State-to-state reaction dynamics of HF($v=2$) with Ba and Sr

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(Received 29 December 1980; accepted 7 August 1981)

HF gas molecules in $v=2$ are produced in a beam-gas reaction system using an intracavity, multiply resonant HF chemical laser to consecutively pump HF($v=0$) using the $P_1(4)$ and $P_3(3)$ HF lasing lines. A beam of Ba or Sr reacts with the perturbed reagent gas to form the metal monohalide. The internal state distribution of the MF product is probed using pulsed laser induced fluorescence. In both reactions, products are seen with internal energies out to nearly the exothermic limit, but fractional vibrational energy releases are small and apparently decrease with increasing reagent vibration. State-to-state cross sections for $v=2$ reagents, relative to those for $v=1$ and $v=0$ are reported.

INTRODUCTION

The simple atom exchange reactions of the group IIA atoms with HF to form the metal monohalides has served over the past few years to illustrate several conceptual principles in reaction dynamics. The first of these were the studies of Cruse, Dagdigian, and Zare of the nascent internal state distributions of metal halide products in several reactions of Ba atoms with hydrogen halides in the ground $v=0$ state. Subsequent studies by Pruet and Zare investigated the production of new product internal states resulting from the pumping of HF molecules to $v=1$ by a resonant HF chemical laser. Two experiments were further extended by Karny and Zare to the endothermic reactions of Sr and Ca with HF by providing the required energy with vibrational excitation of the HF. These latter reactions were also utilized in studies by Karny, Estler, and Zare of product alignment and steric effects by judicious selection of the polarization of the vibrational excitation light pulse.

The reactions of Ba and Sr with HF have received continued attention recently. Gupta, Perry, and Zare studied the effects on product state distributions of adding translational energy instead of vibrational energy to the reaction. We have also restudied the vibrationally excited reaction using a unique dual beam technique to allow full recovery of individual vibrational state-to-state cross sections. There is already therefore, a great wealth of excellent state specific experimental data for reactions of $v=0$ and $v=1$ HF.

It is the goal, of course, to study these reactions as a function of reagent internal energy, but as yet this functionality has been sampled at only two points, $v=0$ and $v=1$. In principle, one can excite overtones of the hydrogen halides, as has been demonstrated recently in energy transfer experiments, but production of sufficient populations of excited molecules under molecular beam conditions to observe state selected products has not yet been demonstrated. We, however, succeeded in observing the reactions of HF($v=2$) with Ba and Sr by exciting the HF from $v=0$ using IR–IR double resonance through the $v=1$ level. This has been accomplished by making a single HF laser doubly resonant on connected fundamental and hot band transitions, and results in a production of approximately 2% of the molecules in the $v=2$ state. This technique is similar to the one used by Osgood, Sackett, and Javan to excite HF to $v=2$ and $v=3$. We have utilized our dual beam apparatus to study these reactions and are able to report detailed state-to-state cross sections for reactions of $v=0$, 1 and 2 HF with Ba and Sr.

EXPERIMENTAL

For any reaction which proceeds readily from a thermal vibrational distribution, the effects of exciting a small fraction of the reagents to a nonthermal vibrational state are difficult to discern. In such cases the product population is still dominated by products of the thermal reagents. The molecular beam apparatus employed was designed to minimize this problem, which in the present case, occurs for the Ba reaction with HF. Sr does not react appreciably with thermal HF. The apparatus was originally discussed in detail in an earlier study. Two molecular beams are formed from a single oven containing two orifices. Both beams enter a common scattering chamber giving two reaction zones, separated by about 20 cm. One of these reaction zones serves as a "blank" reaction while the other serves as a "sample" containing products of vibrationally excited reagents. The "sample" side is located within the cavity of an HF chemical laser. After waiting 20–40 μs after the HF chemical laser pulse, both reaction zones are probed simultaneously by a common dye laser pulse to obtain excitation spectra of the product metal monohalides. Two simultaneous spectra are thus generated and recorded using separate photomultiplier and boxcar integrator channels, followed by digitization into a multichannel averager. The advantage of this technique over earlier techniques lies mainly in its ability to eliminate noise due to probe laser fluctuations.

