Ultrafast absorption spectroscopy of photodissociated CF2Br2: Details of the reaction mechanism and evidence for anomalously slow intramolecular vibrational redistribution within the CF2Br intermediate

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Ultrafast time-resolved absorption spectroscopy in the hard ultraviolet has been used to investigate the photodissociation of gas-phase CF_2Br_2 photolyzed at 248 nm. The broadband spectra obtained in the 250–265 nm region have shown that absorption of a single photon activates a two-step sequential elimination of the molecule's two bromine atoms, leaving the product CF_2 radical in the ground or first-excited vibrational state of its ν_2 bending mode. The spectra also demonstrate the direct detection of the vibrationally hot CF_2Br intermediate species itself. We interpret the ~ 6 ps time scale over which the diffuse CF_2Br spectrum evolves as evidence for slow intramolecular vibrational redistribution within this molecule.

Spectroscopic access to the diffuse and discrete electronic absorption bands of molecules with only a few degrees of freedom makes the elucidation of general principles of ultrafast photodissociation dynamics much more straightforward. Unfortunately, the vast majority of small molecules absorb only at ultraviolet wavelengths, requiring with their study the added expense and complication of ultrafast laser sources that operate in this region. It's therefore no surprise that nearly all ultrafast photochemistry experiments performed in the ultraviolet take advantage of high-sensitivity zero-background detection methods, most commonly laser-induced fluorescence.[1] Nevertheless, the possibility that much less sensitive absorption techniques offer advantages complementary to those of fluorescence methods has motivated us to reexamine the absorption technique. These advantages include the ease of interpretation of a linear spectroscopy, the ability to obtain broadband spectra using a probing supercontinuum, and the ability to detect intermediate species whose lifetimes are short compared with their fluorescence lifetimes. These advantages can be purchased at the cost of a laser system able to deliver high-energy ultrashort pulses (> 1 mJ), and by requiring the photochemical reaction under investigation to produce photoproducts with large absorption cross sections (> 10^{-18} cm^2) at a high quantum yield (~ 1). Exactly so, ultrafast broadband absorption spectroscopy in the near uv has been recently applied to dissociation studies of thallium halides[2] and diatomic bismuth molecules.[3]

We present here initial results of time-resolved absorption experiments performed at shorter uv wavelengths. The experiment uses 700 fs, 10 mJ photolysis pulses at 248 nm, and synchronized, supercontinuum probe pulses derived from the same laser source.[4] The reaction studied is the photolysis of CF_2Br_2, which produces the spectroscopically well characterized CF_2 radical[5,6] by elimination of the molecule's two bromine atoms.[7-11] The spectra obtained have allowed us to describe in new detail the nature of the reaction pathway, and to interpret the expected appearance of the discrete CF_2 absorption spectrum as unimolecular reaction of a vibrationally hot CF_2Br intermediate species. Of per-

haps greater interest is our unexpected direct detection of the ground-electronic-state CF_2Br intermediate species itself: This molecule exhibits a continuous absorption in the ultraviolet whose amplitude and spectral shape both evolve in time. We tentatively attribute this time dependence to the influence of intramolecular vibrational redistribution on the molecule's uv absorption spectrum. Even more significantly, the 6 ps time scale over which the spectrum evolves implies that the initial vibrational excitation in CF_2Br is unusually stable against vibrational redistribution.

