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The effect of collisions in the multiphoton decomposition of 1-bromo 2-fluoroethane

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The multiphoton decomposition (MPD) of 1-bromo 2-fluoroethane, CH_2BrCH_2F, with a pulsed CO_2 infrared laser is reported. The decomposition study was done at constant fluence and at pressures up to 2 kPa. Empirical representations of the pressure dependence of the MPD are reported. A collision-dependent reaction scheme is presented to explain the pressure dependence of the up-pumping through the vibrational manifold.

I. INTRODUCTION

In a recent paper on the MPD of chloroform-*d*, $CDCl_3$, as a function of pressure, a new method of analysis and interpretation of intermolecular vibrational energy transfer was introduced.[1] This present study is one in a series being done to establish the applicability of this method of MPD analysis. The new method expresses the decomposition probability as a multivariable power series expansion of target and product gas partial pressures and takes into account the discrete composition changes of the reaction mixture as the many-pulse experiment proceeds.

The previous experiments[1] with $CDCl_3$ determined, for the fluences and pulse durations used, that the interaction term h_{11} for vibrational energy transfer between excited $CDCl_3$ and the melange for accumulating product "buffer" gases was positive. This was interpreted as a positive collisional energy transfer from one of the components of the product buffer gas, namely, C_2Cl_4 to $CDCl_3$. It was suggested that this transferred energy added to the energy of the $CDCl_3$ molecule and that this energized molecule could then absorb additional photons, circumventing any anharmonic bottleneck, thereby enhancing the decomposition, and/or, simply decompose faster because the energy transferred through the energy pooling mechanism increased the unimolecular decomposition rate. The C_2Cl_4 was implicated because it also had significant photon absorption at the wavelength used to excite the target $CDCl_3$ and was, therefore, also "hot". In this way photon energy initially absorbed by C_2Cl_4 could be transferred to the target, $CDCl_3$, which subsequently decomposed; so-called collision-assisted photosensitizing.

The bromofluoroethane experiment was proposed because it was known that none of the decomposition products absorb at the laser wavelength used to excite the target. Collisions of hot target gas with cold product buffer gas would result in channeling energy out of the target and into the buffer, thereby deactivating the target and decreasing the decomposition probability. It was predicted that the interaction parameter h_{11} would in this instance be negative.

Other studies of bromofluoroethane have been reported but they have dealt primarily with the product ratio for the vinyl fluoride and vinyl bromide decomposition channels.[2,3]

II. EXPERIMENTAL

The laser light source, and experimental method, used are described in Ref. 1. The laser operated in the TEM_{00} mode using $^{12}CO_2$ and was tuned to the $P(28)$ line of the 9 μm band. The pulse was approximately 150 ns long with no discernible tail. The laser beam was focused with a 50 cm BaF_2 lens to a beam waist radius of 0.50 ± 0.04 mm. The cell, fitted with NaCl windows, was 3.7 cm long with a radius of 1.1 cm and was placed at the focal point. The gas inlet to the cell was through a short capillary tube so that the volume of the cell and the cylindrical optical volume were the same to within 1%.

The fluence was calculated from the laser radiant energy E given the form for the fluence at beam center for a Gaussian radial profile normalized to the input radiant energy

$$\phi = 2E/\pi r_w^2,$$

where r_w is the radius of the focused laser beam waist.

The CH_2BrCH_2F was purchased from ICN Biomedicals Inc. and used as received after degassing by freeze-pump-thaw cycling. Initial sample pressures were measured with an MKS Baratron gauge. Infrared spectra were recorded with a Bomem DA3.02 spectrometer.

At the end of each irradiation period, the content of the cell was analysed with the infrared spectrometer. The areas of the resulting absorption peaks were compared with areas of peaks from known amounts of CH_2BrCH_2F and H_2CCHF. The areas were measured between 987 and 1116 cm^{-1} for bromofluoroethane and between 1122 and 1196 cm^{-1} for vinyl fluoride. The error in the vinyl fluoride pressures was the sum of two terms; an estimated error of ± 20 Pa, the pressure at which the signal to noise in the infrared spectra was equal to two, plus 5% in the pressure readings to account for variability in defining the baseline for the absorption peak area measurement.

