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PHOTODISSOCIATION OF $\text{CF}_2\text{Br}_2$ AT 248 NM BY THE
MOLECULAR BEAM METHOD

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ABSTRACT

The photochemistry of CF$_2$Br$_2$ at 248 nm has been studied using the crossed laser-molecular beam technique. The only primary reaction channel observed is atomic bromine elimination: 

\[
\text{CF}_2\text{Br}_2 \rightarrow \text{CF}_2\text{Br} + \text{Br}
\]

Laboratory angular and time-of-flight distributions of the CF$_2$Br and Br primary products were measured and used to derive the center-of-mass (c.m.) product recoil energy and angular distributions for this reaction. The average c.m. recoil energy of the products is 21.3 kcal/mole. The shape of the c.m. angular distribution indicates that the transition dipole moment is polarized parallel to the Br-Br direction in CF$_2$Br$_2$. The molecular bromine elimination reaction, 

\[
\text{CF}_2\text{Br}_2 \rightarrow \text{CF}_2 + \text{Br}_2
\]

does not occur to a measurable extent at 248 nm. However, CF$_2$ radicals are produced in abundance under collision-free conditions, due to the efficient secondary photodissociation of some of the CF$_2$Br primary product.
PHOTODISSOCIATION OF CF₂Br₂ AT 248 NM BY THE MOLECULAR METHOD

I. INTRODUCTION

Two studies of KrF (248 nm) laser photolysis of CF₂Br₂ in gas cells have already been reported.¹,² Sam and Yardley¹ observed prompt fluorescence between 250-460 nm when they irradiated CF₂Br₂ with a KrF laser pulse. Most of the fluorescence could be assigned to ν₂ = 5 and 6 progressions of the CF₂ A¹B₁ → X¹A₁ electronic transition. The fluorescence intensity was linear in excitation intensity under their conditions (they report laser intensities between 10-100 MW/cm², corresponding to energy fluences of 0.12-1.2 J/cm² for their 12 ns pulse width). Sam and Yardley suggested that the CF₂ fluorescence might result from the following two-step process. First, ground electronic state CF₂ radicals are formed in the reaction

(1) CF₂Br₂ → CF₂ (X¹A₁) + Br₂.

Then, the CF₂ A¹B₁ (060) and (050) levels are populated by resonant absorption from the X (000) level:

(2) CF₂ X (000) → CF₂ A (060, 050).

The linear power-dependence of the fluorescence intensity can be explained if the second resonant absorption step is saturated.

The identification of reaction (1) as the primary photodissociation process is only speculation. However, there is little doubt that step (2) is correctly assigned. The origin of the 2₅₀ vibronic transition in CF₂ occurs at 248.4 nm,³ which is within the KrF laser bandwidth, so this transition is particularly favorable. The 2₆₀ origin occurs at
251.9 nm, but rotational transitions involving \( K'' = 16 \) will still be resonant. \( ^4_5 \psi_0^n \) transitions with \( n < 5 \) require higher and higher \( K'' \) values to put them in resonance with the KrF laser line. The fact that these transitions are not observed to an appreciable extent indicates that few ground electronic state \( CF_2 \) radicals are formed in such high rotational levels.

Wampler, Tiee, Rice, and Oldenborg\(^2\) performed a similar experiment on \( CF_2Br_2 \) and obtained results generally in good agreement with those of Sam and Yardley. However, there was one significant discrepancy. Wampler et al. observed a quadratic power dependence of the \( CF_2 \) fluorescence intensity for energy fluences between 3 and 9 J/cm\(^2\). This clashes with the linear power dependence reported by Sam and Yardley. In any case, Wampler et al. also rationalized their results in terms of reactions (1) and (2), but they assumed that step (2) is not saturated.

We have used the crossed laser-molecular beam method to study the photochemistry of \( CF_2Br_2 \) at 248 nm under collision-free conditions. The only primary reaction channel observed is Br atom elimination:

\[
(3) \quad CF_2Br_2 \rightarrow CF_2Br + Br.
\]

Laboratory angular and time-of-flight distributions of the \( CF_2Br \) and Br products were measured and used to derive the center-of-mass product recoil energy and angular distributions for reaction (3). No evidence for reaction (1) was obtained. Br\(_2\) elimination is not an important photodissociation channel at 248 nm. However, \( CF_2 \) radicals are produced under collision-free conditions, due to efficient secondary photodissociation of the \( CF_2Br \) primary product:
The secondary CF$_2$ and Br product yields exhibit a nearly linear power dependence, indicating that the second absorption step is strongly saturated.

