#### DOI: 10.1002/cphc.200800180

# Photodissociation of Dibromobenzenes at 266 nm by the Velocity Imaging Technique

Xiao-Peng Zhang,<sup>[a]</sup> Zheng-Rong Wei,<sup>[b]</sup> Wei-Bin Lee,<sup>[a]</sup> Ting-Jung Chao,<sup>[a]</sup> and King-Chuen Lin\*<sup>[a]</sup>

A velocity imaging technique combined with (2 + 1) resonanceenhanced multiphoton ionization (REMPI) is used to detect the primary  $Br(^2P_{3/2})$  fragment in the photodissociation of o-, m-, and p-dibromobenzene at 266 nm. The obtained translational energy distributions suggest that the Br fragments are produced via two dissociation channels. For o- and m-dibromobenzene, the slow channel that yields an anisotropy parameter close to zero is proposed to stem from excitation of the lowest excited singlet  $(\pi,\pi^*)$ state followed by predissociation along a repulsive triplet  $(n,\sigma^*)$ state localized on the C–Br bond. The fast channel that gives rise to an anisotropy parameter of 0.53–0.73 is attributed to a bound

1. Introduction

Research into the photochemistry of halogenated molecules is of importance, because of their environmental impact and fundamental interest in their photodissociation dynamics. Of the aryl and alkyl halides, the photodissociation processes of aryl halides are more complicated, as more electronic states are involved thus making multiple dissociation channels probable. For instance, in the Br fragmentation of dibromobenzenes, one singlet and three triplet states are reachable upon excitation at 266 nm, and five repulsive singlet and triplet states nearby give rise to  $Br + C_6H_4Br$ .<sup>(1)</sup> The complicated interaction among these electronic states may lead to various photodissociation pathways, including predissociation via intersystem crossing (ISC), hot molecular dissociation from a repulsive surface.<sup>[2-10]</sup>

The femtosecond pump-probe technique<sup>[1,8-12]</sup> and photofragment translational spectroscopy (PTS)<sup>[2-7,13-19]</sup> have been popularly utilized in photodissociation studies of aryl halides. Femtosecond laser spectroscopy provides information on dissociation rate constants for the related routes by detecting the parent molecular cations or fragment cations after loss of a halogen atom. On the other hand, PTS gives insight into the fractions of translational and internal energy deposition and the anisotropy parameters in photolysis, by monitoring the time-of-flight (TOF) mass spectra of the fragments at different laboratory angles. To the best of our knowledge, velocity imaging detection coupled with resonance-enhanced multiphoton ionization (REMPI) as an alternative has been much less adopted, except in the photodissociation of iodobenzene.<sup>[20-22]</sup>

Knowledge of the translational energy and angular distributions of the photofragments may be extracted from the obtained fragment images by means of the velocity imaging triplet state with smaller dissociation barrier. For p-dibromobenzene, the dissociation rates are reversed, because the barrier for the bound triplet state becomes higher than the singlet-triplet crossing energy. The fractions of translational energy release are determined to be 6–8 and 29–40% for the slow and fast channels, respectively; the quantum yields are 0.2 and 0.8, and are insensitive to the position of the substituent. The Br fragmentation from bromobenzene and bromofluorobenzenes at the same photolyzing wavelength is also compared to understand the effect of the number of halogen atoms on the phenyl ring.

technique.<sup>[23, 24]</sup> The branching ratio of spin-orbit ground- and excited-state halogen may also be determined by selecting a particular wavelength in REMPI. This technique offers different insights into photodissociation behavior that should help further understanding of the dynamical complexity. For instance, in a recent study of the photodissociation of o-, m-, and p-bromofluorobenzenes at 266 nm,<sup>[25]</sup> we found two dissociation channels for all the molecules. The anisotropy parameters obtained were close to zero, which supports the observation of slow dissociation lifetimes by femtosecond laser spectroscopy.<sup>[10]</sup> In contrast, our dynamic features of decomposition differ from those by PTS,<sup>[16]</sup> in which only one dissociation channel is considered. The discrepancy might arise from differences in laser pulse duration or data analysis. In addition to Br(<sup>2</sup>P<sub>3/2</sub>), a minor  $Br({}^{2}P_{1/2})$  product was also found. This product has not been reported by the other two methods.