The experimental apparatus is depicted in Fig. 1. The 248 nm laser system used to produce both the pump and probe pulses consists of a chain of two commercial KrF amplifiers seeded by the upconverted, amplified output of a synchronously pumped mode-locked dye laser.[12] The 30 mJ output pulse of this system is then split into two separate pulses of equal energy: One of these serves as the photolyzing pump pulse, while the other is focused through a 1.5 m steel pressure cell containing krypton gas at 250 psi to generate the broadband continuum probe. The continuum pulse, after interrogating evolving photoproducts in the sample cell, is wavelength resolved in a 0.64 m grating spectrometer fitted with an image-intensified optical multichannel analyzer. With the maximum spectral resolution of 0.07 nm available with this system, we find that the rms spectral noise when averaging 100 shots is as low as 0.2%. This value can be translated into a useful system figure of merit defined by the minimum detectable product $\eta\sigma$, of the quantum yield and the photoproduct's absorption cross section. Assuming a pump pulse energy of 10 mJ and a spot size in the sample cell of 0.1 cm^2 (the case in our experiments), $\eta\sigma$ is about 2×10^{-20} cm^2. Absorption spectra are obtained by a single-beam method in which separate averaged spectra captured with and without blocking of the pump beam are numerically divided. The resulting error in the absorption base line is 2%–3%.

Absolute synchronization of the pump and probe pulses is accomplished *in situ* by taking advantage of two facts: First, since the main ultrashort pump pulse is preceded by a weak prepulse of amplified spontaneous emission (ASE), a
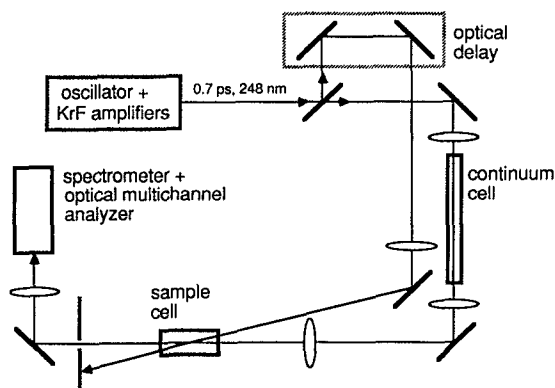
FIG. 1. Pump–probe apparatus for time-resolved spectroscopy in the ultraviolet. The rms spectral noise of the continuum probe is 0.2% after averaging 100 shots.

small amount of photoproduct CF$_2$ [primarily in the $\tilde{X}\,^1A_1(0,0,0)$ ground state] exists in the cell when the pump pulse arrives. Second, since the strong $\tilde{X}\,^1A_1(0,0,0) \rightarrow \tilde{A}\,^1B_1(0,6,0)$ transition of CF$_2$ is coincident with the pump pulse at 248 nm,[8] this initial population of molecules is easily bleached, thus giving a spectroscopic marker showing the arrival time of the main pulse. Detailed spectroscopy of the $\tilde{X}\,^1A_1(0,0,0) \rightarrow \tilde{A}\,^1B_1(0,5,0)$ transition at 252.0 nm performed near zero-time delay demonstrates that the temporal resolution of the system is limited by the width of the pump pulse—about 700 fs. This value is determined by measuring the relative pump–probe time delay for the amount of bleaching of the CF$_2$ absorption to evolve from 25% to 75% of its final value. Moreover, since the $(0,0,0) \rightarrow (0,4,0)$ and $(0,0,0) \rightarrow (0,3,0)$ transitions at 255.2 and 258.5 nm, respectively, also appear in the ASE-produced spectra, a measure of the frequency chirp in the probe continuum can be obtained by noting the times at which the three absorption signals reach half their initial values during the bleaching process. Within the temporal resolution of the system, we detect no measurable chirp over the frequency range spanned by the three transitions ($\Delta\tau/\Delta\lambda < 20$ fs/nm).

