

LETTERS TO THE EDITOR

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COMMUNICATIONS

Effect of reagent orientation and rotation upon product state distribution in the reaction $\text{Sr} + \text{HF} (\nu = 1, J) \rightarrow \text{SrF} (\nu', J') + \text{H}^a$

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While the dependence of chemical reactivity upon reagent orientation and rotation has been studied for a few systems (e. g., K , $\text{Rb} + \text{CH}_3\text{I}$,¹ and $\text{F} + \text{H}_2$),² the role that these dynamical variables play in determining the product energy distribution is poorly understood. We present a study of the effect of rotational energy and orientation of HF molecules on the SrF product state distribution in the reaction $\text{Sr} + \text{HF} (\nu = 1, J) \rightarrow \text{SrF} (\nu', J') + \text{H}$. These experiments were carried out under single-collision conditions using an HF laser to prepare the reac-

tants and a tunable dye laser to probe the product state distribution by laser-induced fluorescence. The SrF vibrational distribution is found to depend markedly upon the rotation and orientation of the HF reactant.

The experimental setup (Fig. 1) is essentially identical to that described previously.³ A beam of Sr atoms enters a scattering chamber containing HF at low pressure ($\leq 1 \times 10^{-4}$ torr). The output of a pulsed, grating-tuned HF laser [$P_1(2) - P_1(6)$] is directed perpendicular

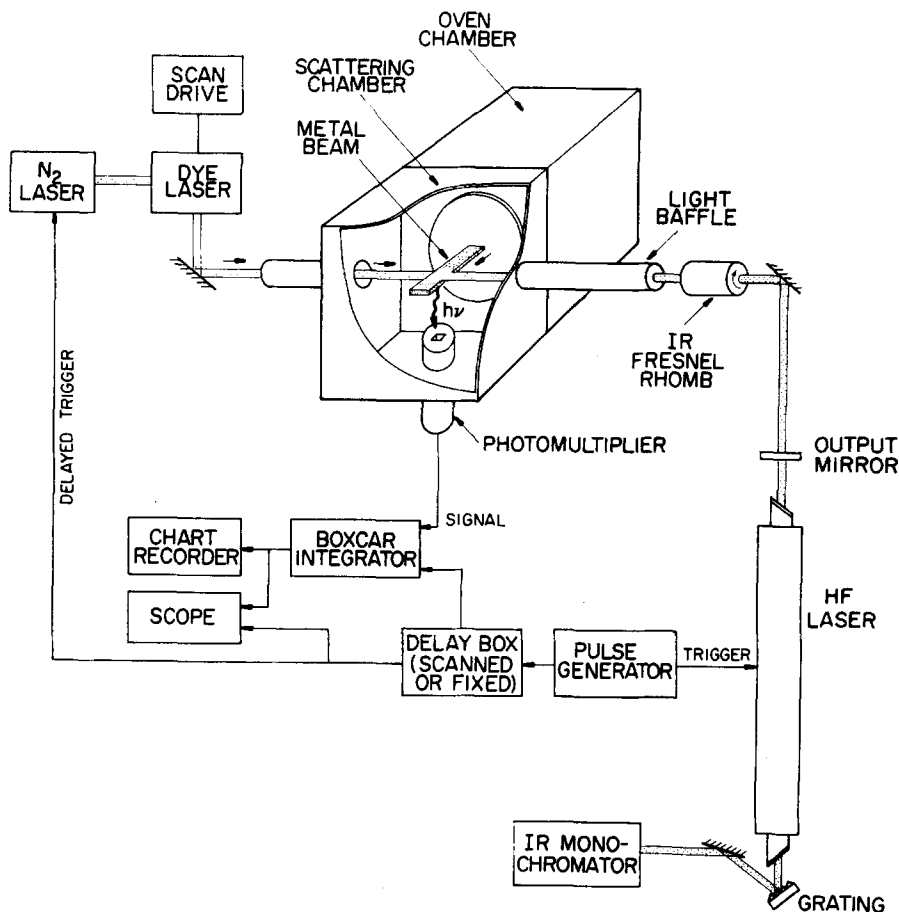


FIG. 1. Cutaway drawing of the apparatus.