(4) $\text{CF}_2\text{Br} \rightarrow \text{CF}_2 + \text{Br}$. 
EXPERIMENTAL DETAILS

The molecular beam was formed by bubbling Ar carrier gas through a CF$_2$Br$_2$ reservoir maintained at -20°C (CF$_2$Br$_2$ partial pressure = 124 torr$^6$) and expanding the mixture through a 0.12 mm diameter hole at a total stagnation pressure of 500 torr. The tip of the nozzle was heated to 240°C to inhibit cluster formation in the supersonic expansion. The velocity distribution of the CF$_2$Br$_2$ beam was determined by conventional time-of-flight (TOF) measurements. Parameterizing the beam number density velocity distribution in the usual way, $N(v) \propto v^2 \exp[-(v - S)^2/a]$, we obtained as best-fit parameters $a = 0.557$, $S = 10.51$, with $a$ in units of $10^4$ cm/s. This gives a most probable beam velocity of $5.91 \cdot 10^4$ cm/s, and a FWHM velocity spread of 16%. After skimming, the beam passed through two additional differential pumping regions before entering the main vacuum chamber, where it was crossed at right angles by the laser beam. The distance from the nozzle tip to the interaction region was 10.0 cm. The molecular beam was defined to an angular divergence of 1.6°, giving a 2.7 mm beam diameter at the interaction region.

For most of the measurements, the Lambda Physik EMG 101 excimer laser was operated at a repetition rate of 30 Hz, and the average laser power was maintained constant at 3W (100 mJ/pulse). For the power dependence measurements, the average pulse energy was decreased by reducing the concentration of F$_2$ and/or Kr in the laser cavity. The unpolarized, rectangular-shaped laser beam was focussed to a $-4$ mm$^2$ spot at the point where it crossed the molecular beam by a 35 cm focal length, UV-grade fused silica lens. For 100 mJ pulse energies, this results in a (time-integrated) photon flux of $\phi = 3 \cdot 10^{18}$ photons/cm$^2$-
pulse and laser intensities of ~160 MW/cm² (assuming a 16 ns pulse duration, as quoted by Lambda Physik). The absorption cross section of CF₂Br₂ at 248.4 nm is \( \sigma = 6 \cdot 10^{-19} \text{ cm}^2 \). This suggests that the CF₂Br₂ dissociation yield should be entering the saturation region at our highest pulse energies. (At 100 mJ/pulse, the fraction of undissociated molecules should be \( e^{-1.8} = 0.17 \)). However, our results (to be presented in the next section) show that the dissociation yield is still nearly linear in laser power at 100 mJ/pulse. This means that probably not more than half of the CF₂Br₂ molecules are dissociating at 100 mJ/pulse; either the above value for the CF₂Br₂ absorption cross section, or our estimate of the photon flux (or both) must be somewhat too high. A two-fold reduction in the product \( \sigma \cdot \phi \) would give consistency with the experimental results.

Photodissociation products were detected in the plane of the laser and molecular beams by a rotatable ultra-high vacuum mass spectrometer, consisting of an ionizer, a quadrupole mass filter, and a Daly-type ion counter. The distance from the interaction region to the center of the ionizer is 20.8 cm. CF₂Br⁺, Br⁺, CF₂⁺, and CF⁺ TOF distributions were recorded at several detector angles by a 255-channel multiscaler. The scaler was triggered by a reference pulse from the excimer laser. The offset between the reference pulse and the actual laser pulse was only 200 ns and was ignored. TOF distributions were accumulated for between \( 2 \cdot 10^4 \) and \( 10^5 \) laser pulses at each angle. With the detector positioned \( 10° \) from the molecular beam and 100 mJ pulse energies, the observed signal levels ranged from 4.3 counts/pulse at Br⁺ to 0.4 counts/pulse at CF₂Br⁺. No Br₂⁺ signal could be detected (<0.004
counts/pulse at the 1σ confidence level).
RESULTS AND ANALYSIS

A. \( \text{CF}_2\text{Br}_2 \rightarrow \text{CF}_2\text{Br} + \text{Br} \)

The only primary dissociation process at 248 nm is the bromine atom elimination reaction (3). This process was studied by monitoring the parent ion of the \( \text{CF}_2\text{Br} \) product in the mass spectrometer. The measured \( \text{CF}_2\text{Br}^+ \) TOF distributions are shown by the circles in Fig. 1. (The distributions have been normalized to the same peak height at each angle). Note that the time scale in Fig. 1, as well as other TOF distributions to be shown later, includes the transit time of the ions through the mass spectrometer. (For our operating conditions, the ion transit time in \( \mu s = 1.8 \sqrt{M} \), where \( M \) is the detected ion mass in amu's). To convert to laboratory velocities, the displayed flight times must be corrected for ion transit time and divided into 20.8 cm.

The laboratory angular distribution of \( \text{CF}_2\text{Br} \) is shown in Fig. 2. The points were obtained by integrating and normalizing the \( \text{CF}_2\text{Br}^+ \) TOF distributions in Fig. 1. At each angle, background subtraction was performed by averaging the 20 channels preceding the peak in the TOF distribution. The error bars in Fig. 2 represent plus and minus two standard deviations of the statistical counting error.

