Nonadiabaticity and intramolecular electronic energy transfer in the photodissociation of 1-bromo-3-iodopropane at 222 nm

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The photodissociation of 1-bromo-3-iodopropane $(1,3-C_3H_6BrI)$ at 222 nm is studied with crossed laser-molecular beam experiments. Irradiation at this wavelength excites an $n(Br) \rightarrow \sigma^*(C-Br)$ transition which promotes the molecule to an approximately diabatic excited state potential energy surface which is dissociative in the carbon-bromine bond. This surface intersects an approximately diabatic surface of $n(I) \rightarrow \sigma^*(C-I)$ character at extended C-Br distances; this surface is dissociative in the carbon-iodine bond. Crossings from the surface initially accessed to the intersecting surface correspond to intramolecular excitation transfer from the carbon-bromine to the carbon-iodine bond. The incidence of such transfer and hence of carbon-iodine bond fission depends upon the strength of the off-diagonal potential coupling of the two diabatic states. These experiments test the dependence of the coupling and consequent energy transfer upon the separation distance of the C-Br and C-I chromophores. The data show C-Br fission dominates C-I fission by a ratio of 4:1 and determine the center-of-mass translational energy distributions and angular distributions of these processes. The measured anisotropy parameters are β (C–Br)=1.6±0.4 and β (C–I)=0±0.2. A third photofission process, IBr elimination, also contributes to the observed signal. The results of the study of C-Br and C-I fission are compared to previous studies on similar molecules to understand how the branching depends on the relative positioning of the C-Br and C-I chormophores. © 1995 American Institute of Physics.

I. INTRODUCTION

Much experimental¹⁻⁸ and theoretical⁹⁻¹¹ research has focused on describing the radiationless transfer of electronic energy or electronic excitation either from one molecule to another or from one chromophore to another within the same molecule. An elementary theoretical model developed by Förster¹² treats the interaction between the donor and acceptor of electronic excitation as a simple Coulombic interaction, a description which is suited to systems in which the donor and acceptor are well separated spatially. In the case in which the interacting chromophores are not well separated, or if the excitation transfer is from one triplet state to another, a model developed by Dexter,¹³ which extends the Förster model by accounting for the exchange interaction between electrons, has been applied.⁵⁻⁷ In both the Förster and the Dexter mechanisms, the probability (or rate) of excitation transfer decreases with increasing spatial separation of the chromophores.

Much of the experimental work on the transfer of electronic excitation has been done in condensed phases^{4–7} and has often involved transfer of excitation between different donor and acceptor molecules.^{11–13} However, some recent work has been done in the gas phase^{1–3,8} and has concentrated on intramolecular energy transfer, in which the donor and acceptor chromophores are located upon the same molecule.

An often overlooked aspect of electronic energy transfer phenomena is the role that the breakdown of the Born– Oppenheimer (adiabatic) approximation plays in such processes.^{9,14} Recent experimental studies by Butler and co-workers¹⁵⁻¹⁹ have emphasized and described the nonadiabatic effects in intramolecular excitation transfer for a variety of small organic compounds containing chromophores such as carbonyl groups as well as carbon-halogen bonds. This work continues such studies by using crossed lasermolecular beam studies to examine the incidence of carbonbromine and carbon-iodine bond fission in 1-bromo-3iodopropane $(1,3-C_{3}H_{6}BrI).$ In this system, the chromophores are the C-Br and C-I bonds, separated by methylene unit spacers. The C-Br bond may be considered the donor chromophore initially excited by ultraviolet radiation. Excitation at 222 nm may be described at zeroth order primarily as an $n(Br) \rightarrow \sigma^*(C-Br)$ transition, one which would be expected to lead to dissociation of the carbonbromine bond. Transfer of electronic energy to the C-I bond acceptor chromophore, after initial stretching of the C-Br bond, would, in a zeroth order description, replace the $n(Br) \rightarrow \sigma^*(C-Br)$ character of the excitation with an excitation characterized by a $n(I) \rightarrow \sigma^*(C-I)$ transition. This would correspond to a crossing from an approximately diabatic surface dissociative in the C-Br bond to one dissociative in the C-I bond. Fission of the C-I bond can occur as the result of such a surface crossing.

The experiments presented here measure the photofragment velocities and angular distributions at 222 nm with a crossed laser-molecular beam apparatus to determine the branching ratio of C–Br/C–I fission and compare it to the results of experiments on the similar CH₂BrI and 1,2-C₂F₄BrI systems.^{20–22} In the CH₂BrI system there is no spacer between the C–Br and C–I chromophores, whereas in the 1,2-C₂F₄BrI system the chromophores are separated only by the carbon–carbon single bond. Comparison of our results here with these systems allows analysis of the dependence of excitation transfer upon the spatial separation of the carbon– bromine and carbon–iodine chromophores. Studies employing a linearly polarized radiation source identify the orientation of the electronic transition moment excited in the photodissociation and indicate how molecular conformation and the direction of the absorbing electronic transition moment influences the energy transfer. The nonadiabatic character of the processes studied is discussed.