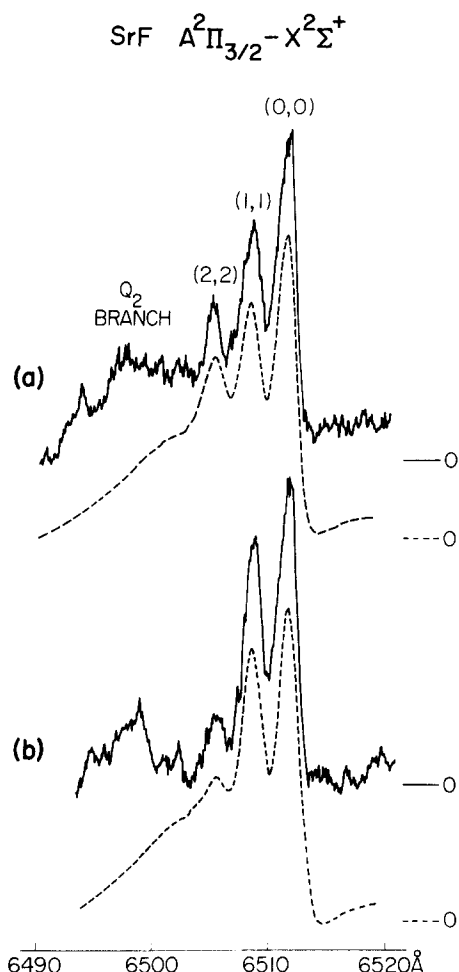


FIG. 2. Excitation spectra for Sr + HF ($v=1, J=1$) with the HF molecule preferentially aligned (a) perpendicular or (b) parallel to the approach direction of the Sr atom. Computer simulations (dashed curves) give the following internal state distributions: (a) $v_0:v_1:v_2=1.00:0.63:0.29$; and (b) $v_0:v_1:v_2=1.00:0.72:0.13$, using a rotational temperature of 800 K for all vibrational levels. The baselines have been offset to aid comparison.

to the metal beam, preparing HF ($v=1, J=1-5$). Its electric vector \mathcal{E} is aligned either parallel or perpendicular to the metal beam by use of a rotatable half wave Fresnel rhomb (ZnSe) placed between the HF laser and the scattering chamber. In analogy to the previous study on In, Tl + I_2^* , the polarized excitation source produces preferentially oriented molecules with respect to the oncoming beam of strontium atoms.⁴ In this manner we can alter the approach geometry of the reagents. Specifically, when \mathcal{E} lies along the metal beam, collinear approach predominates while when \mathcal{E} is perpendicular to the metal beam, noncollinear (broadside attack) is more probable. As shown previously,³ essentially no reaction occurs for Sr with ground state HF molecules, while vibrationally excited HF readily reacts to form SrF whose internal state distribution is determined by measuring the $A^2\Pi_{3/2}-X^2\Sigma^+$ excitation spectrum.

Figure 2 compares the SrF excitation spectra obtained for reaction with HF ($v=1, J=1$) when the reagent molecule is preferentially oriented perpendicular to the metal

beam [Fig. 2(a)] and parallel to the metal beam [Fig. 2(b)]. The dashed curve underneath each spectrum is a computer simulation of the excitation spectrum which is used to determine approximate rotational temperature and vibrational distribution of the SrF product. It is clearly seen that broadside attack favors the population of the $v'=2$ level in the SrF product. If we believe that product internal excitation is correlated with the degree of attractive energy release along a potential path,⁵ then this result supports recent theoretical calculations indicating that for the reactions of alkali atoms with hydrogen fluoride the minimum energy path is along a bent configuration.^{6,7}

Figure 3 compares the SrF excitation spectra obtained for reaction with HF ($v=1, J=3$) in Fig. 3(a) to that of HF ($v=1, J=1$) in Fig. 3(b) for the same polarization direction of the HF laser (perpendicular to metal beam). Again the dashed curves are computer simulations for both cases. The increase in the SrF product vibration in going from $J=1$ to $J=3$ is typical for $J=1$ compared to $J>1$ for all J values up through $J=5$. However, the variation in the SrF $v'=2$ population with HF ($v=1, J>2$) is within our signal-to-noise ratio (10%). The product of the laser intensity [on the $P_1(2)$ and $P_1(3)$ lines] and the thermal population of HF ($v=0, J=1, 2$) is approximately equal for both cases. Moreover, the increase in available energy in going from HF ($v=1, J=1$) - HF ($v=1, J=2$) is less than 10% of the energy between SrF (v