The signal to noise at the bromofluoroethane absorption was much better; the minimum signal-to-noise error was ± 4 Pa. The vinyl fluoride peak overlapped the bromofluoroethane peak. This was corrected for by subtracting from the bromofluoroethane areas the area due to vinyl fluoride. This added to the bromofluoroethane error to give a total experimental uncertainty of 6% for each point.

[a)] Contribution No. 10168.

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III. ANALYSIS

The method of analysis has been described earlier.[1] To observe a measurable change in the amount of CH_2BrCH_2F due to multiphoton decomposition, it is necessary to irradiate the cell with a large number of pulses from the CO_2 laser. During this many pulse experiment, the partial pressure of the CH_2BrCH_2F will decrease. N_0 is the initial number of molecules in the cell and $f(\phi,\alpha,\beta)$ is the single-pulse decomposition probability: a function of fluence ϕ (the distinction between fluence and intensity cannot be made in this study), of the CH_2BrCH_2F partial pressure α, and of the partial pressure of the buffer gas β. The buffer gas includes all gases other than the target gas that can affect the decomposition probability. The amount of CH_2BrCH_2F left after m pulses, N_m, is

$$N_m = N_0 \prod_{k=1}^{m} (1 - f_k(\phi_k, \alpha_{k-1}, \beta_{k-1})). \tag{1}$$

(Note that the volume ratio defined in Ref. 1 is equal to one for this study and is not included in these equations.) It was assumed that the functional dependence of $f(\phi,\alpha,\beta)$ on fluence and pressures is given by

$$f(\phi,\alpha,\beta) = \sum_{i=1} \sum_{j=0} h_{ij}(\phi)\alpha^{i-1}\beta^{j}. \tag{2}$$

For the experiments described here the variation in fluence over the measurements was purposely small. The laser fluence was adjusted to be approximately 5.1 J/cm². The shot-to-shot variation was about 20%.

TABLE I. Results of the fit of the experimental data to Eqs. (3) and (4). The observed minus calculated, $O-C$, is given along with the weighted squared error (the contribution to the chi-square) for each datum. In the fits each datum is weighted as the squared inverse of the experimental error (see text). The bromofluoroethane pressure α_m and the vinyl fluoride pressure β_m are treated as separate data points.