II. EXPERIMENT

A crossed laser-molecular beam apparatus^{23,24} was used to measure the velocities and angular distributions of fragments from the photodissociation of 1,3-C₃H₆BrI. Upon photodissociation with a pulsed 2640 Questek excimer laser, the neutral products scatter from the intersection region of the laser and molecular beam with laboratory velocities determined by the vector sum of the molecular beam velocity and the center-of-mass recoil velocity imparted to each fragment upon dissociation. Those fragments scattered into the acceptance angle of the differentially pumped detector travel 44.1 cm to an electron bombardment ionizer and are ionized by 200 eV electrons. After mass selection is accomplished via a quadrupole mass filter, the ions are counted with a Daly detector and multichannel scaler with respect to their time of flight (TOF) from the interaction region after the dissociating laser pulse. Angular distributions of photofragments are obtained with a linearly polarized laser beam by measuring the variation in signal intensity with the direction of the electric vector of the laser in the molecular-beam/detector scattering plane.

The molecular beam is formed by expanding gaseous 1,3-C₃H₆BrI, at its vapor pressure at 70 °C, seeded in He to give a total stagnation pressure of 300 Torr. The 1,3-C₃H₆BrI/He mixture was expanded through a 0.076 mm diameter nozzle heated to 170 °C. The peak beam velocity was 1.35×10^5 cm/s with a full width at half maximum (FWHM) of 11%. The velocity of the parent molecular beam was measured by directing the molecular beam into the detector and raising a chopper wheel into the beam. To measure the velocities of neutral photofragments, the source was rotated to 15° away from the detector in the plane containing the beam and the detector axis. Laser polarization angles and molecular beam source angles reported in this work are given with respect to the detector axis and defined as clockwise with respect to laser polarization and counterclockwise with respect to the orientation of the molecular beam.

For the unpolarized experiments used to determine the C–Br/C–I branching ratio, the unpolarized laser light, typically at 40 mJ/pulse, intersects the molecular beam to photodissociate the molecules. The signal at $m/e^+=79$ (⁷⁹Br) and 127 (¹²⁷I) was also studied at a lower power (15 mJ/pulse in the interaction region) to identify any signal from two-photon processes. The light was focused at the interaction region to a 5 mm² spot. Polarized spectra were typically taken at 7 mJ/pulse with the same focus in the interaction region. For the collection of the branching ratio data, quadrupole resolution was adjusted to 1.0 amu FWHM for



FIG. 1. The ultraviolet absorption spectrum of liquid-phase $1,3-C_3H_6BrI$ at 300 K. Contributions from $n(I) \rightarrow \sigma^*(C-I)$ and $n(Br) \rightarrow \sigma^*(C-Br)$ transitions are shown.

 $m/e^+ = 79$ (Br⁺) and for $m/e^+ = 127$ (I⁺). For the polarized anisotropy studies, the plane-polarized laser light was dispersed into two linearly polarized components using a single crystal quartz Pellin–Broca prism. The horizontal component was rotated to the desired angle using a half-wave retarder. To average out systematic errors, the polarization dependent signal was integrated in repeated short scans alternating between each polarization angle.

The only detectable signal observed in these difficult measurements at 222 nm came from ⁷⁹Br⁺, ¹²⁷I⁺, and $m/e^+=42$ (C₃H₆ fragment). (Obtaining data at other masses was prohibited by the high propensity for this molecule to clog the nozzle, the low vapor pressure, and the low laser powers.) Signal could be fit to the C-Br and C-I photodissociation channels, in addition to a third channel corresponding to IBr elimination. For these measurements, we operate under conditions which effectively eliminate formation of clusters in the supersonic expansion. The combination of seeding in helium rather than argon, operating at modest stagnation pressures, heating the nozzle to 170 °C, and using a very low seed ratio accomplishes this. To assure our spectra are not contaminated by the photodissociation of dimers, we do not rely on the dimer giving signal at the dimer ion mass (dimers fragment to monomers and give monomer daughter ions in the mass spectrometer). Rather, we rely on eliminating any signal due to dimers which occurs in our time-offlight spectra. The spectator monomer in a photodissociating dimer is imparted with only small recoil velocities, so would appear close to the center-of-mass velocity in time-of-flight spectra taken at 15° source angles. (This is easy and common to see in the photodissociation of CF₃I and CH₃I for argon seeded expansions or expansions which use too high a seed ratio or too low a nozzle temperature.) We are very sensitive to this dimer signal due to the Jacobian transformation; none of our spectra of 1,3-C₃H₆BrI show any contamination.