By taking advantage of the velocity imaging technique coupled with REMPI, we aim to investigate the photodissociation of *o*-, *m*-, and *p*-dibromobenzene at 266 nm. In a similar study using femtosecond pump-probe spectroscopy, Davidsson et al.<sup>[1]</sup> recently found a common slow dissociation channel

[a]	Dr. XP. Zhang, Dr. WB. Lee, TJ. Chao, Prof. KC. Lin
	Department of Chemistry, National Taiwan University, Taipei 106 (Taiwan) and
	Institute of Atomic and Molecular Sciences
	Academia Sinica, Taipei 106 (Taiwan)
	Fax: (+886) 2-23621483
	E-mail: kclin@ccms.ntu.edu.tw
[b]	ZR. Wei
	State Key Laboratory of Magnetic Resonance and
	Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics Chinese Academy of Sciences, Wuhan 430071 (P.R. China)

WWILEY InterScience

leading to the Br fragment. Its dissociation rate increases when the distance between the bromine atoms on the phenyl ring decreases or the number of substituted bromine atoms increases. They also found that the other fast dissociation channel, only available for o- and m-dibromobenzene, was opened up due to the symmetry lowering from  $C_{2v}$  to  $C_s$ . Nevertheless, with the velocity imaging technique we found that all the molecules may undergo dissociation via two channels. One dissociation channel has large fractions of translational energy release along with positive anisotropy parameters, indicative of very short dissociation lifetimes that are in accord with those obtained by femtosecond laser spectroscopy.<sup>[1]</sup> In contrast, the other channel is found to have anisotropy parameters close to zero. The ground-state  $Br({}^{2}P_{3/2})$  is the primary bromine product detectable. With the aid of reported ab initio potential energy calculations,<sup>[1]</sup> the photodissociation pathways are discussed in detail and also compared to the cases of bromobenzene and bromofluorobenzenes to understand the halogen effect.

### **Experimental Section**

The velocity imaging apparatus, similar to that used previously,<sup>[25,26]</sup> consisted of a molecular-beam source chamber and a main chamber, both of which were pumped to remain at a low pressure of  $\approx 2 \times 10^{-7}$  Torr. The samples of *o*-, *m*-, and *p*-dibromobenzene (99% purity) were used without further purification. Each was carried by helium gas at 1 atm through a pulsed valve with a 0.6-mm-diameter orifice (General Valve Co.) operating synchronously with the laser pulses at 10 Hz, and expanded into the source chamber. After passing through a 1 mm diameter skimmer and a collimator, the molecular beam was intersected perpendicularly by a linearly polarized laser beam in a two-stage ion lens region. The skimmer was mounted 30 mm downstream from the nozzle to divide the source chamber from the main chamber, which comprised an electrostatic lens, TOF drift tube, and two-dimensional position-sensitive detection system.

A 308 nm XeCl excimer pumped dye laser (FL3002, Lambda Physik) with a pulse duration of 15–20 ns and operating at 10 Hz was the only radiation source employed. Its output beam was frequency-doubled to emit at about 266 nm with the energy range of 100–200  $\mu$ J (AutoTrack III, InRad), followed by linear polarization perpendicular to the flight tube direction, and focused at the skimmed beam with a lens of focal length 200 mm. The *o*-, *m*- and *p*-dibromobenzene molecules were then photolyzed and the bromine-atom fragments were successively ionized by the (2+1) REMPI technique.

The resulting ions of Br or Br\* were extracted and accelerated into a 36 cm long field-free drift tube along the molecular-beam direction, followed by projection onto a two-stage microchannel plate (MCP) and a phosphor screen (FM3040, Galileo). The MCP could be gated within a minimum duration of 250 ns for mass selection. The ion image on the phosphor screen was recorded by a charge-coupled device (CCD) camera (200XL4078, Pixelfly). All the ion signals without gate restriction could be acquired by a photomultiplier tube, instead of the CCD camera, and then transferred to a transient digitizer for display of the TOF mass spectrum. The laser power dependence of the ion intensity was measured directly from the transient digitizer.