In early "alternate sampling" techniques a single reaction zone and fluorescence detector were used in which the HF pumping laser was only fired on every other shot of the probe laser and the alternate shot signals were subtracted in an A–B mode boxcar integra-

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tor. In principle the alternate sampling technique will produce equivalent results, but requires extensive averaging to reduce shot to shot laser noise to extract the signal, risking degradation of the molecular beam system during spectral scans. It must be emphasized that the signal fluctuation will in general exceed the dye laser energy fluctuation due to the fact that individual molecular absorption lines are narrower than the dye laser frequency envelope. This causes the signal to fluctuate due to mode hopping as well as due to intensity changes.

The pulsed HF laser uses a single row of resistively ballasted electrodes along a 1 meter discharge tube. As in the first experiments with this apparatus, the totally reflecting cavity end mirror is beyond the molecular beam chamber to allow intracavity irradiation of the "sample" reaction zone. There is no output coupler on the laser per se, although sapphire windows on the laser tube do provide a monitor output and the sapphire windows on the beam apparatus also couple out some radiation. We did not measure absolute laser energies, although typical single line output energies for these lasers are in the 100 - 500 µJ range. Because we are using a total reflector end mirror and measure the laser power at one of eight possible sapphire window reflections, we estimate the effective intracavity laser power to be in the 1 - 5 mJ range. Although a grating is used and the discharge tube windows are at Brewster's angle, the laser is presumed to be unpolarized, due to the high gain of the laser system.

A retro-reflection grating is used to force oscillation onto a low gain, low J line fundamental transition which is needed to pump the thermally populated rotational levels in the beam apparatus. To obtain double resonance pumping the zero order reflection from the grating is returned with a plane mirror back through zero order and into the cavity. This very low level of feedback is sufficient to cause three high gain hot band lasing lines to oscillate. Figure 1 illustrates the optical paths for the Littrow and zero order coupling. Assignment of the hot band transitions to the P(3), P(4), and P(5) lines reveals that setting the retro-reflection coupling to allow the P(4) line to oscillate provides the necessary frequencies for the double resonance. Although the hot-band feedback is weak, these lines still reach gain before the fundamental transition, but continue to lase after the fundamental transition begins. Thus only part of the hot band light is utilized in the double resonance scheme.

The use of double resonance to provide the v = 2 excitation necessarily allows simultaneous production of v = 1 molecules in the reaction zone. This results in difficult complications in data reduction, especially in the absence of an accurate knowledge of the fraction of v = 2 and v = 1 molecules present.

Our previous experiments using only v = 1 utilized the P(2) line in HF as the excitation frequency. Laser intensity at the P(2) line is weaker by a factor of 6 than the P(4) line, but overlaps a larger thermal population. We previously estimated that excitation by the P(2) line resulted in an effective reagent fraction v = 1 of 3.5%.11 The higher energy of the P(4) line apparently compensates for the decreased population because preliminary studies using the P(4) line alone resulted in a slightly larger production of higher product vibrational levels. This conclusion assumes that reagent rotation has little effect on the reaction rate, although recent results of Disper, Gels, and Brooks causes some worry on this point.12 We therefore conclude that the P(4) line saturates the transition in the scattering gas, resulting in an effective excitation fraction of about 5%.

The assumption of near saturation is not based on an observation of signal intensity versus pump laser energy. A rough indication that saturation is occurring is obtained by comparing the absolute signal intensities in the first experiments of this type2 with present results. Extra cavity pumping in those first experiments utilized pulse energies of 100 µJ on the P(2) transition. Intracavity pumping with the present laser operating on the same transition results in a signal which is three to four times larger, but utilizes a pulse energy of from 10 to 50 times larger.

When the hot band transition is also present, its intensity (during the time of the fundamental lasing) is about one third that of the fundamental line, but the hot band absorption coefficient is almost twice that of the fundamental.13 Thus the hot band transition should be near saturation also. A combination of two unpolarized lasing lines would result in a three level saturation ratio of 9:7:5 for the v = 0, J = 4; v = 1, J = 3; and v = 2, J = 2 levels, respectively.