III. RESULTS AND ANALYSIS

The ultraviolet absorption spectrum of liquid phase $1,3-C_3H_6BrI$, obtained at 300 K using a Perkin–Elmer 330 UV spectrometer, is shown in Fig. 1. Comparison with the



FIG. 2. Laboratory TOF spectrum observed at $m/e^+=79$ (⁷⁹Br). The signal is integrated for 300 000 laser shots. The solid line fit to the data points corresponds to expected signal for the $P(E_T)$ for C–Br bond fission shown in Fig. 3.

absorption spectra of similar haloalkanes^{21,22,25,26} indicates that excitation at 222 nm should excite purely the $n(Br) \rightarrow \sigma^*(C-Br)$ transition. The $n(I) \rightarrow \sigma^*(C-I)$ approximately diabatic state is excited at longer wavelengths²⁷ near 260 nm and should not be populated by the initial exciting radiation. As noted in studies of the Rydberg state absorption spectroscopy of 1,3-C₃H₆BrI,²⁵ Rydberg transitions begin at 200 nm and hence Rydberg states should not be accessed by 222 nm excitation.

A. Primary photofragmentation channels

1. C–Br bond fission

The TOF spectrum observed at $m/e^+ = 79$ (⁷⁹Br) is shown in Fig. 2. The dominant peak of the signal can be fit to one dissociation channel, fission of the C-Br bond. Data taken at lower laser powers showed that the small shoulder on the fast side of the main peak is due to multiphoton processes. The small, broad signal to the slow side of the peak can have contributions from the Br⁺ daughter ion of the C₃H₆Br fragment from C-I bond fission and also from IBr elimination (see later section). The translational energy distribution $[P(E_T)]$ derived from forward convolution fitting of the main peak in the signal to a C-Br bond dissociation process is shown in Fig. 3. This $P(E_T)$ is peaked well away from zero, reaching it's maximum at 12.5 kcal/mol out of a possible 60 kcal/mol of available energy (discounting possible spin-orbit excitation of the bromine atom, which would subtract 10.5 kcal/mol from the excitation energy). This kinetic energy distribution is characteristic of the evolution of a dissociating molecule upon a repulsive electronic surface. The data do not resolve the fractions of Br atoms formed in the ${}^{2}P_{1/2}$ versus the ${}^{2}P_{3/2}$ spin-orbit states.

2. Assigning the signal at $m/e^+ = 127 (^{127}I^+)$

The TOF spectrum obtained at $m/e^+ = 127$ (¹²⁷I) is shown in Fig. 4. While the main signal peaking near 270 μ s is clearly due to C–I fission, there are a few possible photofragmentation channels that could contribute to the slow



FIG. 3. $P(E_T)$ for C–Br bond fission determined by forward convolution fit of the experimental Br⁺ TOF spectrum in Fig. 2.

shoulder between 320 and 450 μ s. We first considered the possibility that the fast peak resulted from formation of spin-orbit ground state iodine and the slow shoulder from formation of spin-orbit excited state iodine, but the resulting kinetic energy distributions were inconsistent with the expected kinetic energy partitioning. In comparison with other iodoalkane photofragmentation studies,²⁸⁻³⁰ we expect that these two dissociation channels will partition roughly the same fraction of the available energy to product translation. The average kinetic energy of the primary C-I bond fission in the main peak is 17 kcal/mol, which is 22% of the 77 kcal/mol of available energy if only spin-orbit ground state products give this signal. If we then try to assign the slow shoulder to formation of spin-orbit excited I atoms, we find that the $P(E_T)$ which fits the slow signal has an average kinetic energy of only 6 kcal/mol out of a possible 55 kcal/ mol (77 kcal/mol-22 kcal/mol of spin-orbit excitation) or 11% of the available energy after subtracting that in electronic excitation of the products. This discrepancy is inconsistent with previous studies on energy partitioning in these two product channels in the iodoalkanes, so the signal in the slow shoulder must be due to contribution from other photo-



FIG. 4. Laboratory TOF spectrum observed at $m/e^+=127$ (¹²⁷I⁺). Signal is integrated for 300 000 laser shots. Contributions to the fit of the spectrum for C–I fission, C–Br fission, and IBr elimination are shown.



FIG. 5. $P(E_T)$ for primary C–I fission determined from forward convolution fitting of the I⁺ TOF spectrum to C–I fission, C–Br fission, and IBR elimination.

fragmentation processes. The $P(E_T)$ for primary C–I bond fission that fit the main peak in the spectrum is given in Fig. 5, and is likely the result of overlapping contributions from both spin–orbit product channels.