α_0(kPa)		Pulses m	Fluence J/cm²	α_m kPa	$O-C$ kPa	Weighted Sq Error	β_m kPa	$O-C$ kPa	Weighted Sq Error
0.67		500	5.2	0.66	0.02	0.1	0.02	− 0.00	0.0
0.67		1 500	5.3	0.63	0.03	0.3	0.03	− 0.03	2.2
0.67		3 500	5.2	0.59	0.03	0.6	0.06	− 0.05	4.6
0.67		1 000	5.4	0.60	− 0.02	0.2	0.04	− 0.01	0.1
0.67		2 000	5.4	0.59	0.01	0.0	0.07	− 0.00	0.0
0.67		4 000	5.3	0.55	− 0.00	0.0	0.09	− 0.03	1.0
0.67		7 000	5.2	0.49	− 0.04	1.3	0.08	− 0.05	3.9
1.33		250	5.2	1.25	− 0.03	0.1	0.08	0.03	1.6
1.33		750	4.9	1.13	− 0.05	0.4	0.18	0.03	0.9
1.33		1 000	5.0	1.14	0.01	0.0	0.15	− 0.04	2.5
1.33		1 250	5.0	1.00	− 0.09	2.0	0.24	0.01	0.1
1.33		2 000	5.3	0.96	− 0.04	0.5	0.32	0.00	0.0
1.33		3 000	5.1	0.99	0.07	1.0	0.29	− 0.10	7.5
1.33		3 000	4.9	0.94	0.01	0.0	0.41	0.02	0.3
1.33		5 000	5.0	0.94	0.08	1.6	0.35	− 0.11	8.0
1.33		5 000	4.5	0.85	− 0.01	0.0	0.46	0.01	0.1
1.33		7 500	4.7	0.77	− 0.06	1.4	0.52	0.05	1.2
1.33		10 000	4.8	0.77	− 0.07	1.5	0.56	0.08	2.7
2.00		250	5.3	1.77	− 0.09	0.6	0.22	0.09	7.7
2.00		750	5.4	1.53	− 0.04	0.2	0.49	0.09	3.9
2.00		1 000	5.3	1.44	− 0.01	0.0	0.51	− 0.02	0.1
2.00		1 000	5.0	1.47	0.02	0.0	0.56	0.03	0.5
2.00		1 250	5.5	1.36	0.02	0.0	0.65	0.03	0.3
2.00		2 000	5.6	1.20	0.06	0.5	0.84	0.02	0.1
2.00		2 000	5.1	1.17	0.03	0.1	0.80	− 0.02	0.1
2.00		3 000	5.2	1.05	0.02	0.1	0.89	− 0.04	0.3
2.00		3 000	5.4	1.07	0.04	0.4	0.93	0.01	0.0
2.00		4 000	5.1	0.95	− 0.03	0.3	0.97	0.00	0.0
2.00		5 000	5.3	0.91	− 0.06	0.8	1.03	0.05	0.4
2.00		5 000	5.2	0.93	− 0.05	0.7	0.96	− 0.03	0.1
2.00		6 000	5.2	0.89	− 0.07	1.4	1.08	0.09	1.4
2.00		7 000	5.3	0.86	− 0.10	2.9	1.08	0.09	1.4
2.00		7 500	5.1	0.98	0.02	0.1	1.04	0.05	0.4
2.00		10 000	5.0	0.92	− 0.04	0.4	1.11	0.11	2.2
	β_0(kPa) CH_2CHF								
0.89	1.78	750	5.0	0.88	− 0.01	0.0	1.73	0.04	0.1
0.89	1.78	2 000	5.0	0.87	− 0.02	0.1	1.72	0.03	0.1
1.33	1.33	1 000	5.1	1.29	0.21	6.0	1.41	− 0.10	1.2
1.33	1.33	2 000	5.2	1.22	0.20	6.0	1.45	− 0.11	1.4
1.33	1.33	5 000	5.1	1.14	0.13	2.9	1.53	− 0.05	0.2

TABLE II. The model parameters and, in parentheses, their standard deviations in units of the least significant figures.

h_{20}	$1.27(8)\times10^{-4}\text{kPa}^{-1}$
h_{11}	$-8.09(6)\times10^{-4}\text{kPa}^{-1}$
h_{21}	$7.3(7)\times10^{-4}\text{kPa}^{-2}$
S	$0.95(2)$

The target gas partial pressure after m pulses, α_m, was calculated from

$$\alpha_m = (N_m/N_0)\alpha_0. \tag{3}$$

In this study the buffer gas came from two sources; the multiphoton decomposition products and, for some experiments, the initial partial pressure of gas other than the bromofluoroethane target gas, β_0. The buffer gas accumulated with successive pulses and so a pulse-dependent buffer gas contribution was assumed. For the mth pulse,

$$\beta_m = S(\alpha_0 - \alpha_{m-1}) + \beta_0. \tag{4}$$

The S constant depends on the stoichiometry of the decomposition and the channel ratio. Implicit in the above equation is that the initial added buffer gas has the same composition as the MPD product gas. Experimentally this was not strictly true. The initial added buffer gas was always just H_2CCHF, whereas the decomposition products contained HBr as well. In general the several molecular components making up the product buffer gas must be accounted for separately, however, in this study it was assumed that the contribution to the pressure effect from HBr could be neglected. With this assumption the product buffer gas was treated as a single entity; H_2CCHF. The effective h_{ij} coefficients were determined empirically given the experimental values of α_m and β_m for initial pressures α_0 and β_0.