This analysis leaves completely unanswered any questions concerning the effects of laser cavity mode frequency structure which would preferentially select certain velocity groups relative to the laser propagation direction. These effects would drastically reduce the excitation fractions below the saturation values, and the simultaneous operation of two such mode structures would essentially eliminate any possibility of exciting
molecules to \( v = 2 \). The fact that we do see reaction from \( v = 2 \) insures that the effect of mode structure is not disastrous, and the size of the \( v = 2 \) effect that we do see is consistent with the assumption that mode effects are inoperative. For our laser, the longitudinal modes would be separated by 0.0016 cm\(^{-1}\) giving 18 modes in the Doppler width. We are thus requiring a combined power broadening and/or cavity mode width of about 0.001 cm\(^{-1}\) to justify ignoring these effects.

We do, however, assume that we are slightly below saturation on the hot band, and that the hot band lasing pulls additional population from the ground state in a three level system. We estimate that with both lines lasing we have a rotationally summed reagent vibrational distribution of \( 0.94 : 0.04 : 0.02 \) for the \( v = 0 \), \( v = 1 \), and \( v = 2 \) levels, respectively. The latter two numbers have rather large uncertainties which may significantly affect some of the state-to-state cross sections calculated from the data.

Excitation spectra were acquired in several experiments over a period of a few weeks. The raw data were stored on tape as digitized fluorescence intensity versus probe laser wavelength. To construct final excitation spectra and difference spectra, the best indications of the effects of \( J \) on the reagents could then be recorded and compared with the digitally obtained difference spectra from the raw data. In some cases this blocked versus unblocked data was used to help normalize the difference spectra reactive to the pure \( v = 0 \) reagent results.

Franck–Condon factors for the BaF products \( (C^2\Pi_{1/2} - X^2\Sigma_g, \Delta v = 0) \) were obtained from the work of Cruse et al.\(^1\) for \( 0 \leq v \leq 9 \) and extrapolated for \( 10 \leq v \leq 19 \). The extrapolations should be quite good due to the very slow change in the \( \Delta v = 0 \) band sequence. For the SrF products \( (A^3\Pi_{5/2} - X^2\Sigma_g, \Delta v = 0) \) we have used unity values for all the levels since the \( \Delta v = 0 \) sequence is at least two orders of magnitude stronger than the \( \Delta v = 1 \) sequence.\(^1\)

Because we are using successive \( P \) branch transitions to excite HF, the reagents differ in \( J \) as well as in \( v \). As mentioned above, Dispert et al.\(^1\) have looked at the rotational dependence of the total cross section for the \( K + \text{HCl} \) reaction and saw a decrease in the total cross section of about a factor of 0.7 for each increase in \( J \) of one, although most of the effect was apparently evident for the lowest \( J \) values of \( J = 1 \) and \( J = 2 \). If a similar behavior is assumed for the present systems, then we may have underestimated the total cross sections that should be applied to equal rotational states. The effect of rotation on the product state \( J \) distribution has not been examined experimentally, and is assumed here to be negligible.

**BaF** \( (v = 2) \) RESULTS

Excitation spectra of BaF are shown in Fig. 2 for pure HF \( v = 0 \); \( v = 0 + v = 1 \); and \( v = 0 + v = 1 + v = 2 \). The third of these spectra continues to show band intensity for an additional four vibrational levels beyond those pictured, but digital channel storage limitations prevented their inclusion in the figure. Subtracting the contribution of \( v = 0 \) reagents (recorded as the “blank” reaction excitation spectrum) from the \( v = 0, 1, \) and \( 2 \) reagent produced product excitation spectrum leads to Fig. 3(a). This is the difference spectrum which shows the difference in the state-to-state cross section between a pure \( v = 0 \) reagent and a combined \( v = 1, v = 2 \) reagent population. Figure 3(b) is reproduced from our earlier work showing this difference spectrum between \( v = 0 \) and \( v = 1 \) reagents.