The slow shoulder in the I⁺ TOF spectrum can result from contributions from the daughter ion from the momentum-matched C_3H_6I fragment from C–Br fission and from the I⁺ daughter ion from the IBr elimination product. Although the relative contribution from these two sources that fits the slow shoulder is not unique, a linear combination of these two channels does give a good fit to the slow shoulder. The contribution to the fit from the C_3H_6I fragment from C–Br fission is calculated from the $P(E_T)$ in Fig. 3 and the arrival times of the IBr fragment is calculated from momentum matching the signal attributed to the C_3H_6 + IBr channel in the $C_3H_6^+$ spectrum shown in the next section.

3. Signal observed at $m/e^+ = 42 (C_3H_6^+)$

Figure 6 shows the very small signal observed for $C_3H_6^+$. Plotted with the data are three contributions to the fit, two corresponding to daughter ions of the C_3H_6I and the C_3H_6Br



FIG. 6. TOF spectrum observed at $m/e^+=42$ (C₃H₆⁺). The signal is integrated for 360 000 laser shots. Contributions to the fit from C–I fission, C–Br fission, and IBr elimination are labeled.



FIG. 7. $P(E_T)$ proposed for IBr elimination obtained from forward convolution fit of the I⁺ TOF spectrum shown in Fig. 4. The slow portion of this $P(E_T)$ which is uncertain is shown in dotted line.

fragments from the fission of the C-Br and C-I bonds (these fits are calculated from the $P(E_T)$'s already shown) and one from the C₃H₆ fragment from IBr elimination. In molecular beam experiments on CH2BrI where IBr elimination also occurred, the signal from IBr at the parent ion was extremely weak; we were unable to detect signal at the parent ion for this molecule. However, signal from the I^+ daughter ion of IBr was also evident in fitting the signal in the slow shoulder in the $m/e^+ = 127$ spectrum in Fig. 4, helping to confirm the assignment. The proposed $P(E_T)$ that gave the fits shown in Figs. 4 and 6 to the signal from IBr elimination products is shown in Fig. 7. We indicate with the dotted line that we could have attributed some of the slower signal in the $C_3H_6^+$ spectrum to IBr elimination rather than C-I and C-Br fission fragments, resulting in considerable uncertainty in the slow side of this $P(E_T)$. Note that the total available energy for product translation upon IBr elimination is 50 kcal/mol if IBr is formed in its ground state and only 15 kcal/mol if it is formed in the excited ${}^{3}\Pi_{1}$ state as was found in the photodissociation of CH₂BrI.²² Hence, the $P(E_T)$ shown in Fig. 7, which extends to 25 kcal/mol, excludes the possibility of the formation of exclusively excited state IBr photoproducts. However, if the C₃H₆ radical formed during the process of IBr elimination is simultaneously stabilized by hydrogen migration to form H₂CCHCH₃, an additional 62 kcal/mol is available to be partitioned into translation, and it may be postulated that IBr is eliminated in its excited state. Some of the broad signal on the slow side of the peak observed for C–Br fission in Fig. 2 could also be attributed to the Br^+ daughter ion of IBr, but we did not attempt to fit this signal. Because the signal at $m/e^+=42$ is so small, we were unable to do a laser power dependence; thus the poor base line at very early arrival times may in part arise from the twophoton signal, but more likely arises from a systematic error we have observed in many of our spectra with extremely low signal levels and long accumulation times.

B. Determination of C–Br to C–I bond fission branching ratio

To determine the branching ratio between C–Br and C–I fission, the integrated signal intensity at 79 Br and 127 I was

measured over those portions of the TOF spectra corresponding to atoms from each of these primary bond fission processes. All kinematic, ionization cross sections, and isotope abundancy factors were accounted for. To average out systematic errors, the TOF spectra for ⁷⁹Br and ¹²⁷I were integrated for an equal number of laser shots, changing the mass every 5000 shots, with a total of 30 scans for each. The TOF signal in the raw data was integrated over the main peak for the Br⁺ TOF and the fast portion of the spectrum in the I⁺ TOF. To calculate the absolute branching ratio from the integrated signal intensities, we begin by correcting the integrated signals at Br⁺ and I⁺, $N_{lab}^{Br^+}(15^{\circ})$ and $N_{lab}^{I+}(15^{\circ})$, for the ionization cross sections of each atom and their isotopic abundancies³¹

$$\frac{N_{\rm lab}^{\rm Br \ atoms}(15^{\circ})}{N_{\rm lab}^{\rm I \ atoms}(15^{\circ})} = \frac{N_{\rm lab}^{\rm Br^{+}}(15^{\circ})\sigma_{\rm ion}^{\rm I}f(^{79}{\rm Br/Br})}{N_{\rm lab}^{\rm I^{+}}(15^{\circ})\sigma_{\rm ion}^{\rm Br}f(^{127}{\rm I/I})}.$$
 (1)