### 2. Results and Discussion

### 2.1. Molecular Photodissociation

As shown in Figure 1, the TOF mass spectrum of *m*-dibromobenzene (1,3-dibromobenzene) fragmentation at  $\approx$  266 nm yields several major peaks at *m/e* 12, 24, 36, 48, 79, and 81,



**Figure 1.** TOF mass spectrum of photofragments obtained in the photolysis of *m*-dibromobenzene at 266.55 nm. The Br<sup>+</sup> ion signal is formed by the (2+1) REMPI process, while the remaining peaks result from nonresonant ionization.

corresponding to C<sup>+</sup>, C<sub>2</sub><sup>+</sup>, C<sub>3</sub><sup>+</sup>, C<sub>4</sub><sup>+</sup>, <sup>79</sup>Br<sup>+</sup>, and <sup>81</sup>Br<sup>+</sup>, respectively. Among them, the isotopic variants <sup>79</sup>Br<sup>+</sup> and <sup>81</sup>Br<sup>+</sup> are enhanced with (2+1) REMPI via the 5p<sup>4</sup>P<sup>0</sup><sub>3/2</sub>  $\leftarrow$  4p<sup>2</sup>P<sup>0</sup><sub>3/2</sub> two-photon transition at 266.55 nm, while the remaining peaks result from the nonresonant processes. The parent peak C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub><sup>+</sup> is missing in the mass spectrum, in part because the dissociation lifetimes of the excited state prepared at 266 nm are so short that a great number of excited molecules have dissociated prior to absorbing an additional photon for ionization.

To further confirm that the bromine atoms are produced by molecular photodissociation, the power dependence of Br<sup>+</sup> produced by *m*-dibromobenzene at 266.55 nm is measured. The results yield a straight line with the slope of 3.3, which indicates that Br is obtained during one-photon dissociation, followed by ionization through (2+1) REMPI. The final ionization step is partially saturated. The laser energy applied throughout the experiments is not large enough to open up significantly the other channel of dissociative ionization, that is,  $C_6H_4Br_2^+ \rightarrow$  $C_6H_4Br^+ + Br$ . It will otherwise consume at least five photons; the consequence is not supported by our power-dependence measurement. This dissociation channel is, however, found in the femtosecond laser experiments,<sup>[1]</sup> in which the time-resolved profiles of molecular cations  $C_6H_4Br_2^+$  were probed for determining the lifetimes of the excited molecules before the Br atom leaves.

### 2.2. Translational Energy and Angular Distributions

Raw ion images of  $Br(^{2}P_{_{3/2}})$  acquired with velocity imaging detection from the photodissociation of *o*-, *m*-, and *p*-dibromobenzene at 266.55 nm are shown in Figure 2. Each image was accumulated over 40 000 laser shots, and the background was



**Figure 2.** Ion images of Br from the photodissociation of *o*-, *m*-, and *p*-dibromobenzene at about 266 nm. The left half is the raw ion image, while the right half is the inverse Abel-transformed image. The laser is linearly polarized along the vertical direction.

removed by subtracting a reference image collected at off-resonance wavelength under the same conditions. When the laser is tuned to 266.61 nm, a much weaker  $Br^{*}({}^{2}P_{1/2})$  ion signal can be detected only in the photodissociation of *m*-dibromobenzene at the higher laser energy of 200 µJ (Figure 3). Each



**Figure 3.** a) Raw ion image and b) inverse Abel-transformed ion image of Br\* from the photodissociation of *m*-dibromobenzene at approximately 266 nm. The laser is linearly polarized along the vertical direction. c) The corresponding center-of-mass translational energy distribution of the Br\* fragment. The arrow indicates the maximum kinetic energy available for one-photon dissociation. Each data point ( $\bullet$ ) corresponds to the relative signal intensity in arbitrary units. The deconvoluted Gaussian components are denoted by the solid lines.

raw image is a two-dimensional projection of the three-dimensional speed and angular distributions with cylindrical symmetry around the polarization axis of the photolyzing laser. The corresponding three-dimensional spatial distributions of the fragments are reconstructed based on inverse Abel transformation (Figures 2 and 3).

The speed distribution of the bromine fragments can be extracted by integrating the reconstructed three-dimensional speed distribution over all angles at each speed. The subsequent center-of-mass translational energy distribution is obtained from the speed distribution by considering the energy conservation.<sup>[25,26]</sup> The individual results of Br\* and Br fragmentation from dibromobenzenes are displayed in Figures 3 c and



**Figure 4.** Center-of-mass translational energy distributions of the Br fragments produced from the photodissociation of o-, m-, and p-dibromobenzene at about 266 nm. The arrows indicate the maximum kinetic energy available for one-photon dissociation. Each data point ( $\bullet$ ) corresponds to the relative signal intensity in arbitrary units. The deconvoluted Gaussian components are denoted by the solid lines.