The data in Figs. 1 and 2 were used to determine the center-of-mass (c.m.) translational energy and angular distributions for the products of reaction (3). As usual, a trial-and-error fitting procedure was used. The c.m. angular distribution must be of the form

\[ w(\theta) = \frac{1}{4\pi} [1 + \beta P_2(\cos \theta)], \]

where \( \theta \) is the angle between the electric vector of the laser light and
the final (c.m.) recoil direction of the products. The anisotropy parameter, $\theta$, is constrained to lie in the range $-1 \leq \theta \leq 2$. A completely flexible point form for the product translational energy distribution, $P(E_T)$, was used. $E_T$ represents the combined c.m. translational energy of the CF$_2$Br and Br products.

The shapes of the laboratory TOF distributions are mainly sensitive to the $P(E_T)$, while the shape of the laboratory angular distribution is mainly sensitive to $\theta$. We started with the TOF distributions. We set $\theta = 0$ and found a triangular-shaped $P(E_T)$ which had about the right mean energy and width to fit the peaks in the TOF distributions. This $P(E_T)$ was then used to calculate the laboratory angular distribution of CF$_2$Br, and $\theta$ was adjusted until the calculated and experimental angular distributions agreed. The $P(E_T)$ was then refined, and $\theta$ readjusted, until a good simultaneous fit to all of the data was obtained. The final fits are shown by the solid curves in Figs. 1 and 2. They were calculated using the solid-line $P(E_T)$ shown in Fig. 3 and $\theta = 1.21$. This $P(E_T)$ has a mean translational energy of 23.5 kcal/mole and a FWHM energy spread of 6.3 kcal/mole. The two dashed curves in Fig. 2, calculated using the same $P(E_T)$ but different values of $\theta$, illustrate the sensitivity of the data to the anisotropy parameter.

B. CF$_2$Br$_2 \rightarrow$ CF$_2$ + Br$_2$

With the mass spectrometer tuned to Br$_2^+$ (m/e = 160), we measured the TOF distribution shown in Fig. 4. This distribution was summed over $10^5$ laser pulses with the detector positioned 10° from the molecular beam. This proves that Br$_2$ elimination does not occur to any significant extent at 248 nm.
C. Secondary Photodissociation of CF$_2$Br

The CF$^+$ TOF distribution measured at 10° is shown in Fig. 5. A sharp feature, which is clearly due to fragmentation of CF$_2$Br to CF$^+$ in the ionizer, is seen superimposed on a broad underlying background signal. TOF distributions of CF$_2^+$ (not shown) are qualitatively similar, although the ratio of the underlying signal to the CF$_2$Br signal is much smaller than in the case of CF$^+$. The underlying CF$^+$ and CF$_2^+$ signals must be assigned to CF$_2$ radicals. CF$_2$ radicals could arise spontaneously if some of the CF$_2$Br primary products are formed with internal energies exceeding the CF$_2$-Br bond energy. It turns out (see Sec. IV) that this is actually possible, but only if ground electronic state Br atoms are produced in reaction (3). However, the excess energy available for the spontaneous decay would be quite small, and all that would be expected in the CF$^+$ and CF$_2^+$ TOF distributions would be a slight broadening at the base of the CF$_2$Br peak. This effect is not observed. Therefore, we do not believe that spontaneous CF$_2$Br decay is occurring to any significant extent.

In fact, the fastest CF$^+$ and CF$_2^+$ signals are much too fast to be accounted for by spontaneous unimolecular decay of hot CF$_2$Br. The underlying CF$^+$ and CF$_2^+$ signals can only be due to CF$_2$ radicals produced via secondary photodissociation of CF$_2$Br, reaction (4). From the fastest observed CF$^+$ signal (marked by the arrow in Fig. 5), we calculate that the CF$_2^+$-Br products of reaction (4) are formed with a maximum c.m. recoil energy of ~70 kcal/mole. The large amount of translational energy released in the secondary reaction explains why the CF$_2$ signal is so smeared out in the laboratory.
Br⁺ TOF distributions measured at four laser pulse energies are shown in Fig. 6. These measurements were also made at 10°. Contributions from the CF₂Br and Br products of reaction (3) are clearly seen, superimposed on an underlying signal which is assigned to secondary Br atoms produced in reaction (4). The fastest Br⁺ signal arrives later than the fastest CF⁺ and CF₂⁺ signals (even after correcting for ion flight times), which is consistent with our assignment of the underlying signals to secondary photodissociation of CF₂Br.

The four Br⁺ TOF distributions in Fig. 6 have all been normalized to the same peak height. The raw signal under the Br peak is linearly proportional to the laser pulse energy over the range shown, indicating that the primary absorption step is linear in this range. Fig. 6 shows that the ratio of the secondary Br signal (Br_II) to the primary Br signal (Br_I) is nearly independent of laser power. This can be true only if the second absorption step is strongly saturated, even at our lowest pulse energy. The absorption cross section of CF₂Br is evidently much larger than that of CF₂Br₂ at 248 nm.