The relative abundancies of the ⁷⁹Br and ¹²⁷I isotopes used were 0.5069 and 1.0000, respectively, and the relative ionization efficiencies of the atoms were estimated from the atomic polarizabilities.³² The flux of neutral products detected in the TOF spectra was corrected for the angular and velocity distributions of the scattered products, the Jacobian factors in the conversion from the center of mass to the laboratory frame, and flux measured in time versus kinetic energy space. This correction was accomplished via a standard program, RPCMLAB3,³³ which calculates the expected signal at each mass f_{diff}^X given a 1:1 branching ratio. Correcting for this relative differential scattering efficiency gives the final product branching ratio as

$$\frac{\text{C-Br fission}}{\text{C-I fission}} = \frac{N_{\text{lab}}^{\text{Br atoms}}(15^\circ) f_{\text{diff}}^{\text{I}}(15^\circ)}{N_{\text{lab}}^{\text{I} \text{ atoms}}(15^\circ) f_{\text{diff}}^{\text{Br}}(15^\circ)}.$$
 (2)

The C–Br:C–I fission branching ratio determined from the data in this way was 4.0:1.

Note that if we try to fit all signal observed at $m/e^+ = 127$ to C–I fission processes the branching ratio of C–Br to C–I fission obtained would be 2.0:1. However, we found that attributing the slow shoulder in the $m/e^+ = 127$ TOF spectrum to C–I fission was inconsistent with the expected fraction of the available energy partitioned to the ground and spin–orbit excited dissociation channels (see Sec. III B), so was much better fit to the daughter ions of the C₃H₆I fragments from C–Br fission and the IBr product. Thus, our best estimate of the primary C–Br:C–I bond fission branching ratio is 4.0:1.

C. Photofragment anisotropies

The angular distribution of photofragments with respect to the electric vector of exciting polarized radiation in a single photon process can be characterized by an anisotropy parameter β . In the classical electric dipole expression, the angular distribution is given as³⁴

$$w(\theta_{\rm c.m.}) = (1/4\pi) \{ 1 + \beta [P_2(\cos \theta_{\rm c.m.})] \}, \qquad (3)$$



FIG. 8. Laboratory angular distribution of Br atoms. Fits for β =2.0, 1.6, and 1.2 are shown.

where, in the limit of a photodissociation process which is fast on a time scale with respect to molecular rotation and which is characterized by axial recoil, β is given by³⁵

$$\beta = 2P_2 \cos \alpha, \tag{4}$$

where α is the angle between the molecular transition dipole excited by the laser and the recoil axis of the dissociation. For a photodissociation process in which the transition dipole is parallel to the recoil axis $\beta=2$, while if the transition dipole is perpendicular to the recoil axis $\beta=-1$. A value of zero for the anisotropy parameter indicates that the angular distribution of photofragments is isotropic.

Figure 8 shows the integrated Br^+ signal versus Θ_{lab} , the angle between the laser electric vector and the axis of the detector. Curves shown with the data represent forward convolution fits to the signal, converting between the c.m. frame and the lab frame using the measured molecular beam velocity and the $P(E_T)$ derived from the unpolarized data, for values of β ranging from 1.2 to 2.0. This markedly anisotropic angular distribution is indicative of a transition moment predominantly parallel to the recoil axis, in this case simply the carbon-bromine bond. This result is consonant with the angular distributions of Br^+ obtained for the n(Br) $\rightarrow \sigma^*(C-Br)$ excitations in CH₂BrI and 1,2-C₂F₄BrI.^{20,22}

In principle, it should be possible to predict the angular distribution of fragments resulting from C-I bond fission if the structure of the parent molecule 1,3-C₃H₆BrI is known. Then the parameter β might be calculated by determining the angle between the carbon-bromine and carbon-iodine bonds and then using Eq. (4). The molecular structure of several conformers of 1,3-C₃H₆BrI has been theoretically studied by Postmyr.³⁶ These molecular mechanics calculations determine the structures, relative energies, and barriers to interconversion for the four most stable conformers of 1,3-C₃H₆BrI, which are found in order of decreasing stability to be the gauche-gauche (GG), anti-gauche (AG), gaucheanti(GA), and anti-anti (AA) conformers (see Fig. 9). This result is similar to the conformational structures of other 1,3dihalopropanes determined by computational methods as well as electron diffraction experiments.³⁷



FIG. 9. The conformers of $1,3-C_3H_6BrI$. The structure of the molecule is shown in the top schematic diagram. Newman-like projections looking down the carbon backbone of the molecule from the CH₂Br end serve to illustrate the anti–anti (AA), gauche–anti (GA), anti–gauche (AG), and gauche–gauche (GG) conformers. The double dagger marks the position of the middle methlyene unit joining the CH₂Br and CH₂I ends of the molecule.