A survey of the time-resolved spectra obtained with the above system is shown in Fig. 2. Several qualitative observa-
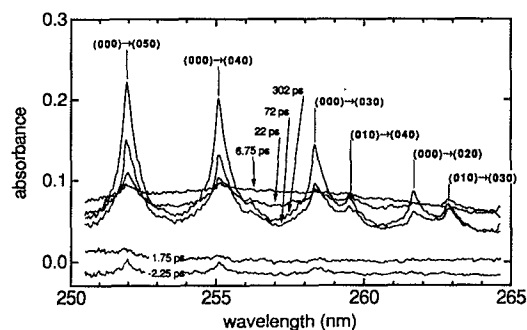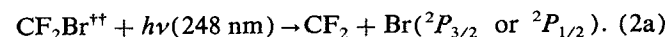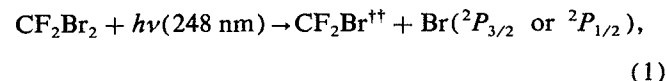

FIG. 2. Time-resolved absorption spectra showing both the evolution of a discrete spectrum belonging to CF$_2$ and a continuous spectrum attributed in the text to vibrationally hot CF$_2$Br. Bleaching of ASE-produced CF$_2$ by the ultrashort pump pulse is seen by comparing the spectra taken at time delays of -2.25 and $+1.75$ ps.

tions can be made about these results: First, the two spectra taken at the -2.25 and $+1.75$ ps time delays illustrate the bleaching of ASE generated CF$_2$ described above. At the larger time delays, the expected appearance of absorption features due to the evolution of CF$_2$ produced by the ultrashort pump pulse is evident. The CF$_2$ line assignments indicated in the figure demonstrate that only the $v_2 = 0$ and $v_2 = 1$ states of the low-frequency bending mode are produced. Using absorbance measurements taken at a time delay of 2 ns in combination with published values of the absolute line strengths,[6] the relative abundance of the two vibrational species upon completion of the reaction is determined to be $[CF_2(v_2 = 0)]/[CF_2(v_2 = 1)] = 6.6$.[13] The most unexpected result, however, is the dramatic shift in the absorption base line between time delays of 0 and 10 ps. This abrupt shift is followed by a slow decay that is approximately commensurate with the increasing strength of the CF$_2$ spectrum, suggesting that the base line signal is actually due to absorption by an unstable reaction intermediate. The remainder of our discussion will be primarily devoted to clarifying the nature of the reaction mechanism, about which conclusions will be crucial to further interpretation of the base line signal.

The most convincing account of the photochemistry of CF$_2$Br$_2$ has been published by Krajnovich et al.[11] (hereafter KZBL). Using mass-spectroscopic data obtained with a jet-cooled molecular beam, these workers argued that the molecule follows the two-step, two-photon reaction pathway

$$CF_2Br_2 + h\nu(248\ nm) \rightarrow CF_2Br^{\dagger\dagger} + Br(^2P_{3/2}\ or\ ^2P_{1/2}),$$

$$(1)$$

$$CF_2Br^{\dagger\dagger} + h\nu(248\ nm) \rightarrow CF_2 + Br(^2P_{3/2}\ or\ ^2P_{1/2}). \quad (2a)$$

In particular, the latter step was favored by KZBL over the possibility of spontaneous dissociation:

$$CF_2Br^{\dagger\dagger} \rightarrow CF_2(\tilde{X}) + Br(^2P_{3/2}). \quad (2b)$$
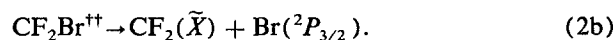
This conclusion, however, demanded that the CF$_2$Br†† absorption cross section at 248 nm be sufficiently large that the second dissociation step (2a) would be fully saturated, thus giving KZBL's observed linear dependence of the CF$_2$-related mass signals on the laser fluence.

We likewise observe a linear dependence of CF$_2$ signals on laser fluence, and therefore eliminate from consideration any prompt nonlinear absorption processes. To distinguish a one-photon mechanism from saturated, sequential absorption of two photons through a resonant intermediate state, it will be useful to derive a lower bound that the two-photon mechanism would impose on the absorbance ratio of the CF$_2$Br†† and CF$_2$ species. With the help of expressions derived by KZBL for the number densities of photogenerated CF$_2$Br†† and CF$_2$ as functions of Φ, the photon fluence, and assuming only that the first step of the reaction occurs in the linear regime, i.e, $\sigma_1 \Phi \ll 1$, where σ_1 is the CF$_2$Br$_2$ adsorption cross section (6.4×10^{-19} cm^2 [14]), the space derivatives in the sample cell of the photon fluence and the absorbances of the two species are