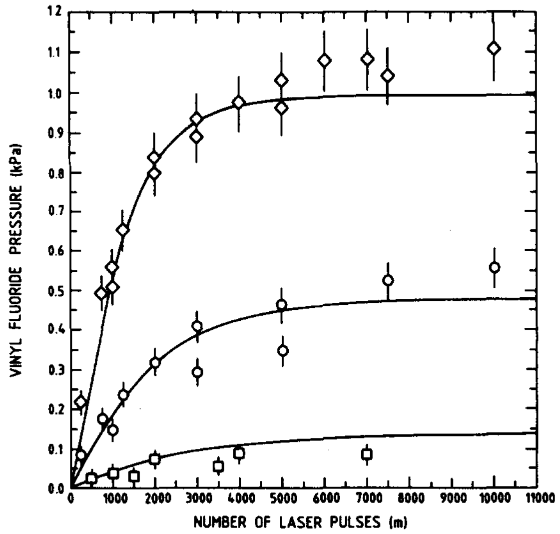

FIG. 2. Pressure of the decomposition product vinyl fluoride vs number of pulses for various initial pressures of CH_2BrCH_2F. The initial pressures in kPa are represented by □ for 0.67, ○ for 1.33, and ◇ for 2.00, respectively.

IV. RESULTS AND DISCUSSION

The experimental results for the multiphoton decomposition of CH_2BrCH_2F are presented in Table I. The determinable model parameters are given in Table II. Some of the results of Table I are also displayed in Figs. 1–3. In Fig. 1 the ratio $N_m/N_0 (= \alpha_m/\alpha_0)$ is plotted to demonstrate the pressure effect more clearly. In the figures, the calculated values appear as continuous lines. In the fits, each datum was weighted by the inverse square of the experimental error defined earlier. The chi-square for the best fit was 93 for 75 degrees of freedom. The experimental minus the calculated

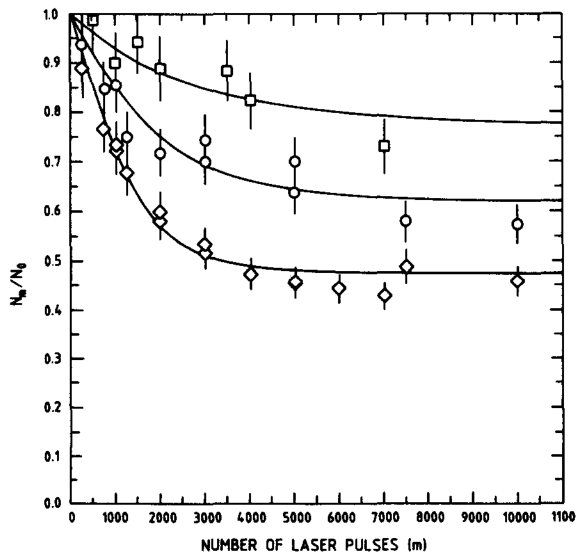

FIG. 1. Fraction of CH_2BrCH_2F remaining, N_m/N_0, vs number of pulses for various initial pressures of CH_2BrCH_2F. The initial pressures in kPa are represented by □ for 0.67, ○ for 1.33 and, ◇ for 2.00, respectively.

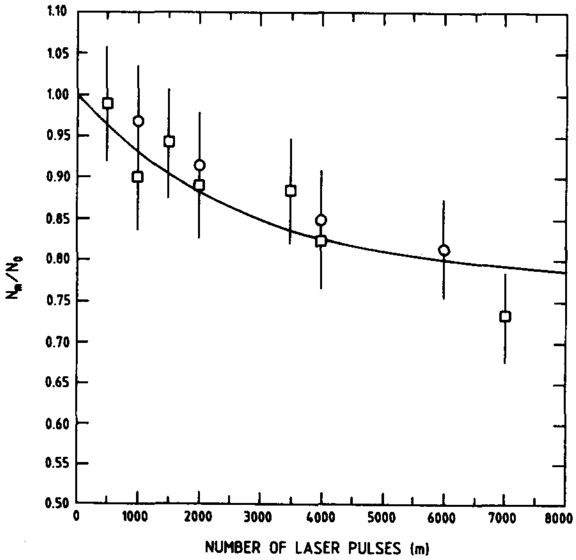

FIG. 3. Fraction of CH_2BrCH_2F remaining N_m/N_0, vs number of pulses for 0.67 kPa CH_2BrCH_2F (□) and 0.67 kPa of CH_2BrCH_2F plus 0.67 kPa added Xe (○).

values ($O - C$), show no obvious correlation with the slight variation in fluence recorded in Table I and therefore support the assumption of constant fluence.