4. Each Br distribution can be well-fitted by two narrow Gaussian curves, whereas the Br\* distribution requires one additional Gaussian curve.

The available energy  $E_{avl}$  for the dissociation process is evaluated by [Eq. (1)]

$$E_{\rm avl} = E_{\rm hv} - D_0 - E_{\rm el} + E_{\rm int} \tag{1}$$

where  $E_{hv}$  is the photon energy,  $E_{el}$  the electronic energy of the bromine atom (0 kJ mol<sup>-1</sup> for Br and 44 kJ mol<sup>-1</sup> for Br\*), and  $E_{int}$  the internal energy of the parent molecule, which is expected to be zero in a supersonic molecular beam under jetcooled conditions. The dissociation energy  $D_0$  of the C–Br bond, for which data are not available in the literature, is as-

## **CHEMPHYS**CHEM

sumed to equal the corresponding values of *o*-, *m*-, and *p*-bromofluorobenzene as evaluated by the PTS method.<sup>[16]</sup> The values of 328.8, 328.8, and 316.2 kJ mol<sup>-1</sup> for *o*-, *m*-, and *p*-dibromobenzene, respectively, are thus adopted. Each  $E_{avl}$  evaluated is listed in Table 1 and marked with an arrow in Figur-

<b>Table 1.</b> Important parameters obtained from bromine fragmentation of 1,2-Br <sub>2</sub> C <sub>6</sub> H <sub>4</sub> , 1,3-Br <sub>2</sub> C <sub>6</sub> H <sub>4</sub> , and 1,4-Br <sub>2</sub> C <sub>6</sub> H <sub>4</sub> ( <i>o</i> -, <i>m</i> -, and <i>p</i> -dibromobenzene) at 266 nm.										
	State	hν [kJ mol <sup>-1</sup> ]	E <sub>avl</sub> [kJ mol <sup>-1</sup> ]	$< E_{\rm t} >$ [kJ mol <sup>-1</sup> ]	f <sub>T</sub>	β				
1,2-	Br	449.4	120.4	9.6	0.08	$0.07 \pm 0.05$				
$\mathrm{Br}_{2}\mathrm{C}_{6}\mathrm{H}_{4}$				48.5	0.40	0.65±0.1				
1,3-	Br	449.4	120.4	7.5	0.06	$0.13 \pm 0.05$				
$Br_2C_6H_4$				34.7	0.29	$0.53 \pm 0.1$				
	Br*	448.9	76.5	5.4	0.07	$0.15 \pm 0.05$				
				31.8	0.42	$0.72 \pm 0.1$				
				60.6						
1,4-	Br	449.4	128.7	8.4	0.06	$0.05 \pm 0.05$				
$\mathrm{Br}_{2}\mathrm{C}_{6}\mathrm{H}_{4}$				48.0	0.37	$0.73 \pm 0.1$				

es 3 c and 4, and indicates the maximum kinetic energy available for one-photon dissociation of the parent molecules. Apparently, all the Br fragments originate from a process of onephoton dissociation, whereas a fraction of the Br\* fragments leading to the broader and higher translational energy component might be produced by two-photon dissociation. The fraction  $f_T$  of each translational energy ( $E_t$ ) component, defined as the ratio of the average translational energy to the available energy, can also be evaluated and is listed in Table 1.

The relative quantum yields  $\Phi(Br^*)$  and  $\Phi(Br)$  are evaluated by [Eq. (2)]

$$\Phi(\mathsf{Br}^*) = \frac{N(\mathsf{Br}^*)}{N(\mathsf{Br}) + N(\mathsf{Br}^*)} = k \frac{S(\mathsf{Br}^*)}{S(\mathsf{Br}) + S(\mathsf{Br}^*)}$$
(2)

and [Eq. (3)]

$$\boldsymbol{\Phi}(\mathsf{Br}) = \mathbf{1} - \boldsymbol{\Phi}(\mathsf{Br}^*) \tag{3}$$