If the second absorption step is strongly saturated, then most of the CF₂Br should be blown apart, and the ratio of the surviving CF₂Br to primary Br signals should decrease at least linearly as the laser power is increased. (We will discuss this point more quantitatively in the Discussion Section) However, Fig. 6 shows that the CF₂Br:Br_I ratio decreases rather slowly (at most by a factor of 3) as the laser power is increased by a factor of 30. To explain this fact, it is necessary to postulate that the absorption cross section of the primary CF₂Br products is not uniformly large. While some (probably most) of the CF₂Br
radicals formed in reaction (3) absorb very efficiently at 248 nm, a significant fraction of the CF$_2$Br, by virtue of its particular internal excitation, does not absorb so strongly, permitting it to survive and be detected even at our highest laser pulse energy (100 mJ). If the above conclusion is correct, then the $P(E_T)$ which was derived earlier from the CF$_2$Br data probably does not accurately reflect the product translational energy distribution for reaction (3). As we shall see, this is actually the case: the conclusions drawn in part A will have to be modified.

In Fig. 7, the Br$^+$ TOF distributions measured at 100 mJ and 10 mJ pulse energies are displayed again after approximately subtracting out the secondary photodissociation signal. The fits were calculated using the solid-line $P(E_T)$ in Fig. 3 and $\beta = 1.21$. The CF$_2$Br:Br ratio was freely adjusted to fit the relative peak heights. This ratio differs by only a factor of 2.5 for the two distributions, compared to the $>10$-fold change which would be expected if all CF$_2$Br primary products had an equal probability of absorbing a second photon. The solid-line $P(E_T)$ in Fig. 3 obviously produces a terrible fit to the Br peak in these TOF distributions. The calculated Br peak is too fast and too narrow.

The $P(E_T)$ for reaction (3) was adjusted to fit the Br peak in the Br$^+$ TOF distributions. The best-fits shown in Fig. 8 were calculated from the dashed-line $P(E_T)$ in Fig. 3 still using $\beta = 1.21$. Since nothing unusual can happen to the Br primary product, this dashed-line $P(E_T)$ should reflect the true distribution of recoil energies for the products of reaction (3). This $P(E_T)$ has a mean translational energy of 21.3 kcal/mole and a FWHM energy spread of 8.0 kcal/mole.
The difference between the two $P(E_t)$'s in Fig. 3 indicates that most of the CF$_2$Br radicals which survive (i.e., which do not undergo secondary photodissociation) are formed with higher than average recoil energies, or lower than average internal energies. Thus, the internally hottest CF$_2$Br radicals are mainly responsible for the observed secondary photodissociation signal, while the colder CF$_2$Br radicals do not absorb so strongly at 248 nm.
IV. DISCUSSION

Our results clearly indicate that Br-elimination is the only important primary photodissociation channel at 248 nm. The concerted Br$_2$-elimination does not occur to a measurable extent. From the dashed-line P($E_T$) in Fig. 3, we conclude that the CF$_2$Br + Br primary products are formed with a mean c.m. translational energy of 21.3 kcal/mole. The C-Br bond dissociation energy in CF$_2$Br$_2$ is approximately 66 kcal/mole. Since a 248 nm photon corresponds to 115 kcal/mole of available energy, an average of 115 - 66 - 21 = 28 kcal/mole remains in the internal (vibrational, rotational, electronic) degrees of freedom of the CF$_2$Br and Br products. The minimum observed CF$_2$Br + Br recoil energy of ~10 kcal/mole gives a maximum product internal energy of ~39 kcal/mole. The only excited electronic state which is energetically accessible is the $^2$P$_{1/2}$ fine-structure state of the Br atom, which lies 10.54 kcal/mole above the $^2$P$_{3/2}$ ground state. Our mass spectrometer has no way of telling which Br fine-structure state is produced. However, the absence of any shoulder or strong asymmetry in the derived P($E_T$) suggests that only one bromine electronic state is actually produced.

The fact that we do not observe any evidence for spontaneous unimolecular decay of CF$_2$Br (see Results and Analysis C) may have some bearing on the question of which bromine electronic state is produced. We estimate that the C-Br bond strength in CF$_2$Br is around 35 kcal/mole. If Br($^2$P$_{3/2}$) atoms are formed in reaction (3), then the average and maximum CF$_2$Br internal energies are 28 and 39 kcal/mole, respectively, and the hottest CF$_2$Br radicals should be above the CF$_2$-Br dissociation threshold. If Br($^2$P$_{1/2}$) atoms are formed, then the average
and maximum \( \text{CF}_2\text{Br} \) internal energies are 17 and 28 kcal/mole, respectively. No spontaneous \( \text{CF}_2\text{Br} \) decay would be possible in this case. Thus, our failure to observe evidence for spontaneous \( \text{CF}_2\text{Br} \) decay would seem to favor the conclusion that \( \text{Br}(^{2}\text{P}_{1/2}) \) atoms are formed in reaction (3). However, given the uncertainties in the \( \text{CF}_2\text{Br}-\text{Br} \) and \( \text{CF}_2-\text{Br} \) bond dissociation energies, this conclusion cannot be taken too seriously. Also, if a large fraction of the \( \text{CF}_2\text{Br} \) internal energy is in the form of rotation, then even \( \text{CF}_2\text{Br} \) radicals containing \( > 35 \) kcal/mole internal energy might be prevented from dissociating by a centrifugal barrier. Because of these complications, we really cannot decide on the basis of our results which \( \text{Br} \) fine-structure state is produced in reaction (3).