Preliminary fits showed the only statistically significant expansion coefficients influencing the quality of the fits were h_{20}, h_{11}, and h_{21}. Consequently, in the final fit all other h_{ij} parameters were fixed at zero (see Table II).

The pressure dependence of MPD can be generally understood in terms of three processes: rotational hole filling,[4] vibrational energy pooling,[5] and circumvention of an anharmonic bottleneck.

Rotational hole filling is often invoked as an explanation for decomposition probability increasing with pressure. The laser-depleted effective ground-state rotational population is refilled through collision-induced rotational transitions from population outside the initial laser frequency bandwidth. Increasing the effective ground-state population in this way allows more radiation to be absorbed, leading to a pressure-dependent decomposition enhancement. These collision-induced rotational transitions are usually rotational to rotational (RR) and rotational to translational (RT) energy transfers. Vibration to rotation (VR), collisional energy transfer is generally thought to be inefficient.[6]

RT energy transfer is often investigated by the addition of a monoatomic buffer gas. The monoatomic, having no vibrational or rotational structure, can only accomodate vibrational to translational (VT) or RT energy transfer between a vibrationally hot polyatomic and itself. The probability of VT is small because the vibrational energy quantum is so large. Conversely, rotational energy separations are much smaller and rotational energy transfer from a polyatomic to translational energy of a monoatomic is more probable.[7] Therefore, an added monoatomic gas will promote rotational hole filling through RT energy transfer, but will not contribute to any vibrational energy transfer processes such as anharmonic bottleneck breaking or energy pooling. If RT energy transfer contributed to the pressure effect observed in this study, then addition of xenon to bromofluoroethane should result in an increased decomposition yield. In Fig. 3 some of the MPD results of 0.67 kPa CH_2BrCH_2F and 0.67 kPa CH_2BrCH_2F, plus an added 0.67 kPa Xe are plotted. Within experimental error the addition of the monoatomic buffer gas has no effect on bromofluoroethane MPD at these pressures and so RT energy transfer can be excluded as an explanation for the pressure effect observed in this study.

Rotational hole filling can also be caused by RR collisions. The laser excites vibrational levels, but if, as is generally observed,[6] VR energy transfer is inefficient, then the rotational population should be relatively unexcited. RR collisions between unexcited rotational populations would then be responsible for an enhancement of the MPD with increasing pressure. If this were true, then addition of a buffer gas, like H_2CCHF, with its unexcited ground rotational states, should enhance the MPD of bromofluoroethane. Experimentally it is found that the decomposition is lowered with the addition of the buffer gas. If RR induced rotational hole filling is occurring, then it is being overwhelmed by some other effect.

The pressure effect can be understood in terms of vibrational to vibrational (VV) energy transfer. The two possibilities, overcoming of an anharmonic bottleneck and energy pooling, cannot be separated by this study and the experimentally determined h_{ij} parameters may contain contributions from each. Both mechanisms are essentially the same. If the vibrational energy transfering collisions happen during the laser pulse then the collision partners can absorb additional photons. This will prove important when vibrational anharmonicity renders photons, initially resonant with the initial rungs up the vibration ladder, out of resonance with later, higher, rungs. In this instance a bottleneck to further photon up-pumping occurs that can be alleviated with collision-assisted vibrational energy transfer. This can only happen during the pulse. The other VV mechanism, energy pooling, can happen both during and after the pulse. Vibrational energy transfer results in one of the collision partners becoming more energetic, and since the unimolecular decomposition rate constant increases rapidly with energy, this translates into an increase in the decomposition. The mechanism of overcoming an anharmonic barrier is differentiated from energy pooling by when photons are absorbed relative to the collisions. It is useful to associate the h_{ij} parameters with Lindemann-like[8] collision reactions. For example, vibrational energy pooling can be described by the following collision sequences:

$$\mathrm{A} \overset{h\nu}{\Rightarrow} \mathrm{A}^*,$$

$$\left.\mathrm{A}^* \overset{k_1^*}{\Rightarrow} \mathrm{B}\right\} h_{10},$$

$$\left.\begin{array}{c} \mathrm{A}^* + \mathrm{A}^* \overset{k_2}{\underset{k_{-2}}{\rightleftarrows}} \mathrm{A}^{**} + \mathrm{A} \\ \mathrm{A}^{**} \overset{k_1^{**}}{\Rightarrow} B \end{array}\right\} h_{20},$$

$$\left.\mathrm{A}^* + \mathrm{B} \overset{k_2'}{\underset{k'_{-2}}{\rightleftarrows}} \mathrm{A}^{*-\delta} + \mathrm{B}^{\delta}\right\} h_{11},$$

where the superscripts * indicate a generalized excitation energy distribution due to photon absorption or collision. The number of *'s is a qualitative representation of the energy and δ indicates a lower energy than a *. The k_1 is the energy-dependent unimolecular kinetic rate constant and the k_2's are bimolecular rate constants. The model parameters associated with each reaction are also listed. For an h_{ij} the sum of $i + j - 1$ is the number of collisions in the reaction sequence where i molecules of A and j molecules of B collide. Here A is assumed to be the only candidate that can decompose at this fluence so there are no $i = 0$ terms. The anharmonic barrier breaking description is obtained from the above energy pooling description by simply inserting in each of the sequences, after each collision, a line like

$A^{m*} \overset{h\nu}{\Rightarrow} A^{n*}$ to represent the possibility of further photon absorption after the collisional energy transfer circumvents an anharmonic barrier.

In this study the relevant collisional activation sequences are represented by the h_{20}, h_{11}, and h_{21} terms in the model. The fact that h_{10} was indeterminable indicates that, for these experimental conditions, decomposition without a collision is not significant when compared to the collisional activation sequences. If, upon excitation, most of the molecules do not possess enough energy for rapid decomposition (relative to collisional deactivation), then in order to decompose, energy-transferring collisions with other excited species will become important.

The main objective of the present study was to investigate the role of the product buffer gas during the course of the many pulse experiment. Recall the previous study on chloroform-*d*, described briefly in the introduction.[1] In that study, the MPD product gas C_2Cl_4 was vibrationally hot as it also absorbed the radiation used to decompose the target gas. Collisions with the vibrationally hot product gas were seen to enhance the decomposition of $CDCl_3$. The target gas for this study, bromofluoroethane, was chosen because its decomposition products did not absorb at the illumination wavelength and so the product buffer gases would be vibrationally cold. For this study it was predicted that the product buffer gases should quench the decomposition. Verification of this can be seen graphically in Fig. 1 where the N_m/N_0 ratio is seen to level off at high pulse numbers. Also in Table I results are listed that show the addition of 1.78 kPa of "product" vinyl fluoride to 0.89 kPa of bromofluoroethane all but quenches the decomposition.

In the chloroform-*d* experiment the h_{11} model parameter was positive. This was interpreted as representative of the product buffer gas collisional enhancement of the $CDCl_3$ MPD. If the interpretation of these model parameters is reasonable then, in this instance where the product buffer gas is cold, h_{11} should be negative. As predicted, the h_{11} parameter is negative (Table II).

The method of analysis outlined in this paper determines parameters that can be interpreted as the relative contributions to the decomposition probability from various collisional schemes. The positive h_{ij}'s when multiplied by the partial pressures raised to the appropriate powers, give the relative contributions of the various collision sequences to the product yield. Likewise, the negative h_{ij}'s account for the relative contributions of the various collision sequences to the overall deactivation. The rationale for a negative h_{11} was outlined above. A positive h_{20} is understood in terms of a collision between two hot target molecules, neither hot enough to decompose on its own, to produce one very hot molecule and one somewhat colder molecule. This either alleviates an anharmonic barrier allowing further photon absorption and subsequent decomposition, or, the very hot molecule, by virtue of its increased internal vibrational energy, simply decomposes with an increased unimolecular rate. The single collision parameters h_{20} and h_{11}, can thus be understood in terms of activation and deactivation processes.