where *N*(Br\*) and *N*(Br) are the numbers of Br\* and Br fragments; *S*(Br\*) and *S*(Br) are the ion intensities that are measured individually. The factor *k*, which relates the obtained bromine ion signal to its state population, can be evaluated by performing a calibration experiment of Br<sub>2</sub> photolysis under the same conditions. The *k* value was thus determined to be 0.595. The results for  $\Phi(Br^*)$  and  $\Phi(Br)$  are listed in Table 2.  $\Phi(Br)_{low}$  and  $\Phi(Br)_{high}$  are defined as the quantum yield evaluated from the low and high translational energy components as resolved in Figure 4. If  $\Phi(Br)$  is considered as unity,  $\Phi(Br)_{low}$  and  $\Phi(Br)_{high}$  are evaluated to be about 0.20 and 0.80, respectively, irrespective of the relative positions of the two Br atoms on the phenyl ring. In the photodissociation of *m*-dibromobenzene, the low and middle translational energy components for the Br\* product, confined within the arrow mark, are considered as the gravely mark and considered as the state of the relative positions for the Br\* product.

 Table 2. Relative quantum yields of Br and Br\* for different translational energy components.

	$\Phi(Br)_{total}$	$\Phi(Br)_{low}$	$\Phi(Br)_{high}$	$\Phi(Br^*)_{total}$
1,2-Br <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	1	0.2	0.8	0
$1,3-Br_2C_6H_4$	0.91	0.17	0.74	0.06 <sup>[a]</sup>
$1,4-Br_2C_6H_4$	1	0.19	0.81	0

[a] Considering only the portions (confined at low energy below the marked arrow in Figure 3 c) resulting from one-photon molecular dissociation.

ered to originate from the one-photon dissociation and their sum amounts to 67%, contributing 6% of the total quantum yield (Table 2). The quantum yields  $\Phi(Br)$  differ from those by femtosecond laser spectroscopy.<sup>[1]</sup> The latter method gave results of 0.3, 0.6, and 1 for the slow dissociation channel and 0.7, 0.4, and 0 for the fast channel in *o*-, *m*-, and *p*-dibromobenzene, respectively.

In a photodissociation process, the angular distribution  $l(\theta)$  of the fragment can be obtained by integrating the reconstructed spatial distribution over a suitable range of speed at each angle. It may be characterized by an anisotropy parameter  $\beta$ , as expressed by Equation (4)<sup>[27,28]</sup>

$$I(\theta) = (4\pi)^{-1} [1 + \beta P_2(\cos \theta)]$$
(4)

where  $\beta$  is limited between 2 and -1,  $P_2(\cos\theta)$  is the secondorder Legendre polynomial, and  $\theta$  is the angle between the laser polarization direction and the recoil velocity vector of fragments. The  $\beta$  value can be obtained by least-squares fitting to the angular distribution. *p*-Dibromobenzene is demonstrated as an example; the fit is given in Figure 5. The upper and lower fitting curves determine the uncertainty. The  $\beta$  values obtained in this manner from the Br and Br\* images are listed in Table 1. Note that information on the possible alignment of the Br fragment may be lost in one-laser experiments. This could slightly affect the measured anisotropy parameter.

The  $\beta(Br)$  and  $\beta(Br^*)$  values obtained for the lower-speed components during the photodissocation are approximately zero. The anisotropic feature of the fragments indicates that the dissociation lifetime is comparable to a molecular rotation period. In contrast,  $\beta(Br)$  of the higher-speed components and  $\beta(Br^*)$  of the middle-speed component are about 0.53–0.73, which suggests that the molecular dissociation results mainly from a parallel transition.

#### 2.3. Photodissociation Channels

By using femtosecond laser spectroscopy at 270 nm, Davidsson and co-workers<sup>[1]</sup> obtained the dissociation lifetimes of (13.3, 2.9), (7.5, 1), and 18.2 ps for *o*-, *m*-, and *p*-dibromobenzene, respectively. Two dissociation channels are found in *o*- and *m*-dibromobenzene, whereas the fast channel is blocked in *p*-dibromobenzene. The common slow channel is anticipated to involve predissociation via ISC. With the aid of ab initio one-dimensional potential energy curves along the C–Br bond disso-



**Figure 5.** Determination of  $\beta$  by the fit of angular distribution for *p*-dibromobenzene. a)  $\beta = 0.05 \pm 0.05$  for the slow dissociation channel, and b)  $\beta = 0.73 \pm 0.1$  for the fast dissociation channel.