The derived value of the asymmetry parameter for reaction (3), \( \beta = 1.21 \), provides information on the orientation of the transition dipole moment in the \( \text{CF}_2\text{Br}_2 \) molecule and the symmetry of the upper electronic state. The electronic transition at 248 nm involves the promotion of a non-bonding bromine electron to a \( \text{C-Br} \) anti-bonding orbital. (Of course, since the two \( \text{C-Br} \) bonds are equivalent, the non-bonding and anti-bonding orbitals are delocalized over both \( \text{Br} \) atoms or \( \text{C-Br} \) bonds). By symmetry, only three orientations of the transition dipole moment, \( \mathbf{\mu} \), with respect to the \( \text{Br-C-Br} \) plane are possible: (i) \( \mathbf{\mu} \) perpendicular to the \( \text{Br-C-Br} \) plane \( (B_2 \leftarrow A_1 \) transition); (ii) \( \mathbf{\mu} \) bisecting the \( \text{Br-C-Br} \) bond angle \( (A_1 \leftarrow A_1 \) transition); (iii) \( \mathbf{\mu} \) parallel to the line through the two \( \text{Br} \) atoms \( (B_1 \leftarrow A_1 \) transition). We will assume that the equilibrium geometry of \( \text{CF}_2\text{Br}_2 \) is the same in the ground and excited electronic states, and that the \( \text{Br} \) atom which is ejected leaves along the \( \text{C-Br} \) bond direction. We will also assume that any "smearing" of the
c.m. anisotropy, due to effects such as overall rotation of CF₂Br₂ between absorption and dissociation, or the finite amplitude of the bending vibrations, is small. Then, the asymmetry parameter should be related to the angle, α, between the transition dipole moment and the C-Br bond direction according to

\[ \beta = 2 P_2(\cos \alpha). \]

For the three possible cases mentioned above, we would expect: (i) \( \alpha = 90^\circ, \beta = -1.0 \); (ii) \( \alpha = 54.7^\circ, \beta = 0.0 \); (iii) \( \alpha = 35.3^\circ, \beta = 1.0 \).

Only case (iii) is near the experimental result. Therefore, the transition dipole moment is polarized parallel to the Br-Br direction, and the excited electronic state must have \( B_1 \) symmetry.

The kinetics of the two-step photodissociation process leading to the formation of CF₂ radicals and secondary Br atoms is easily worked out. We will assume a rectangular-shaped laser pulse of duration \( \tau \) with photon intensity \( I \) (photons/cm²·sec). The time-integrated photon flux for the single pulse is then \( \Phi = I\tau \) (photons/cm²·pulse). We will denote the absorption cross sections (in cm²) of CF₂Br₂ and CF₂Br by \( \sigma_1 \) and \( \sigma_2 \), respectively, and assume for now that \( \sigma_2 \) is the same for all of the CF₂Br primary products. The rate equations for the two-step process

\[ \text{CF}_2\text{Br}_2 \xrightarrow{k_1 = \sigma_1 I} \text{CF}_2\text{Br} + \text{Br}_2 \]
The equations are:

\[ \frac{dn_{CF_2Br(t)}}{dt} = -\sigma_1 \cdot I \cdot n_{CF_2Br_2}(t) \]

\[ \frac{dn_{Br_I(t)}}{dt} = \sigma_1 \cdot I \cdot n_{CF_2Br_2}(t) \]

\[ \frac{dn_{CF_2Br(t)}}{dt} = \sigma_1 \cdot I \cdot n_{CF_2Br_2}(t) - \sigma_2 \cdot I \cdot n_{CF_2Br}(t) \]

\[ \frac{dn_{Br_{II}(t)}}{dt} = \frac{dn_{CF_2(t)}}{dt} = \sigma_2 \cdot I \cdot n_{CF_2Br}(t). \]

