due allowance being given for rotational excitation of the product, it is apparent that the reaction dynamics for these systems differ significantly from those observed in more covalently bonded systems in that more than half the excess energy of reaction has the fate of appearing in product translational energy.

V. ACKNOWLEDGMENTS

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