$$\frac{d\Phi}{dx} = -\frac{1}{\sigma_2}\frac{da_{CF_2Br}}{dx} - \frac{2}{\sigma_{CF_2}}\frac{da_{CF_2}}{dx},$$

$$\frac{da_{CF_2Br}}{dx} = \frac{n_0\sigma_1\sigma_2}{\sigma_2 - \sigma_1}[1 - e^{-\sigma_2\Phi}],$$

$$\frac{da_{CF_2}}{dx} = \frac{n_0\sigma_1\sigma_{CF_2}}{\sigma_2 - \sigma_1}[\sigma_2\Phi - (1 - e^{-\sigma_2\Phi})]. \quad (3)$$

In these expressions, σ_2 and σ_{CF_2} are the absorption cross sections of $CF_2Br^{\dagger\dagger}$ and CF_2, respectively, while n_0 is the number density of CF_2Br_2 molecules (5×10^{17} cm^{-3} in our experiment). The linearity assumption for the first dissociation step, in fact, holds quite well in practice; $\sigma_1\Phi$ in the experiment is at most 0.07. Since nearly all of the incident pulse is absorbed in the sample cell, explicit integrals can be obtained for the two absorbances by using the first relation above to affect a change of variables. With an initial fluence of Φ_0 entering the sample cell, the ratio of the $CF_2Br^{\dagger\dagger}$ and CF_2 absorbances is then given by the expression

$$\frac{a_{CF_2Br}}{a_{CF_2}}$$

$$= \frac{\sigma_2\int_0^{\sigma_2\Phi_0}[(1 - e^{-\xi})/(2\xi - (1 - e^{-\xi}))]d\xi}{\sigma_{CF_2}\int_0^{\sigma_2\Phi_0}[(\xi - (1 - e^{-\xi}))/(2\xi - (1 - e^{-\xi}))]d\xi}.$$

It can be shown that this ratio is a monotonically increasing function of σ_2. It therefore suffices to evaluate the above expression in the limit $\sigma_2 \to 0$ in order to establish an absolute lower bound on the absorbance ratio. The result is

$$\frac{a_{CF_2Br}}{a_{CF_2}} > \frac{4}{\sigma_{CF_2}\Phi_0}.$$

Taking the experimental values of $\Phi_0 = 1 \times 10^{17}$ cm^{-2} and $\sigma_{CF_2} = 2 \times 10^{-17}$ cm^2 (for the $(0,0,0) \to (0,5,0)$ transition),[15] the ratio of the absorbances should be > 2 if the two-photon mechanism is correct. [An exact numerical integration of the differential equations (3), which includes the effect of the finite length of the sample cell, gives a minimum absorbance ratio of 1.9.]

Referring again to Fig. 2, and in particular to the spectrum taken at 1.75 ps, we can see by extrapolation of the spectrum to 248 nm that it is very unlikely that the absorption is large there.[16] We can now say with some confidence that at least in our short-pulse experiment, elimination of the second bromine atom occurs purely *spontaneously*.

More can be said in support of the case for spontaneous dissociation in the second step: As pointed out above, the spectra of Fig. 2 indicate that the $(0,0,0)$ and $(0,1,0)$ states are produced in the ratio of 6.6:1, with no evidence for the production of any higher excited states. This means that little excess energy is available in the reaction, as would be expected for CF_2Br_2 photoproducts that arise from absorption of a single photon. That the evolution of the CF_2 spectrum occurs relatively slowly as compared to what would be expected for parent $CF_2Br^{\dagger\dagger}$ molecules with an additional energy boost of 40 300 cm^{-1} is further evidence for near-threshold spontaneous dissociation. In fact, since KZBL observe a 2210 cm^{-1} wide distribution of center-of-mass translational energies for the first dissociation step 1(a), the large ratio of the abundances of the $(0,0,0)$ and $(0,1,0)$ states suggests that only molecules in the top end of this distribu-

tion have energies that exceed the dissociation threshold. Indeed, an estimate for the quantum yield of CF_2 in our experiment gives a value of only $\sim20\%$, a figure which is consistent with KZBL's easy detection of stable $CF_2Br^{\dagger\dagger}$ molecules in their mass spectrometer.