These equations are easily solved for the final concentrations of the various species at the end of the laser pulse \( n_o \) is the initial concentration of \( CF_2Br_2 \):

\[ \frac{n_{CF_2Br_2}}{n_o} = e^{-\sigma_1 \phi} \]

\[ \frac{n_{Br_I}}{n_o} = 1 - e^{-\sigma_1 \phi} \]
\[
\frac{n_{CF_2Br}}{n_0} = \frac{\sigma_1}{\sigma_2 - \sigma_1} \left[ e^{-\sigma_1 \phi} - e^{-\sigma_2 \phi} \right]
\]
\[
\frac{n_{Br_{II}}}{n_0} = \frac{n_{CF_2}}{n_0} = 1 + \frac{\sigma_1 e^{-\sigma_2 \phi} - \sigma_2 e^{-\sigma_1 \phi}}{\sigma_2 - \sigma_1}
\]

We know that, under the conditions of our experiment, the first absorption step is in the linear region. Therefore, \(\sigma_1 \phi \leq 1\). If the second step is also in the linear region, then the ratio \(n_{Br_{II}}/n_{Br_{I}}\) should be small and have a linear dependence on \(\phi\), as is easily verified from the above expressions. However, our power dependence measurements showed that \(n_{Br_{II}}/n_{Br_{I}}\) is almost independent of \(\phi\) over a 30-fold range. This requires \(\sigma_2 \gg \sigma_1\), or \(\sigma_2/\sigma_1 \gg 1\).

In Fig. 9, the calculated concentrations of \(Br_{I}, CF_2Br\) and \(Br_{II}\) are shown as a function of \(\sigma_1 \phi\) for the case \(\sigma_2/\sigma_1 = 10\). (This case is only chosen for illustration.) The linear \(\phi\)-dependence of \(n_{Br_{II}}/n_{Br_{I}}\) at low \(\phi\) (\(\sigma_2 \phi \leq 1\), or \(\sigma_1 \phi \leq 0.1\)), and the approach to the limiting condition \(n_{Br_{II}}/n_{Br_{I}} = 1\) as \(\phi\) increases, are evident in this figure. To keep \(n_{Br_{II}}/n_{Br_{I}}\) essentially constant over a 30-fold range of \(\phi\), and still not saturate the primary absorption step, it is necessary to assume an even larger \(\sigma_2/\sigma_1\) ratio. Then the transition from a quadratic to a linear \(\phi\)-dependence of the secondary \(Br\) signal will occur at an even lower value of \(\sigma_1 \phi\).

On the basis of Fig. 9, the ratio \(n_{CF_2Br}/n_{Br_{I}}\) should decrease somewhat faster than linearly with \(\phi\) as \(\phi\) increases. The experimental \(n_{CF_2Br}/n_{Br_{I}}\) ratio decreased by only a factor of \(\sim 3\) for a 30-fold
increase in $\phi$. This discrepancy indicates that it is incorrect to assume that $c_2$ is the same for all of the CF$_2$Br primary products. A subset of the CF$_2$Br formed in reaction (3) must absorb weakly, if at all, at 248 nm. The presence of this subset causes the experimental $n_{\text{CF}_2\text{Br}}/n_{\text{Br}}$ ratio to fall off more slowly with $\phi$ than expected on the basis of the simple two-step model described above. The difference between the $P(E_T)$'s derived from the CF$_2$Br and Br TOF data (Fig. 3) supports this conclusion. The dashed-line $P(E_T)$, derived from the Br data, reflects the actual translational energy release in the primary dissociation reaction. The solid-line $P(E_T)$, derived from the CF$_2$Br data, is narrower and skewed to higher recoil energies, indicating that the CF$_2$Br radicals which survive are mainly those formed with low internal energies. The magnitude of the CF$_2$Br absorption cross section at 248 nm must depend strongly on CF$_2$Br internal energy.

In principle, it should be possible to approximately determine the form of the product translational energy distribution for the secondary photodissociation reaction from the shapes of the underlying secondary Br and CF$_2$ signals in the Br$^+$ and CF$^+$ TOF distributions. If the laser light had been polarized parallel to the CF$_2$Br$_2$ beam direction, then both the c.m. and laboratory angular distributions of the CF$_2$Br primary product would have had cylindrical symmetry about the molecular beam direction, and the existing computer program could have been used to calculate the laboratory angular and TOF distributions of the CF$_2$ and Br$_{II}$ products, given an assumed form for the $P(E_T)$ and anisotropy parameter for reaction (4). In our experiment, the laser was unpolarized. In this case, the c.m. angular distribution of CF$_2$Br is cylindrically
symmetric not about the molecular beam direction, but about the laser
propagation direction, and the laboratory angular distribution of CF₂Br
has no simplifying symmetry at all. This makes the determination of the
product energy distribution for the secondary dissociation process very
difficult.