It is expected for molecules with significant (greater than 1 kcal/mol) barriers to interconversion between conformers, that the conformational composition of molecules in a supersonic beam seeded with He will correspond to the Boltzmann distribution of conformers at the nozzle temperature.³⁸ Postmyr's results find that all barriers to interconversion in 1,3-C₃H₆BrI are greater than 2 kcal and would predict that the distributions of conformers in the jet would be 52.3% GG, 23.6% AG, 18.8% GA, and 5.5% AA. The values of β one would expect for these conformers would be -0.493 (GG), -0.634 (AG), -0.549 (GA), and -0.693 (AA), given that the molecule absorbs via a transition moment parallel to the C–Br bond. The average value of β that one would anticipate observing experimentally would be -0.547.

Figure 10 shows the integrated I^+ signal versus Θ_{lab} . The signal has been integrated over that part of the TOF spectrum corresponding to primary C-I fission. The distribution is very isotropic; possible β values which fit this data range between 0.2 and -0.2. The fairly perpendicular distribution expected from the molecular mechanics calculations is not observed. If the molecular geometries obtained in those calculations are accurate, the isotropic distribution we observe may be interpreted as the result of some combination of several phenomena. One possible explanation may be that the geometry of the molecule changes somewhat upon promotion to the excited state, resulting in an angle between the carbon-bromine and carbon-iodine bonds which would produce a more isotropic distribution. Alternatively, some rotation of the molecule during the photofission process would reduce the anisotropy of the carbon-iodine signal. This rotation might also explain the fact that the C-Br angular dis-



FIG. 10. Laboratory angular distribution of the I signal corresponding to primary C–I fission. Fits for β =-0.2, -0.1, 0.1, and 0.2 are shown.

tribution, while strongly anisotropic, is fit by β values of less than 2, which is the limiting case of a purely parallel transition. A third possible explanation is that C–I bond fission results preferentially from absorption via a transition moment perpendicular to the C–Br bond. It has been noted previously that the $n \rightarrow \sigma^*$ transition on a carbon–halogen bond should consist of parallel and perpendicular components with the parallel predominating.²⁰ If C–I bond fissure results more preferentially from the perpendicular component of absorption on the C–Br bond, a less perpendicular, or more isotropic, angular distribution would result. We return to this point in the Discussion.

IV. DISCUSSION AND CONCLUSIONS

These experiments have determined that irradiation of 1,3-C₃H₆BrI at 222 nm results in three competing dissociation processes, C-Br fission, C-I fission, and IBr elimination. The translational energy distributions of the photofragments for each process peaks well away from zero. For each process the $P(E_T)$ peaks at an energy which is much less than the energy available to be partitioned into translation, suggesting that much of the energy of the fission process is partitioned into rotation, vibrational energy in the alkyl backbone of the molecule, and possible spin-orbit excitation of the halogen atom fragment. For the case of primary C-Br fission, the angular distribution of photofragments has been characterized to be strongly anisotropic and indicates that the fission process occurs via an excitation which is predominantly parallel to the C-Br bond, as has been found in the case of previous studies of C-Br fission following an $n(Br) \rightarrow \sigma^*(C-Br)$ excitation. In contrast, the angular distribution observed for C-I fission was found to be more isotropic.

The primary motive for this research was comparison of the ratio of the incidence of C–Br to C–I fission to previous results obtained in studies of smaller alkanes substituted with bromine and iodine atoms. The work of Butler and co-workers²² finds virtually no C–I fission occurs following excitation of an $n(Br) \rightarrow \sigma^*(C-Br)$ transition on CH₂BrI. For a similar study on 1,2-C₂F₄BrI, Krajnovich *et al.* find a branching ratio of 0.5:1 for C–Br:C–I fission following a similar excitation. This study finds a C–Br:C–I branching ratio of 4:1 for the case of 1,3-C₃H₆BrI.