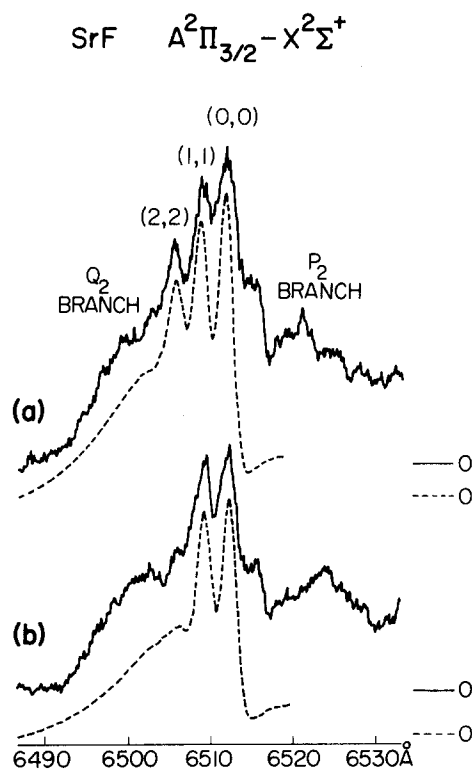


FIG. 3. Excitation spectra for (a) Sr + HF ($v=1, J=3$) and (b) Sr + HF ($v=1, J=1$) for the same laser polarization (perpendicular to metal beam). Computer simulations (dashed curves) give the following internal state distributions: (a) $v_0:v_1:v_2=1.00:0.77:0.36$; and (b) $v_0:v_1:v_2=1.00:0.79:0.08$, using a rotational temperature of 800 K for all vibrational levels. The baselines have been offset to aid comparison.

= 2) and SrF ($v=1$). Therefore we conclude that the effect of populating higher vibrational levels in the SrF product by increasing the HF rotation is caused by some dynamic effect, rather than merely by energetic considerations.

The excitation spectra are found to be extremely sensitive to the metal oven temperature, which affects the velocity distribution of the Sr beam. As a result, spectra could only be compared on the same run, i. e., it is not valid to compare Fig. 2(a) with Fig. 3(b). Orientational effects on the reaction with $v=1$, $J > 1$ levels were also studied. However, we were unable to detect small changes in the $v'=2$ population with HF orientation for these cases. Clearly the effect of reagent orientation and rotation coupled with the sensitivity to reagent translation requires more investigation. However, the results presented here provide the first experimental evidence of a preferred bent approach geometry in an atom plus diatom exchange reaction for populating certain internal states of the products.

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Double resonance on the active medium of an optically pumped submillimeter laser: HCOOH

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In this Communication, we report the first observation of double resonance on the active molecules of an optically pumped submillimeter (submm) laser.

While usual double resonance signals are coming from absorption (or dispersion) features of a molecular sample, in this experiment they are observed as a change in the power emitted by optically pumped molecules. In an optically pumped submm laser, molecules are pumped by the ir radiation of a CO₂ laser in resonance with a transition to an excited vibrational state, thus creating a population inversion between rotational energy levels. This leads to emission of submillimeter radiation at the frequency of rotational transitions. A saturating microwave power is sent into the submm cavity and the submm output power is monitored as a function of the microwave frequency ν . In our experimental setup, the

polarization of the microwave electric field is perpendicular to that of the laser field. Sharp resonances are observed when ν is coming into resonance with transitions concerning levels involved in the submm laser operation.

The relevant energy levels are given in Fig. 1. The experiment has been performed with the HCOOH laser. When pumped with the 9 R 40 line of the CO₂ laser, cascading emissions are observed at 403 721.6 MHz and 381 336.9 MHz. They correspond to the $v_6=1 J_{K_a, K_c} = 18_{3,16} \rightarrow 17_{3,15}$ and $v_6=1 17_{3,15} \rightarrow 16_{3,14}$ transitions, respectively, as recently assigned by Dangoisse *et al.*¹ Only the first line has been used in our experiments. The emission is monitored with a "cat-whisker" millimeter wave harmonic generator (Custom Microwave).

Either frequency modulation of the microwave at a