Following the procedure of spectral normalization and subtraction developed in the Appendix, the effect of pure \( v = 2 \) reagents can be obtained and converted to state specific cross sections. The excitation fraction

![FIG. 2. Excitation spectrum of BaF products using the C^2Π_{1/2} - X^2Σ_g system. The three traces are offset to display all features. Four additional bands out to (19, 19) can be observed but are not shown in the figure.](image)

![FIG. 3. A. Difference spectrum between pure v = 0 reagents and a mixture of v = 1 and v = 2 reagents. Sharp features near (0, 0) and (1, 1) are artifacts of the subtraction process. B. Difference spectrum between pure v = 0 reagents and v = 1 reagents, reproduced from Ref. 7.](image)
values used were $\beta_1 = 0.05$, $\beta_2 = 0.04$, $\gamma_2 = 0.02$. Figure 4 and Table I show the resulting state-to-state cross sections. Included are previous results for reaction from $v = 0$ and $v = 1$. The results are reported as relative $\sigma(v, v')$ where $v$ is the reagent vibrational level and $v'$ is the product vibrational level.

It is instructive to individually evaluate the uncertainties in the $\sigma(v, v')$ values which are due to measurement error and due to errors in assumed excitation fractions. This was not done explicitly in earlier results for the $\sigma(1, v')$ values, but is easily done using Eqs. (8) and (9) of the Appendix. To simplify this we assume all Franck-Condon factors are unity and normalize the data such that the signal intensities of the first reactive vibrational level are numerically equal to the relative cross sections of Tables I and II.

**Table I.** Ba+HF($v$)$\rightarrow$BaF($v''$)+H relative cross sections.

| $v''$ | $\sigma(0, v'')^a$ | $\sigma(1, v'')^b$ | $|\delta\sigma_1|$ | $|\delta\sigma_2|$ | $\sigma(2, v'')$ | $|\delta\sigma_3|$ | $|\delta_{\delta\sigma_3}|$ |
|-------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 0     | 0.32           | 0.32           | 0.04           | 0.02           | 0.32           | 0.1            | 0.04           |
| 1     | 0.33           | 0.33           | 0.04           | 0.02           | 0.33           | 0.1            | 0.04           |
| 2     | 0.21           | 0.21           | 0.04           | 0.02           | 0.21           | 0.1            | 0.04           |
| 3     | 0.07           | 0.07           | 0.04           | 0.02           | 0.21           | 0.1            | 0.04           |
| 4     | 0.03           | 0.185          | 0.01           | 0.07           | 0.185          | 0.025          | 0.15           |
| 5     | 0.01           | 0.157          | 0.01           | 0.07           | 0.157          | 0.025          | 0.15           |
| 6     | 0.158          | 0.01           | 0.07           | 0.158          | 0.025          | 0.15           |
| 7     | 0.159          | 0.01           | 0.08           | 0.161          | 0.025          | 0.15           |
| 8     | 0.163          | 0.01           | 0.08           | 0.161          | 0.025          | 0.15           |
| 9     | 0.158          | 0.01           | 0.08           | 0.161          | 0.025          | 0.15           |
| 10    | 0.052          | 0.01           | 0.05           | 0.098          | 0.025          | 0.1            |
| 11    | 0.028          | 0.01           | 0.03           | 0.095          | 0.025          | 0.06           |
| 12    | 0.017          | 0.01           | 0.02           | 0.079          | 0.025          | 0.04           |
| 13    | 0.009          | 0.01           | 0.01           | 0.073          | 0.025          | 0.04           |
| 14    | 0.010          | 0.01           | 0.01           | 0.072          | 0.025          | 0.04           |
| 15    | 0.009          | 0.01           | 0.01           | 0.072          | 0.025          | 0.04           |
| 16    | 0.008          | 0.01           | 0.01           | 0.072          | 0.025          | 0.04           |
| 17    | 0.007          | 0.01           | 0.01           | 0.072          | 0.025          | 0.04           |
| 18    | 0.006          | 0.01           | 0.01           | 0.072          | 0.025          | 0.04           |
| 19    | 0.005          | 0.01           | 0.01           | 0.072          | 0.025          | 0.04           |

*Reference 1.*

*Reference 7.*

$\delta$ and $\delta^2$ are secondary errors due to difficulty in measuring a zero difference signal.