ciation,<sup>[1]</sup> these authors proposed that the predissociation is through curve crossing between the lowest singlet excited state, S<sub>1</sub>( $\pi\pi^*$ , B<sub>2</sub>) [or S<sub>1</sub>( $\pi\pi^*$ , A')], and the repulsive triplet (n, $\sigma^*$ ) states (T<sub>6</sub>–A" in *o*-dibromobenzene, T<sub>4</sub>–A" in *m*-dibromobenzene, and T<sub>5</sub>–B<sub>1</sub> in *p*-dibromobenzene). For clear interpretation, a simplified energy diagram for the molecular dissociation is shown in Figure 6, which includes only the potential energy curves mentioned in this work.<sup>[1]</sup> The singlet–triplet crossing points for *o*- and *m*-dibromobenzene are  $\approx$  0.2 eV higher than the S<sub>1</sub> state, as excitation at 266 nm is equivalent to 4.66 eV.

The  $S_1-B_2$  state for *p*-dibromobenzene is stabilized, even lying below the  $T_2$  and  $T_3$  states, with an energy  $\approx 0.5$  eV lower than the corresponding states of *o*- and *m*-dibromobenzene. The  $S_1-T_5$  curve crossing point is at about 4.6 eV, very close to the excitation energy. Davidsson's group ascribed the obtained single dissociation channel to this predissociation pathway.

The  $\beta$  value is associated with a molecular rotation period that relies on the temperature of the molecular beam. In our system, the rotational temperature is known to be 100 K by fitting the ro-vibrational band profiles of the  ${}^{1}B_{2}({}^{1}\sum_{u}^{+})$  state of  $CS_{2}.^{[29]}$ Peebles and Peebles<sup>[30]</sup> reported Fourier-transform microwave spectra of a chemical analogue, ARTICLES

<sup>79</sup>Br bromobenzene, which gave rise to the rotational constants of A=5667.750, B=994.9018, and C=846.2567 MHz. The moment of inertia corresponds to  $1.46 \times 10^{-38}$ ,  $8.42 \times 10^{-38}$ , and  $9.85 \times 10^{-38}$  g cm<sup>-2</sup>, respectively. Given the rotational energy,  $E_r = h^2 j(j+1)/8\pi^2 I_m$  (h: Planck's constant;  $I_m$ : moment of inertia; *j*: rotational quantum number), the maximum value of *j* can be populated up to 13, 32, and 34, associated with the rotational constants A, B, and C at 100 K, if the same rotational energy is assumed along each rotational degree of freedom. Therefore, based on the molecular rotation period,  $t_r = h/2\pi j B_m$  ( $B_m$ : rotational constant),<sup>[31]</sup>  $t_r$  may be estimated to be 2.2, 4.9, and 5.4 ps for three different rotational degrees of freedom. The average  $t_r$  becomes 4.2 ps if the rotational period in each degree of freedom has the same contribution. Another chemical analogue, 1,3,5-tribromobenzene, has the moment of inertia of  $4.68 \times 10^{-37}$ ,  $2.338 \times 10^{-37}$ , and  $2.342 \times 10^{-37}$  g cm<sup>-2</sup> along the three principal coordinates.<sup>[32]</sup> The corresponding molecular rotation period is evaluated similarly to be 12, 8.7, and 8.7 ps, and thus the average  $t_r$  becomes 9.8 ps. Despite the lack of rotational constants available for dibromobenzenes, their moments of inertia lie in between those of bromobenzene and 1,3,5-bromobenzene, and thus the average molecular rotation period may be estimated to be  $9.8 \ge t_r \ge 4.2$  ps. The slow dissociation lifetimes of 13.3, 7.5, and 18.2 ps for o-, m-, and p-dibromobenzene, respectively, are comparable to the average  $t_{r}$  and thereby the alignment of fragmentation may be substantially reduced. As listed in Table 1,  $\beta$ (Br) yields a corresponding value of  $0.07 \pm 0.05$ ,  $0.13 \pm 0.05$ , and  $0.05 \pm 0.05$ , thus showing the same trend as the dissociation lifetimes. The slow predissociation process allows for more available energy being partitioned into the internal states of the fragment. A large fraction of the internal energy deposition corresponding to 92, 94, and 94% for o-, m-, and p-dibromobenzene is obtained.