Nevertheless, the possibility remains that in KZBL's long-pulse experiment absorption of a second photon is responsible for perhaps some of the detected CF_2, since a long-term absorbance of ~0.05 at 248 nm does eventually evolve. However, this small value for the absorbance leads to a cross section for $CF_2Br^{\dagger\dagger}$ at 248 nm of only 6.2×10^{-19} cm^2, a value that in turn implies that only a minority of KZBL's detected CF_2 radicals should result from the two-photon mechanism. This may account, on the one hand, for the linear dependence on laser fluence of KZBL's CF_2 mass signals, and on the other hand, for their detection of a few unusually energetic CF_2 radicals attributed by them to the two-photon mechanism.

It remains finally to check whether the energy budget of the reaction is consistent with the interpretation of single-photon dissociation. KZBL estimate the energy required to produce a $CF_2(0,0,0)$ radical and two ground-state $Br(^2P_{3/2})$ atoms to be 35 310 cm^{-1}. Adding to this the mean center-of-mass translational energy of 8250 cm^{-1} measured for the first dissociation step (1a), and assuming that the center-of-mass energies of the products of (2b) are negligible, gives a mean energy of 43 560 cm^{-1} expressed in the final potential and translational states of the system. This figure is 3300 cm^{-1} *above* the photon energy, or about 2.5 standard deviations of the (presumably) Gaussian kinetic-energy distribution. Given that the internal energies of the hot $CF_2Br^{\dagger\dagger}$ molecules are likewise normally distributed with the same energy width, this means that only a negligible fraction of the $CF_2Br^{\dagger\dagger}$ population should be above the dissociation threshold, as compared with the 20% value determined in our measurement. However, only a 6.5% reduction in the sum of the two C–Br bond energies is required to bring the predicted CF_2 quantum yield into agreement, a figure that falls comfortably within KZBL's 15% error bar on their bond-energy estimate. This degree of agreement is probably too good to be true. Nevertheless, since the $^2P_{1/2}$ spin–orbit state of atomic Br lies a sizable 3700 cm^{-1} above the ground state, we can at least tentatively propose that only the bromine ground states are energetically accessible given the measured value of the CF_2 quantum yield.

With the reaction mechanism safely in hand, we can now straightforwardly interpret the broadband absorption in Fig. 2 as due to vibrationally hot CF_2Br produced by direct dissociation[17] of parent CF_2Br_2 molecules upon absorption of a single 248 nm photon. Eighty percent of these are stable and apparently contribute to the long-term diffuse absorption seen in Fig. 2, while the remaining 20% go on to dissociate by unimolecular reaction, giving rise to the discrete CF_2 spectrum and a commensurate decrease in the broadband absorption after 10 ps. Close examination of Fig. 2, however, reveals that these last two effects are not perfectly correlated; most of the decrease in the broadband absorption occurs relatively early in the set of chosen spectra, while most of the increase in the discrete absorption occurs rela-
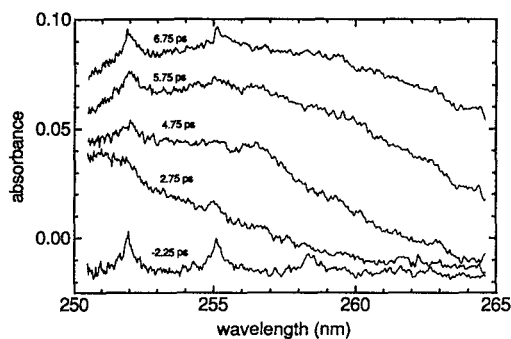
FIG. 3. Evolution of the continuous absorption spectrum at early time delays. Both the amplitude and spectral shapes are time dependent.

tively later. This presents no problem to our interpretation, since there is no guarantee that absorption at a given wavelength is a sum of equal contributions from each molecule in the internal energy distribution.