Previous studies of the branching to different bond fission channels following photoexcitation have considered the coupling between approximately diabatic states which drives this process in the light of the Förster and Dexter models of excitation transfer.^{16,17} These terms may readily be derived from the matrix element expression for the off-diagonal coupling of two approximately diabatic states. If the state initially excited is characterized at zeroth order as an electronic configuration corresponding to an $n(Br) \rightarrow \sigma^*(C-Br)$ excitation, and excitation transfer corresponds to a transition to a zeroth order state characterized by a $n(I) \rightarrow \sigma^*(C-I)$ configuration, the coupling of the two states may be written symbolically as

$$\langle n(\mathrm{Br}) \rightarrow \sigma^{*}(\mathrm{C}-\mathrm{Br}) | H_{\mathrm{el}} | n(\mathrm{I}) \rightarrow \sigma^{*}(\mathrm{C}-\mathrm{I}) \rangle,$$
 (5)

which may be evaluated as an expression of two two-electron integrals 39,40

$$2\langle n(Br)(1)n(I)(2)|e^{2}/r_{12}|\sigma^{*}(C-Br)(1)\sigma^{*}(C-I)(2)\rangle -\langle n(Br)(1)\sigma^{*}(C-Br)(2)|e^{2}/r_{12}|n(I)(1)\sigma^{*}(C-I)(2)\rangle$$
(6)

in which the first term is the Förster expression and the second is the Dexter (exchange) term for excitation transfer. (We note here that purely singlet zeroth order states may be coupled by both the Förster and Dexter terms, while purely triplet zeroth order states are coupled only by the Dexter term. No derivation has been done for systems like the one here characterized by strong spin–orbit coupling, but since these states can be written as linear combinations of wave functions in the more usual basis, we assume that similar expressions can be derived in the strong spin–orbit coupling case.)

Both the Förster and Dexter terms are expected to be distance dependent. The Förster term in particular is often approximated for well-separated chromophores by an expression for the interaction of the transition dipoles^{12,40} and hence to depend inversely on the third power of the spatial separation of the chromophores, with the rate of transfer therefore depending inversely on the sixth power of the separation. The Dexter term is expected to decrease exponentially with increasing separation of the chromophores.^{6,7,13} The distance dependence of these two terms indicates that for the molecules under consideration, the coupling of diabatic states, and hence of C–I bond fission, should decrease with increasing spatial separation of the carbon–bromine and carbon–iodine bonds.

While previous studies of the CH₂BrI and $1,2-C_2F_4BrI$ systems do not clearly support the qualitative distance dependence of excitation transfer described above, the present study of $1,3-C_3H_6BrI$ does evidence such a dependence on distance. The $1,2-C_2F_4BrI$ system, in which the chromophores are separated by a carbon–carbon bond, shows a branching ratio of C–Br to C–I fission of 0.5:1, while in the case of CH₂BrI, in which the chromophores are situated upon the same carbon atom, no incidence of C–I fission is observed. Hence, in these two systems, excitation transfer is observed to increase, not decrease, with increasing spatial separation of the chromophores. While this apparent contradiction might be explained by considering the dependence of the coupling on the relative spatial orientation of the chromophores (see next paragraph), it still leaves the question of the distance dependence largely unanswered. The experiments on 1,3-C₃H₆BrI investigate whether separating the two chromophores by three methylene unit spacers would allow us to observe a decrease in the off-diagonal potential coupling and a concomitant increase in the ratio of C-Br to C-I bond fission. Indeed, excitation of the $n(Br) \rightarrow \sigma^*(C-Br)$ transition in 1,3-C₃H₆BrI shows less excitation transfer, and hence less C–I fission, than exciting the corresponding transition in $1,2-C_2F_4BrI$. The branching ratios for $1,2-C_2F_4BrI$ and 1,3-C₃H₆BrI show that the propane, which has an additional methylene spacer between the C-Br and C-I bonds, has a C-Br:C-I bond fission ratio which is greater than that for the ethane by a factor of 8. This is consonant with the expected distance dependence of the off-diagonal coupling of diabatic states involved in the transfer process.

The photodissociation of CH₂BrI, however, is not explicable merely in terms of the distance dependence of offdiagonal coupling; this system undergoes no discernible C-I fission following $n(Br) \rightarrow \sigma^*(C-Br)$ excitation although both C-Br and C-I chormophores are situated upon the same carbon atom. The germ of understanding this phenomenon lies in consideration of the integrals in Eq. (6). For both the Förster and Dexter contributions to the off-diagonal coupling, the strength of the coupling depends upon the overlap of molecular orbitals involved in these integrals and hence upon the orientation of the chromophores involved in the excitation transfer. One possible explanation which might then be forwarded for the exclusive fission of the C-Br bond in CH₂BrI would be as follows. As the C-Br bond begins elongation after the initial excitation, the Br-C-I bond angle might be expected to approach 90° (this is noted in Ref. 22). At this point, the overlap of the $\sigma^*(C-Br)$ and $\sigma^*(C-I)$ orbitals could become very insignificant, as the two would then be perpendicular to one another. This would make the Dexter term appearing in Eq. (6) very small. Recent experiments^{1,6,7} indicate that the Dexter term may play an important if not a predominant role in excitation transfer in systems with closely situated chromophores. If this were the case for the CH₂BrI system, a small Dexter term, resulting from poor overlap of the anti-bonding orbitals, might drive the selectivity of the dynamics.⁴¹ Similar influences on the coupling arising from the orientation of the chromophores might be significant in the other systems considered as well.