These are two reaction sequences that must be considered for the h_{21} parameter. The first is

$$\left.\begin{array}{c} A^* + A^* \underset{k'_{-2}}{\overset{k'_2}{\rightleftarrows}} A^{**} + A \\ A^{**} + B \underset{k'_{-2}}{\overset{k'_2}{\rightleftarrows}} A^{**-\delta} + B^{\delta} \\ A^{**-\delta} \overset{k_1^{**-\delta}}{\Rightarrow} B \end{array}\right\} h_{21}.$$

This is essentially a buffer gas deactivated h_{20}-type sequence. The A^{**} molecules that do not have time to decompose relative to deactivation by cold B molecules will now be at a lower energy; represented figuratively by $A^{**-\delta}$ above. At this lower energy the unimolecular decomposition rate is much slower but still fast enough that it contributes to the yield.

The second possible h_{21} sequence is represented as

$$\left.\begin{array}{c} A^* + B \underset{k'_{-2}}{\overset{k'_2}{\rightleftarrows}} A^{*-\delta'} + B^{\delta'} \\ A^* + A^{*-\delta'} \underset{k'_{-2}}{\overset{k'_2}{\rightleftarrows}} A^{**-\delta'} + A \\ A^{**-\delta'} \overset{k_1^{**-\delta'}}{\Rightarrow} B \end{array}\right\} h_{21}.$$

The cold B molecules collide with the excited A^* molecules and some of the energy is transfered from A^* to B. The cooled-target molecule, represented figuratively by $A^{*-\delta'}$, can undergo an activating collision with a hot target molecule yielding an even hotter A molecule that then goes on to decompose. The distinction between during and after the pulse cannot be made with the present experiment and so the possibility of absorbing additional photons after the various collisions must be included.

There was no indication of vinyl bromide in the decomposition products and so it is concluded that, under the experimental conditions, the elimination of HBr from CH_2BrCH_2F is the dominant decomposition channel. The parameter *S* was allowed to vary and was found to be equal to 95(2)%. The *S* parameter is the product of the stoichiometric ratio and the channel ratio. In this instance, the stoichiometric ratio is one and so the *S* parameter is just the channel ratio. Earlier work[2,3] suggested another channel where HF was eliminated. This channel was not detected explicitly in this study. The initial assumption that the vinyl fluoride was effectively the only collisionally active decomposition product buffer gas is supported by the same h_{ij} parameters being able to account for all the experimental data, including both the data from decomposition of neat bromofluoroethane where the buffer gas is produced during the course of the irradiation, as well as the data were vinyl fluoride was added before the cell was irradiated. The HBr was not expected to contribute to the efficiency of collisional energy transfer for two reasons; first, much of it was gettered by the walls of the reaction cell, and second, HBr with its low density of vibrational states, relative to vinyl fluoride, is not expected to be as effective in VV transfer.

V. CONCLUDING REMARKS

The pressure dependence of the multiphoton decomposition of CH_2BrCH_2F has been examined and the results have been used as the second example of a new method of analysis for a multipulse decomposition experiment. The decomposition probability was modeled with a two-variable power series expansion in partial pressures of reactant and of product gases and model parameters were determined from a fit to experimental data. The model parameters have been associated with various collision sequences to explain the pressure dependence of CH_2BrCH_2F multiphoton decomposition. It is suggested that the mechanism should rely upon two collisionally assisted processes. First, vibrational up-pumping, as an aid in exciting CH_2BrCH_2F sufficiently to allow unimolecular decomposition (energy pooling). Second, collisionally assisted circumvention of any up-pumping bottleneck due to vibrational anharmonicity. A third process often associated with MPD pressure effects, rotational hole filling, has been shown to be insignificant when compared to the above VV processes. Some of the future work in this laboratory will test the applicability of this new method of analysis to the MPD of other molecules.

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