The error in \( \sigma(2, v'') \) due to intensity errors is now as much as 30% for low product vibrational levels but diminish for most of the high product levels.

Errors due to \( \beta \) and \( \gamma \) are not independent and their correlation depends on the relative laser intensities in the double resonance excitation. If the effects of the first laser are miscalculated then \( \beta \) and \( \gamma \) will be positively correlated since an increase in the first laser pumping effect will increase population in both \( v = 1 \) and \( v = 2 \). Errors in the second laser's effect will cause \( \beta \) and \( \gamma \) to be anticorrelated. We would thus expect errors due to \( \beta \) and \( \gamma \) to be partially correlated. Thus we expect the second term in the expression for \( \delta \sigma_r \) to partially cancel the effect of \( \delta \sigma_p \). If the effect is totally canceled the resulting error is

\[
|\delta \sigma_r| = \frac{\Delta I}{0.04}
\]

If the effect is additive we have

\[
|\delta \sigma_r| = \left| \frac{\Delta I}{0.04} - 2[\sigma(1, v) - \sigma(0, v)] \right|
\]

Because of the sign difference in the absolute value, the two errors are actually comparable so that a partial cancellation of the effects of \( \gamma \) and \( \beta \) occurs. The value of \( \Delta I/0.04 \) is listed in Table I. This error becomes very significant after about \( v = 4 \), but relates only to the scaling of the affected entries in the \( \sigma(2, v) \) column relative to the \( \sigma(1, v)'s \) and \( \sigma(0, v)'s \).

Qualitatively these errors derive as follows: Larger signal fluctuations at low product vibrational levels due to the predominant ground state reagent cause a larger inherent uncertainty in those cross sections. An uncertainty in the excitation fraction for \( v = 1 \) reagents causes a difficulty in scaling the difference signals, such that product vibrational level densities which are most affected by the reagent excitation have relative cross sections for formation which are most affected by a scaling error in \( \beta \). Cross sections for \( v = 2 \) reagents are similarly affected at low product levels by large signal fluctuations and at higher product levels by uncertainties in \( \beta \) and \( \gamma \).  Correlation of \( \beta \) and \( \gamma \) allows cancellation of part of this error.

Aside from the individual rate constants several more qualitative statements can be made by averaging over the detail of the primary results. For each reagent vibrational level, products are seen nearly to the thermodynamic limits of BaF \( v = 6, v = 14, \) and \( v = 24 \) for reagents of HF \( v = 0, v = 1, \) and \( v = 2 \), respectively. The mean product vibrational energy increases from 1.5 to 5.4 kcal for HF \( 1 \) excitation only and the other to \( 8.0 \) kcal representing fractional product vibrational energy release of 21%, 34%, and 29%. It is also interesting to note that of the additional reagent vibrational energy in \( v = 1 \), 35% of it is carried adiabatically to additional product vibration, while only 25% of the additional reagent vibrational energy in \( v = 2 \) (above that in \( v = 1 \)) is carried adiabatically into new product vibrational energy. The total cross section for the reaction is apparently still increasing by going to \( v = 2 \), but as mentioned earlier, this effect cannot be totally attributed to reagent vibration since the rotational state is also changing.