Figure 3 displays in greater detail the evolution of the broadband absorption at early times. Not only is the temporal change in the amplitude of the absorption well resolved, but also a change in its spectral shape. The latter observation could be an artifact of frequency chirp in the probe continuum, but this possibility is discounted in the discussion above of the pump–probe synchronization procedure. Rough inspection of Fig. 3 indicates that the timescale for evolution of the spectrum is about 6 ps.

Since at present little is known of the spectroscopy of the CF$_2$Br radical,[18] we for now restrict ourselves to a simple qualitative picture of the internal dynamics potentially revealed by Fig. 3. By considering only the geometry of the direct dissociation step, it is clear that the initial vibrational excitation of CF$_2$Br is not a statistically mixed distribution. Aside from the large impulse that the CF$_2$Br$\cdots$Br half collision delivers to the central carbon atom, the newly created CF$_2$Br radical is initially distorted from its most likely new equilibrium configuration of a somewhat more flattened pyramid. These two effects add constructively, suggesting that a significant portion of the internal energy resides in the F$_2$–C–Br pyramid bending mode. Since the carbon atom is not located at the center of mass, however, excitation of rotational as well as additional vibrational modes should likewise be expected.

We at this point believe that internal dynamical evolution of CF$_2$Br toward an ergodically mixed distribution of vibrational energy is the most likely interpretation of the rise of the broadband absorption of Fig. 3. Although at present the relatively long wavelength of the broadband absorption allows us to only speculate that the absorption be attributed to the weak C–Br bond itself, the shift of the CF$_2$Br absorption from short to long uv wavelengths is exactly what would be expected as energy is redistributed throughout the CF$_2$Br vibrational manifold.

The apparent 6 ps time scale observed for vibrational redistribution is clearly too large to be a single vibrational period of even the lowest-frequency mode of CF$_2$Br††, despite the high degree of excitation that exists in this molecule. Evidently, many vibrational periods are required for redistribution, implying that the initial excitation may be

somehow stabilized against the complete ergodic mixing normally connected with vibrationally hot, prereactive molecules. Indeed, as we have been recently reminded,[19] subpicosecond redistribution times are the rule rather than the exception for local-mode overtone excitations such as those of C–H bonds in benzene.[20]

On the other hand, very recent experiments reported by Choi and Moore have unambiguously demonstrated the existence of highly excited, yet highly decoupled, "extreme-motion" molecular eigenstates prepared by stimulated-emission pumping of the ν_6 out-of-plane bending mode of HFCO.[21] With this precedent, it is difficult to ignore a possible connection between our time-domain observations of slow vibrational redistribution in CF$_2$Br†† and these workers' frequency-domain measurements of uncongested, narrow spectral features in highly vibrationally excited HFCO.

The present experiments are the first to our knowledge to take advantage of broadband ultrafast absorption techniques to investigate the dissociation dynamics of simple polyatomic molecules. We believe that the evolution of the broadband CF$_2$Br absorption spectrum should be attributed to slow intramolecular vibrational redistribution within this molecule. Some hesitation is justified, however, in accepting our qualitative conclusions until more is understood about the potential energy surfaces and internal dynamics of CF$_2$Br. Nevertheless, these initial experiments have clearly demonstrated the utility of the technique in unravelling reaction mechanisms and detecting unstable reaction intermediates. The confirmation of slow vibrational redistribution within the CF$_2$Br species and the discovery of analogous effects in related molecules motivate current work.

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