From the fastest observed CF⁺ and Br⁺ signals, however, it was possible
to conclude that the maximum c.m. translational energy release in
the secondary photodissociation reaction is around 70 kcal/mole. Using
the average CF₂Br internal energy of 17 kcal/mole (assuming that
Br(²P₁/₂) is formed in reaction (3)), and the CF₂-Br bond strength of 35
kcal/mole, the average energy available to the CF₂ + Br products of
reaction (4) should be approximately 115 + 17 - 35 = 97 kcal/mole.
Again, we cannot say what product electronic states are formed. Besides
ground state CF₂(X¹A₁) and Br(²P₃/₂), the lowest triplet state of CF₂
and spin-orbit excited Br(²P₁/₂) are energetically accessible. At least
some of the CF₂ radicals must be formed in the ground vibrational level
of the X¹A₁ state. These CF₂ radicals then resonantly absorb at 248 nm
to populate the v' = 5 and 6 levels of the A'B₁ state, giving rise to
the fluorescence progressions observed in Refs. 1 and 2.

Unfortunately, the cause of the discrepancy between the linear
power dependence of the CF₂ fluorescence reported by Sam and Yardley,¹
and the quadratic dependence reported by Wampler et al.,² is still not
clear. Our results show that, in the fluence range 0.08-2.5 J/cm², CF₂
radicals are formed with a nearly linear power dependence, even though
they result from secondary photodissociation of CF₂Br. The discrepancy
between Sam and Yardley and Wampler et al. therefore hinges on whether
or not the resonant absorption step,

\[ \text{CF}_2 \tilde{X} (000) \rightarrow \text{CF}_2 \tilde{A} (060, 050), \]

is saturated. At the high power levels used in these experiments, it is hard to believe that the bound-bound transition (2) is not saturated. Because of this, we consider Sam and Yardley's result to be more reasonable. However, we have no explanation for the contrasting result of Wampler et al.

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REFERENCES


4. CF$_2$ is fairly close to being a prolate symmetric top. Since the bond angle is larger in the $\tilde{A}$ state than in the $\tilde{X}$ state (122° vs. 104°), the displacement of the origins of successive K-stacks increases faster in the $\tilde{A}$ state than in the $\tilde{X}$ state. (The spacing of J-levels within a given K-stack is not too different in the $\tilde{X}$ and $\tilde{A}$ states, however, since the rotational constants B and C are similar in both electronic states.) Therefore, for a given $\tilde{A} <\tilde{X}$ vibronic transition, the resonant transition frequency will increase as the K quantum number increases.


6. The CF$_2$ Br$_2$ vapor pressure was measured with a capacitance manometer. In Ref. 7, the vapor pressure equation for CF$_2$ Br$_2$ is given as

\[
\log_{10} P(\text{torr}) = -1387/T(\text{K}) + 7.567;
\]

this equation predicts a CF$_2$ Br$_2$ vapor pressure of 122 torr at -20°C.

7. N. Davidson, J. Am. Chem. Soc. 73, 467 (1951). The value $\sigma = 6 \cdot 10^{-19}$ cm$^2$ at 248.4 nm was interpolated from Davidson's extinction
coefficient measurements at 245 and 250 nm. \( \sigma = 10^{-18} \text{ cm}^2 \)
corresponds to \( \varepsilon_{10}^M = 260 \text{ l/mole-cm} \), where \( \varepsilon_{10}^M \) is the molar decadic extinction coefficient.


9. Although the laser was unpolarized for these experiments, the product angular distribution is still sensitive to the value of the anisotropy parameter, due to the geometry of detection. The unpolarized laser beam can be resolved into two equal components, one parallel and one perpendicular to the molecular beam and the plane of detection. The perpendicular component gives an isotropic contribution to the c.m. product angular distribution in the detector plane, but the parallel component does not.

10. The C-Br bond dissociation energy in CF$_2$Br$_2$ has not been directly determined. However, the C-Br bond dissociation energies in CF$_3$Br and CBr$_4$ are known to be 70.6±1 kcal/mole [K. C. Ferguson and E. Whittle, J. C. S. Faraday I, 68, 295 (1972)] and 56.2±1.8 kcal/mole [K. D. King, D. M. Golden, and S. W. Benson, J. Phys. Chem. 75, 987 (1971)], respectively. Therefore, the C-Br bond dissociation energies in CFBr$_3$ and CF$_2$Br$_2$ should be around 61 and 66 kcal/mole, respectively.

