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BOND SELECTIVE PHOTOCHEMISTRY IN CH_2BrI THROUGH ELECTRONIC EXCITATION AT 210 nm

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ABSTRACT

To explore the possibility of bond selective photochemistry in the excited electronic state, we have studied the photolysis of CH_2BrI in a molecular beam at 210 nm. Following the direct local excitation of a repulsive transition on the C-Br bond at 210 nm, the fragments were detected by time-of-flight mass spectrometry. The dominant channel was found to be C-Br fission (60 percent) releasing an average of 15 kcal/mole into translation with the remainder reacting to form CH_2 + IBr and CH_2 + I + Br. There was no evidence for the primary fission of the C-I bond, making this the first clear example of the selective cleavage of a stronger bond in a molecule over the weakest one.

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The possibility of inducing mode specific or bond selective photo-
dissociation in a polyatomic molecule by varying the nature of the initial
excitation has been of great interest to many workers in the field of laser
chemistry.[1] Although high isotopic selectivity was fully demonstrated
with infrared multiphoton dissociation, due to rapid intramolecular energy
transfer prior to dissociation it was found to be impossible to control the
dissociation mechanism by selection of the vibrational modes through which
energy is deposited into the molecule.[2,3] Even elegant selective studies
of unimolecular reaction dynamics in which energy is depcsited into a parti-
cular local C-H or O-H stretching mode have shown that, at energies not far
above threshold, vibrational energy redistribution occurs in a time scale
fast with respect to isomerization or dissociation, so the experimental
results are largely consistent with statistical predictions.[4,5,6] Dissoc-
iation pathways following electronic excitation of a molecule, however, have
been shown to be critically sensitive to the electronic nature of the initial
excitation.[7] Since it is possible to induce the prompt dissociation of a
chemical bond through direct excitation to a repulsive electronic surface,
it should be possible to achieve selective fission of a stronger bond over
the weaker one in some polyatomic molecules through local electronic
excitation involving a specific chemical bond.

In our previous attempt at the bond selective decomposition of
CF_2BrCF_2I at 193 nm,[8] the initial excitation of a nonbonding electron
in the bromine atom to the antibonding orbital of the C-Br bond (n(Br) $\rightarrow$
σ^*(C-Br) transition) resulted in only 37 percent C-Br bond rupture in the

primary process. Primary C-I bond rupture was found to be 63 percent. The extremely efficient electronic energy transfer from the C-Br to the C-I bond which leads to substantial C-I bond rupture was thought to be partly due to the parallel geometry of the C-Br and C-I bonds in the CF_2Br-CF_2I molecule.

We present here our results on the photodissociation of CH_2BrI at 210 nm, in the absorption peak of the n(Br) $\rightarrow$ σ^*(C-Br) transition, which is clearly separated from the n(I) $\rightarrow$ σ^*(C-I) transition. Since the C-Br and C-I bond angles in CH_2BrI are closer to being perpendicular than parallel, and the electronic excitations involving both C-Br and C-I are dominated by parallel transitions, electronic energy transfer from the C-Br to the C-I bond might not be as efficient as in the case of CF_2BrCF_2I. Excitation of a transition assigned as n(Br) $\rightarrow$ σ^*(C-Br) indeed results in primary C-Br fission with no primary C-I fission. Although the complete dissociation mechanism also contains concerted CH_2 + IBr and CH_2 + I + Br channels, this result is the first clear example of the selective fission of a stronger bond in a molecule over a weaker one. This contradicts the popular conclusion[9,10] from previous broadband experiments in the photodissociation of polyhalomethanes that only the weakest C-X bond breaks in the primary dissociation event at wavelengths >2000 Å.

The experiment was carried out in a high resolution crossed laser-molecular beam apparatus with a rotatable molecular beam source and a fixed mass spectrometric detector. A skimmed supersonic molecular beam of CH_2BrI seeded in argon is crossed by the focused output of a pulsed ArF excimer laser (Lambda Physik 102) Raman-shifted to 210 nm. Fragmentation products travel 36.6 cm to an electron bombardment ionizer; the ions

produced are then mass analyzed and counted with respect to the total flight time from the crossing point of the laser and molecular beam. All the time-of-flight data shown here were taken under the same experimental conditions. The data shown were taken at an angle of 20° from the direction of the molecular beam. The signal counts shown are normalized to counts per 100,000 laser shots with background subtracted.

The time-of-flight spectra from the CH_2I and Br products from C-Br fission at 210 nm are shown in Fig. 1. The Br^+ spectrum also contains a broad slow feature from the dissociation to CH_2 + Br + I which is energetically allowed at 210 nm. The center-of-mass product translational energy distribution for C-Br fission derived from the CH_2I^+ spectrum peaks at 17 kcal/mole with an average kinetic energy release of 15 kcal/mole and a full width at half maximum of 9.2 kcal/mole. This distribution correctly predicts the time-of-flight spectrum of the Br product from C-Br fission as shown by the dashed line in the Br^+ spectrum.