**Sr + HF (\( v = 2 \)) RESULTS**

Because HF \( (v = 0) \) is essentially unreactive with Sr, all of the \( \sigma(0, v) \) cross sections are zero on the scale of the \( \sigma(1, v) \) and \( \sigma(2, v) \). Double resonance pumping of \( v = 2 \) generates a product excitation spectrum which arises from only \( v = 1 \) and \( v = 2 \) reagents. Figure 5 shows the combined \( v = 1, v = 2 \) reagent produced product excitation spectrum compared to the pure \( v = 1 \) reagent produced product excitation spectrum obtained in our laboratory but first seen by Karny et al.\(^3\). Unfortunately, we could not subject one of our reactions zones to \( v = 1 \) excitation only and the other to \( v = 1 \) and \( v = 2 \) excitation to be able to determine the possible change in

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**Table II.** Sr + HF(\( v = 2 \)) - SrF(\( v' \)) + H relative cross sections.

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<th>( \sigma(0, v') )</th>
<th>( \sigma(1, v') )</th>
<th>( \delta \sigma I )</th>
<th>( \sigma(2, v') )</th>
<th>( \delta \sigma q )</th>
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Notes:

* First reported in Ref. 3 but taken from our repeat of the experiment.

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cross section in going from \( v = 1 \) to \( v = 2 \). Since \( v = 1 \) is the first reagent level above the endothermicity, it is entirely conceivable that reaction from \( v = 2 \) may proceed with a significantly higher total cross section. Intensity measurements were made at band head positions by alternately blocking and unblocking the hot band lasing line in the zero order feedback arm of the HF laser. These intensities give a qualitative picture of what the difference spectrum should look like and allowed evaluation of the relative sizes of the two spectra of Fig. 5. In all cases the intensity increased when the hot band transition was present. This increase could be partially due to the fact that in a three level saturation effect a larger population is drawn out of the lowest level than with a two level saturation. The increase could also be due to a real increase in total cross section. It is apparent, however, that \( v = 2 \) reagents populate higher product vibrational levels, since new levels appear in the excitation spectrum.

Our best estimate of the ratio of \( v = 2 \) to \( v = 1 \) reagents present is approximately 1 to 2. Using the assumed excitation ratio between \( v = 1 \) and \( v = 2 \) populations of 2:1, the contribution to the excitation spectrum of Fig. 5 due to \( v = 1 \) reagents can be subtracted according to Eqs. (3c) and (5c) of the Appendix and gives the relative state-to-state cross sections of Table II and illustrated by a bar graph in Fig. 6. Shown for comparison are the rate constants for \( v = 1 \) reagents. Error relationships are also developed in the Appendix resulting in Eqs. (16), (17), and (18). Using the nominal parameters \( \beta_1 = 0.04 \), \( \gamma_2 = 0.02 \), \( \delta_\beta = 0.02 \), \( \delta_\gamma = 0.02 \), and \( \delta_f = 0.01 \) gives for the error in \( (2, v) \):

\[
\begin{align*}
|\delta \sigma_v| &= 2(0.01), \\
\delta \sigma_v &= (f_2 - \sigma(1,v)) \times 0.02, \\
\delta \sigma_v &= -\left(4s(1,v)\right) \times 0.04(0.02). \\
\end{align*}
\]

In this experiment the effect of the first laser does not affect the result since it merely provides a population in the first reactive state and is thus absorbed into the apparatus constant. Errors in the effect of the second laser, however, result in anticorrelation of \( \delta \beta \) and \( \delta \gamma \) such that \( \delta \sigma_v \) and \( \delta \sigma_v \) are now additive. We thus report

\[
|\delta \sigma_v| \approx f(2 - \sigma(1,v)) \times 3.
\]

These values are listed in Table II. Again, the errors due to \( \beta \) and \( \gamma \) are quite large, but primarily represent a scaling error relative to the \( \sigma(1,v) \) values and do not alter the relative values within the list of \( \sigma(2,v) \) results. The relative cross sections from \( v = 2 \) reagents represent an average vibrational energy content of \( 5\frac{3}{2} \) kcal. This means that only 22% of the reagent energy above the reaction endothermicity is partitioned into product vibrational energy. Of the additional reagent vibrational energy in \( v = 2 \) (above that of \( v = 1 \)), 23% is carried adiabatically to product vibration. The total reaction cross section seems to increase only modestly by about 50%.