11. The CF$_2$-Br bond strength was estimated as follows. We assumed that the enthalpy change for the reaction CF$_3$Br \( \rightarrow \) CF$_2$Br + F is the same as for the reaction CF$_3$Cl \( \rightarrow \) CF$_2$Cl + F. Using \( \Delta H_f^0(\text{CF}_3\text{Cl}) = -169.2 \) kcal/mole (Ref. 12), \( \Delta H_f^0(\text{F}) = 18.9 \) kcal/mole (Ref. 12), and \( \Delta H_f^0(\text{CF}_2\text{Cl}) = -66.5 \) kcal/mole (estimated in Ref. 13), the enthalpy change for the latter reaction is calculated to be 121.6 kcal/mole.
Using $\Delta H_f^{\circ}(\text{CF}_3\text{Br}) = -155.1 \text{ kcal/mole}$ (Ref. 12), the heat of formation of $\text{CF}_2\text{Br}$ is then estimated to be $\Delta H_f^{\circ}(\text{CF}_2\text{Br}) = 121.6 - 155.1 - 18.9 = -52.4 \text{ kcal/mole}$. The heats of formation of $\text{CF}_2$ and $\text{Br}$ are quite accurately known: $\Delta H_f^{\circ}(\text{CF}_2) = -44.5 \text{ kcal/mole}$ (Ref. 14) and $\Delta H_f^{\circ}(\text{Br}) = 26.7 \text{ kcal/mole}$ (Ref. 12). Thus, the C-Br bond strength in $\text{CF}_2\text{Br}$ should be given approximately by $-44.5 + 26.7 + 52.4 = 34.6 \text{ kcal/mole}$. This value is probably within $\pm 5 \text{ kcal/mole}$ of the true value.


16. P. M. Kroger, P. C. Demou, and S. J. Riley, J. Chem. Phys. 65, 1823 (1976). These authors observed sequential photodissociation of $\text{CH}_2\text{I}_2$ at 266 nm [$\text{CH}_2\text{I}_2 \rightarrow \text{CH}_2\text{I} + \text{I}$, $\text{CH}_2\text{I} \rightarrow \text{CH}_2 + \text{I}$], and they analyzed the kinetics of the two-step process in the same way described here for $\text{CF}_2\text{Br}_2$.

18. In Ref. 3, King et al. report a low resolution absorption cross section of $4.2 \times 10^{-17} \text{ cm}^2$ at the center of the CF$_2$ 2$^5$ absorption band at 249 nm. This certainly seems large enough to expect saturation of this transition in the excimer laser experiments.
FIGURE CAPTIONS

Fig. 1. Laboratory TOF distributions of \( \text{CF}_2\text{Br} \).  ○ Experimental points (\( \text{CF}_2\text{Br}^+ \) monitored by the mass spectrometer); ———— calculated using the solid-line \( P(E_T) \) in Fig. 3 and \( \beta = 1.21 \).

Fig. 2. Laboratory angular distribution of \( \text{CF}_2\text{Br} \).  ● Experimental points, obtained by integrating the TOF distributions in Fig. 1. Error bars represent two standard deviations. All three curves were calculated using the solid-line \( P(E_T) \) in Fig. 3 and the following values for the anisotropy parameter: ———— \( \beta = 1.11 \); ———— \( \beta = 1.21 \); ———— \( \beta = 1.31 \).

Fig. 3. Center-of-mass translational energy distributions for the products of the Br elimination reaction. ———— obtained by fitting the \( \text{CF}_2\text{Br}^+ \) TOF distributions; ———— obtained by fitting the Br peak in the \( \text{Br}^+ \) TOF distributions.

Fig. 4. Laboratory TOF distribution of the \( \text{Br}_2^+ \) (m/e = 160) mass spectrometer signal measured at \( \Theta = 10^\circ \).

Fig. 5. Laboratory TOF distribution of the \( \text{CF}^+ \) mass spectrometer signal measured at \( \Theta = 10^\circ \).

Fig. 6. Laboratory TOF distribution of the \( \text{Br}^+ \) mass spectrometer signal measured at \( \Theta = 10^\circ \).
Fig. 7. Laboratory TOF distributions of the Br\textsuperscript{+} mass spectrometer signal at two laser pulse energies, after approximately subtracting off the underlying secondary photodissociation signal.  ○ Experimental points;  ——— calculated using the solid-line $P(E_T)$ in Fig. 3 and $\beta = 1.21$. The fast and slow peaks are due to the Br and CF\textsubscript{2}Br products of reaction (3).

Fig. 8. Same as Fig. 7, except that the fits were calculated using the dashed-line $P(E_T)$ in Fig. 3 (still using $\beta = 1.21$).

Fig. 9. Predicted dependences of the CF\textsubscript{2}Br, Br\textsubscript{I} and Br\textsubscript{II} yields on $\sigma_1 \phi$, calculated on the basis of the simple two-step model described in the text for the case $\sigma_2/\sigma_1 = 10$. $\sigma_1$ and $\sigma_2$ are the absorption cross sections of CF\textsubscript{2}Br\textsubscript{2} and CF\textsubscript{2}Br, respectively, and $\phi$ is the (time-integrated) photon flux in the laser pulse. The product concentrations are normalized to the initial CF\textsubscript{2}Br\textsubscript{2} concentration, $n_0$. 
Fig. 2

$N(\Theta)$ vs $\Theta$ (deg)

$CF_2Br_2$ and $CF_2Br + Br$
$CF^+$
Fig. 7
Fig. 8

100 mJ/p

10 mJ/p

N(t)

t (μs)

XBL 832-8012
\[
\frac{\sigma_2}{\sigma_1} = 10
\]

Fig. 9
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