One final point is worth analyzing with respect to the present data. The measured anisotropy parameters show that C–Br fission results from an absorption via a transition moment which is predominantly parallel with respect to the C–Br bond. However, the measured anisotropy for the C–I fission is close to isotropic despite the fact that in all the molecular conformers the C–I bond is roughly perpendicular to the C–Br bond, leading us to expect a perpendicular angular distribution of the C–I fission photofragments. If the molecular conformation predicted in the molecular mechan-



FIG. 11. Schematic representation of the $n(Br) \rightarrow \sigma^*(C-Br)$ and $n(I) \rightarrow \sigma^*(C-I)$ potential energy surfaces along the C-Br and C-I internuclear distances in the approximately diabatic (top) and adiabatic (bottom) representations. Cutaway views at the right are of the Franck-Condon region as seen from the back of the corresponding diagram on the left. The vertical arrow in the lower right frame represents excitation from the ground state to the upper adiabatic via a 222 nm photon. Arrows in this figure show the possible dynamics once the upper, bound adiabat is accessed; the solid arrow illustrates a diabatic process leading to C-Br bond fission, while the dashed arrow shows an adiabatic process in which the molecule remains confined to the upper bound surface. The adiabatic process corresponds to an excitation transfer and may ultimately result in C-I bond fission, as detailed in the text.

ics calculations are correct, there is one way to resolve the discrepancy. It may be that the absorption at 222 nm is carried by a dominant contribution from a parallel $n(Br) \rightarrow \sigma^*(C-Br)$ transition moment but a minor contribution from a perpendicular $n(Br) \rightarrow \sigma^*(C-Br)$ transition moment. Then if the molecules which absorbed via the perpendicular $n(Br) \rightarrow \sigma^*(C-Br)$ transition moment are more strongly coupled to the $n(I) \rightarrow \sigma^*(C-I)$ electronic state at the curve crossing the I atom fragments will show a more parallel angular distribution than expected (close to isotropic rather than perpendicular). We favor this explanation over the other explanations suggested in Sec. III C, such as "smearing" of anisotropy due to rotation during the bond fission process or a change in molecular geometry following the initial excitation. Both of these latter explanations also require that the anisotropy of the signal corresponding to the C-Br fission be dramatically smeared as well, which was not experimentally observed.

Although we have been analyzing the results of these and the previous experiments in an approximately diabatic representation where off-diagonal potential coupling matrix elements drive the intramolecular electronic energy transfer, it is instructive to cast the results in an adiabatic representation. The adiabatic representation makes it clear that a single transition from the diabat repulsive in the C-Br bond to one repulsive in the C-I bond does not result in C-I bond fission, but rather only results in the molecule remaining on the upper bound adiabat (this is why throughout this article we used the wording that the energy transfer "can" result in C-I fission, rather than "will"). Consider the schematic diagrams in the upper frame of Fig. 11 of the two intersecting repulsive electronic states in a diabatic representation, and the figures in the lower frame of the resulting adiabats if offdiagonal potential coupling couples the diabats at all geometries. The upper adiabat, although having an electronic character repulsive in the C-Br bond in the Franck-Condon region, is bound in both bonds. Following the initial excitation of the molecule to the upper, bound surface, the C-Br bond begins to extend. Upon stretching toward the turning point of C-Br vibrational motion upon the upper surface, the dynamics may proceed in either a diabatic or adiabatic fashion. If the dynamics proceeds diabatically, the molecule hops to the lower surface and evolves in a channel resulting in C-Br bond fission. If the dynamics proceeds adiabatically, the molecule continues to evolve on the upper surface, accessing a region of the surface which is of $n(I) \rightarrow \sigma^*(C-I)$ character and consequently repulsive in the C-I bond. The molecule then begins to stretch at the C-I bond and moves upon the upper adiabat until it reaches the avoided crossing between the upper and lower surface. Here again the dynamics may proceed adiabatically or may hop diabatically to the lower surface and evolve in a channel dissociative in the C–I bond. Thus fission of the C-I bond requires that the avoided crossing first be traversed adiabatically on the upper adiabat, resulting in intramolecular electronic energy transfer, then diabatically (resulting in a nonadiabatic hop to the lower dissociative adiabatic potential energy surface) while the C-I bond is stretching. Note that the large branching ratio in favor of C-Br fission shows that the adiabatic approximation is terrible for this system; most of the molecules do not proceed adiabatically the first time they meet the avoided crossing after the initial stretching of the C-Br bond. Instead, they proceed diabatically, hopping to the region of the lower adiabat repulsive in the C-Br bond and undergoing C-Br fission.

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