**DISCUSSIONS AND CONCLUSIONS**

The extension of the reagent energy selection to \( v = 2 \) of HF for reaction with Ba and Sr provides even more detail to consider the dynamics of a specific type of reaction surface, namely a covalent to ionic surface crossing present in this family of reactions. For Ba + HF, it has been shown by Gupta, Perry, and Zare that translational energy is almost as efficient as vibrational energy in overcoming a small apparent barrier, and our recent results show that the product distribution is substantially the same whether reagent vibration or reagent translation is utilized. Now it is also apparent from present results that further increase in reagent vibration extends the high energy tail of the product vibrational energy to nearly the thermodynamic limit, but again causes no great significant shift in the product distribution. In addition, we see evidence of a reduced efficiency of product vibrational energy production, with increased reagent vibrational energy. A similar effect was seen by Gupta et al. for increased reagent translation.
For the Sr + HF reaction, again the product distribution is slightly shifted towards higher energy with increased reagent vibrational energy, in much the same way as Gupta et al. saw it shifted by reagent translational energy. Recent diatomics-in-molecules calculations of various collinear surfaces of the Ca + HCl system by Isaacson and Mackerman have shown that the Ca Cl-H arrangement exhibits a severely restricted pathway between reagents and products due to an collinear to ionic curve crossing. This is in agreement with the surface calculated by Schorr, Green, Chapman, and Zare for the Be + HF system and supports the generalization that all such potential surfaces will exhibit similar features. The present results are consistent then with the picture that due to this restricted pathway to the product valley, all reactive trajectories tend to produce similar product distributions for a given total reactant energy.

ACKNOWLEDGMENTS

This research was supported by the National Science Foundation under NSF CHE76-11468. One of us, (A.T.F.), would like to acknowledge C.A.P.E.S. and the Instituto de Quimica, University of Bahia, Brazil, for support. Part of the optical support of this work was provided through the University of Pennsylvania Regional Laser Laboratory, NSF CHE78-18719.

APPENDIX: GENERATION OF PURE STATE CROSS SECTIONS

The fluorescences signal intensity at a particular product vibronic band due to pure HF (v = 0) reaction can be described as

$$ I(0, v') = k q v_{v'} \sigma(0, v') , $$

where k is an apparatus constant which includes all constant factors in the experiment and is adjusted in the two reaction zones to be equal, q v_{v'} is the Franck-Condon factor for the δω = 0 bands and σ(0, v') is the effective state-to-state cross section for production of the product v' level. When reagents are excited to v = 1, the signal intensity must now be given by

$$ I(0, v') = k q v_{v'} [\alpha(0, v') + \beta(1, v')] , $$

where α is the fraction of HF molecules in v = 0 when only the fundamental line is lasing, β is the fraction of HF molecules excited to v = 1, and σ(1, v') is the state-to-state cross section for forming products at v' from reagents in v = 1. The difference spectrum between the two signals is (since α + β = 1):

$$ \Delta I(v') = k q v_{v'} [\beta(1, v') - \sigma(0, v')] . $$

Thus to generate a pure v = 1 produced excitation spectrum we must add β times the spectrum of pure v = 0 reagent produced products and renormalize by 1/β. Equation (3) also shows that if the state-to-state cross sections are identical for a particular product level, then the removal of the excitation will have no net effect. This fact can be used to confirm the equality of two such cross sections and is independent of the excitation fraction, although the accuracy of the measurement of equality is enhanced by a larger excitation fraction.

If three reagent levels are present due to double resonance excitation, the signal intensity will be given by

$$ I(0 + 1, v'') = k q v_{v''} [\alpha(0, v'') + \beta(1, v'') + \gamma(2, v'')] . $$

Subtracting the v = 0 spectrum [Eq. (1)] gives

$$ \Delta I(v'') = k q v_{v''} [\beta(1, v'') + \gamma(2, v'')] - (\beta + \gamma)(0, v'') . $$

Equation (5) shows that to generate pure v = 2 results we must subtract β times a pure v = 1 spectrum and add β + γ times a pure v = 0 spectrum.