The time-of-flight spectra taken of CH_2Br^+ and I^+ are shown in Fig. 2. There is no signal from CH_2Br^+ which could be attributed to CH_2Br formed by primary C-I bond rupture in the monomer. The I^+ time-of-flight spectrum contains a broad slow signal from the dissociation to CH_2 + Br + I and a faster signal from the CH_2I product from C-Br fission fragmenting to I^+ in the ionizer. The time-of-arrival of CH_2I product shown in Fig. 1 corrected for the slightly longer flight time of CH_2I^+ ions through the quadrupole mass spectrometer is shown to fit the fast signal at I^+ perfectly. There is no signal at faster arrival times which could be attributed to I atoms formed by C-I bond rupture. In experiments

carried out at both 193 and 248 nm, I atoms from C-I fission gave signal at I^+ at faster arrival times than the I^+ signal from CH_2I and a major fraction of CH_2Br was also detected as CH_2Br^+. Apparently,.excitation to a Rydberg state of the I atom in CH_2BrI at 193 nm and the direct excitation of $n \rightarrow \sigma^*$ transitions of both C-I and C-Br at 248 nm, which is in an overlap region between two absorption peaks, resulted in both CH_2Br + I and CH_2I + Br dissociation channels. The lack of a CH_2Br + I channel at 210 nm is clear evidence that dissociation following excitation of the $n(Br) \rightarrow \sigma^*(C-Br)$ transition takes place before the electronic energy can be transferred from $\sigma^*(C-Br)$ to $\sigma^*(C-I)$.

The results presented here show that although excitation of a transition of CH_2BrI at 210 nm assigned as $n(Br) \rightarrow \sigma^*(C-Br)$ results in several competitive dissociation processes, including concerted IBr elimination (<6 percent) and dissociation forming CH_2 + I + Br (35 percent), among the simple bond rupture processes selective fission of the stronger C-Br bond over the weaker C-I bond was observed, contrary to any statistical description of the dissociation process. The evolution of the molecule along this electronic surface which is repulsive in the C-Br bond is faster than the rate of energy redistribution, thus allowing the selective fission of a stronger bond in the molecule.
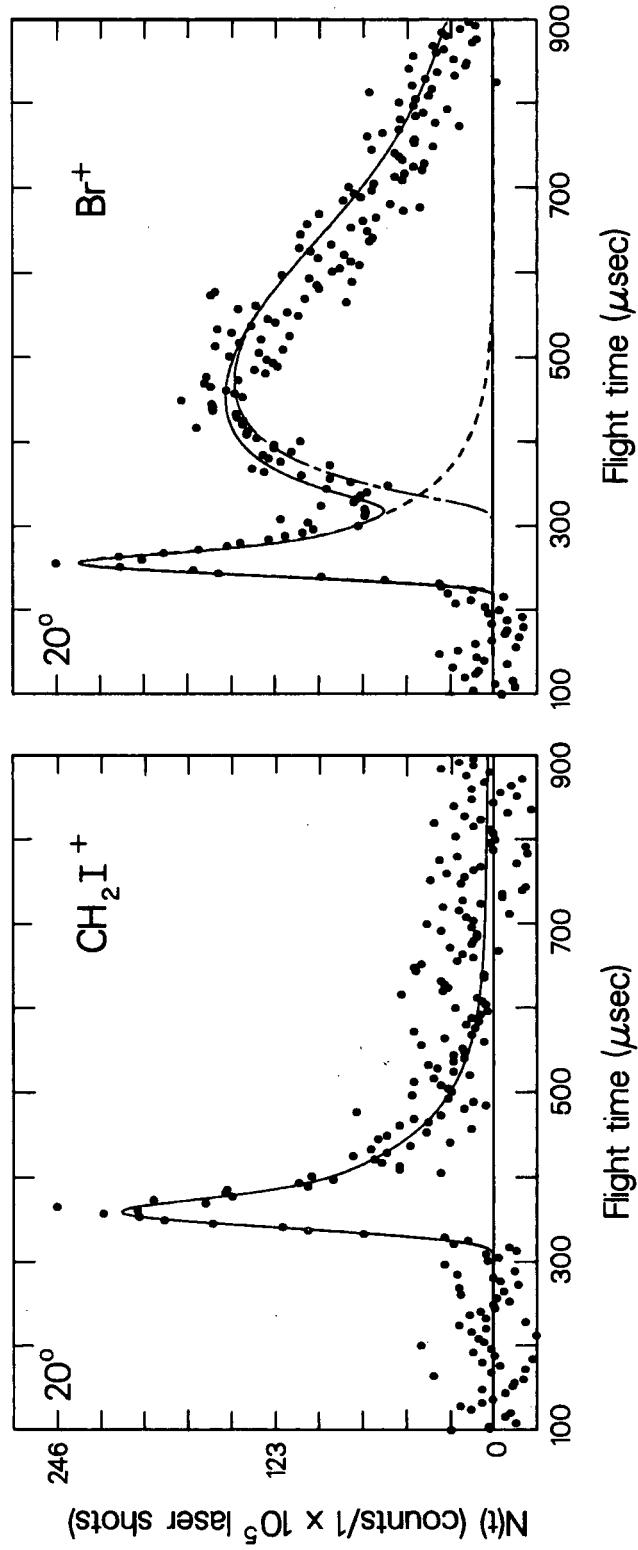
ACKNOWLEDGMENT