For reactions in which v = 0 is endothermic and non-reactive there is no primary difference spectrum so Eqs. (3) and (5) simply become

$$ I_1 = k q v_{v'} \beta(1, v') , $$

$$ I_2 = k q v_{v'} [\beta(1, v') + \gamma(2, v'')] , $$

since we are looking for relative cross sections only we can simply redefine the apparatus constant k = k' β, giving

$$ I_1 = k' q v_{v'} \sigma(1, v') , $$

$$ I_2 = k q v_{v'} \frac{\beta'}{\beta_1} \sigma(1, v') + \frac{\gamma_2}{\beta_1} \sigma(2, v'') $$

which resembles Eq. (2) except that the sum of the two fractional parts β/β1 and γ/β1 may not necessarily equal one. Equations (3), (5), (3c), and (5c) are used to calculate σ(1, v) and σ(2, v) for the reactions studied.

In all cases the relative cross sections are normalized so that the first reactive vibrational level gives a cross section, when summed over product levels, equal to unity.

Error relationships. Error relationships are easily deduced using simple differential error analysis of Eqs. (3) and (6). If we assume all errors are due to measurements of ΔI and estimates of β and γ, that σ(0, v'') values are fixed when calculating σ(1, v''), σ(1, v'') values are fixed when calculating σ(2, v'') values, and the q v_{v''} are all approximately equal to unity, then the following relations are obtained:

Errors in σ(1, v''). Rewriting Eq. (3) under the above assumption and finding the first partial derivatives

$$ \sigma(1, v'') = \frac{\Delta \sigma}{\beta_1} + o(0, v''), $$

$$ \delta \sigma_1 = \frac{\delta \Delta I}{\beta_1} \text{ uncertainty due to measurement} , $$

$$ \delta \sigma_2 = \frac{\delta \sigma_1}{\beta_1} \text{ uncertainty due to excitation fraction} . $$

If all o(0, v) are zero, the errors in σ(1, v) follow from Eq. (3c) giving δσ1 = 0 and |δσ2| = 0.

Errors in (2, v''). Solving Eq. (5) for σ(2, v'') and evaluating the partial derivatives

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\[ \sigma(2, v'') = \frac{\Delta I}{\gamma_2} - \frac{\beta_2 \sigma(1, v'')}{\gamma_2} + \frac{\beta_2 \sigma(0, v'')}{\gamma_2} + \sigma(0, v''), \quad (10) \]

\[ \delta \sigma_I = \frac{\delta \Delta I}{\gamma_2}, \quad (11) \]

\[ \delta \sigma_{\beta_2} = \frac{\sigma(1, v'') - \sigma(0, v'')}{\gamma_2} \delta \beta_2, \quad (12) \]

\[ \delta \sigma_{\gamma_2} = -\frac{\Delta I - \beta_2 [\sigma(1, v'') - \sigma(0, v'')]}{\gamma_2^2} \delta \gamma_2. \quad (13) \]

For the case in which the $\sigma(0, v)$ are zero we obtain from Eq. (5c), that

\[ \sigma(2, v) = \left( \frac{\beta_1}{\beta_2} \right) \frac{I_2 - \sigma(1, v)}{\gamma_2}. \quad (14) \]

Since we are investigating errors we will approximate $\beta_1/\beta_2 \approx 1$, giving

\[ \sigma(2, v) \approx \frac{\beta_2 [I_2 - \sigma(1, v)]}{\gamma_2}. \quad (15) \]

\[ \delta \gamma_I \approx \frac{\delta \beta_2 I_2}{\gamma_2}, \quad (16) \]

\[ \delta \beta_2 \approx \frac{I_2 - \sigma(1, v)}{\gamma} \delta \beta, \quad (17) \]

\[ \delta \gamma \approx \frac{I_2 - \sigma(1, v) \cdot \beta_1}{\gamma} \delta \gamma. \quad (18) \]

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11. We actually used 4.5% in Ref. 7, but failed to consider rotational degeneracy in calculating the saturation fraction. A proper analysis gives closer to 3.5%, which is still within the uncertainty quoted in that work.