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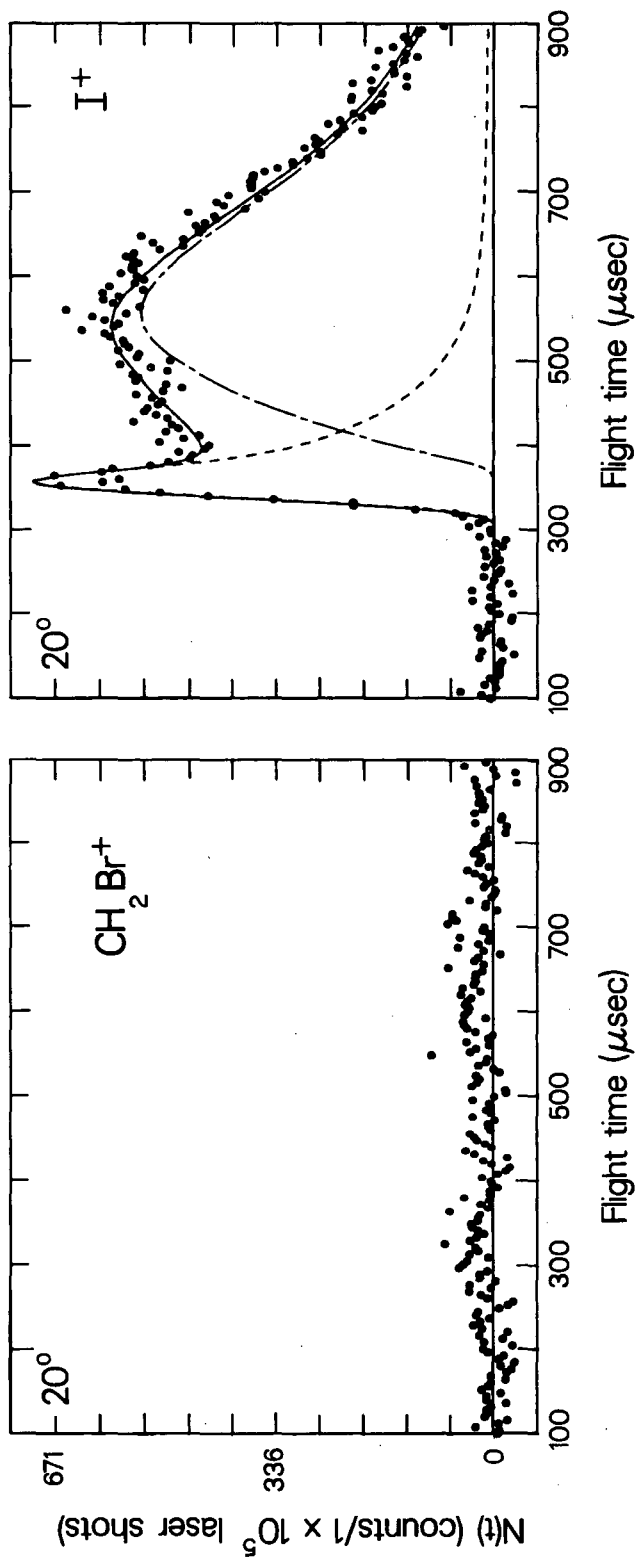
FIGURE CAPTIONS

Fig. 1.   Time-of-flight spectra of m/e = 141, CH_2I^+, and m/e = 81,
$^{81}Br^+$. ● Experimental points. (left) ———— fit to the
CH_2I^+ signal calculated from the product translational energy
distribution for C-Br fission. (right) - - - - calculated
time-of-flight of Br product from C-Br fission from the product
translational energy distribution derived from the CH_2I^+
spectrum, ——— — ——— contribution of Br atoms from
the dissociation to CH_2 + I + Br, ——— total sum. Relative
scaling of calculated fits is arbitrary.

Fig. 2.   Time-of-flight spectra of m/e = 95, $CH_2{}^{81}Br^+$, and m/e = 127,
I^+. ● Experimental points. (right) - - - fit to the fast
signal assuming it is all from fragmentation of CH_2I to I^+ in
the ionizer; fit is calculated from the time of arrival of CH_2I
product at CH_2I^+ shifted by 2 μsec to account for the smaller
precalibrated ion flight time, ——— — ——— contri-
bution from I atoms from the dissociation to CH_2 + I + Br,
——— total sum fit. Relative scaling of calculated fits is
arbitrary.

Fig. 1

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Fig. 2

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