**Figure 6.** Simplified energy diagrams showing one-dimensional potential energy curves along the C–Br bond dissociation for a) *o*-dibromobenzene, b) *m*-dibromobenzene, and c) *p*-dibromobenzene. The excitation energy at 4.66 eV by a laser source is denoted by horizontal dashed lines. The detailed diagrams and calculations are referred to in the work by Liu et al.<sup>[1]</sup>

Davidsson et al.<sup>[1]</sup> proposed that the dissociation pathway for the fast channel is via a bound triplet state  $T_3$  (n $\sigma^*$ , A') followed by IC to T<sub>2</sub>-A', which has a dissociation barrier smaller than the  $S_1-T_6$  or  $S_1-T_4$  ISC point as described above (Figure 6). They also explained the lack of a fast dissociation channel in p-dibromobenzene by attributing it to the fact that the  $T_2(A_1)$ -to- $T_3(B_2)$  IC is forbidden due to symmetry restriction. In our work, p-dibromobenzene shows two dissociation channels (Figure 4). The channel with the slow kinetic component, which gives rise to a  $\beta$ (Br) value of 0.05  $\pm$  0.05, corresponds to that obtained with a dissociation lifetime of 18.2 ns.<sup>[1]</sup> The additional channel with the higher kinetic component, which yields  $\beta$ (Br) and  $f_{\rm T}$  of 0.73  $\pm$  0.1 and 0.37, respectively, is termed a fast dissociation channel that was not reported previously. The reasons for the discrepancy found in the dissociation channels of p-dibromobenzene and the quantum yields mentioned above are not yet known. Different pulse durations between femtosecond and nanosecond lasers might be one of the reasons to cause the discrepancy. Excitation with a femtosecond laser can feasibly lead to multiphoton absorption producing a large number of parent molecular ions, such that the dissociation pathways might differ somewhat from those obtained by nanosecond-pulsed excitation.

Herein, alternative photodissociation pathways for *p*-dibromobenzene are given. According to the potential energy curves (Figure 6), we propose that the fast channel might proceed through  $S_1 \rightarrow T_5$  ISC or the  $T_3$  state, either exit channel correlating to the ground state  $Br(^2P_{3/2})$  product; the dissociation barriers for the ISC point or  $T_3$  are very close to the excitation energy at 4.66 eV. The ISC ( $S_1 \rightarrow T_5$ ) should make the  $T_5$  state carry a mixed property of both parallel and perpendicular transition. Because  $T_3(B_2)$  and  $S_1(B_2)$ , with the same symmetry, are close to each other energetically, the intensity borrowing effect may enhance the  $T_3(B_2) \leftarrow S_0(A_1)$  transition, thereby leading to a Br fragment with mixed character. The obtained positive value of  $\beta$  is attributed to a partial contribution of the parallel transition.

Meanwhile, we propose that the slow dissociation channel might proceed via the  $T_2(A_1)$  state that has a barrier  $\approx 0.2 \; eV$ higher than the excitation energy. This barrier height is comparable to those of the slow channels in o- and m-dibromobenzene, such that these molecules may have similar dissociation rates, as reflected in the dissociation lifetimes and the  $\beta({\rm Br})$ values. Note that the proposed mechanisms simply rely on the state energies and the dissociation barriers along the C-Br dissociation coordinate, but neglect the surface coupling strength and multidimensional character probably involved in the photodissociation process. If the ISC coupling strength is weak, the dissociation rate may turn out to be slow, or involvement of the multidimensional character may change the activation barrier. For instance, in the photodissociation of bromo-3,5-difluorobenzene, the singlet-triplet crossing barrier is reduced when the reaction coordinate combines a C-Br bond stretch and a Br out-of-plane bend on the  $\mathsf{S}_1$  surface.  $^{[33]}$  Given more quantitative dynamical information, prediction of the dissociation rates and the subsequent pathways may be more reliable.

It is worth noting the laser energy dependence of these two dissociation channels; *m*-dibromobenzene is examined as an example. As shown in Figure 7, when the laser energy is dou-



**Figure 7.** Speed distributions of the Br( ${}^{2}P_{3/2}$ ) photofragments obtained from a) *m*-dibromobenzene and b) *m*-bromofluorobenzene<sup>[25]</sup> at different laser energies near 266 nm. Both distributions in (b) were normalized to unity.

bled, the peak positions of the slow and fast dissociation components both shift to the side of higher speeds. It can be speculated that increasing the laser energy helps enhance population excitation to those vibrational levels with poor Franck-Condon factors, including the levels either close to or away from the dissociation barrier. The molecules excited to these levels have different dissociation rates, depending on the energy deficit from the barrier. The increased amount in the higher vibrational levels gain a higher rate to pass through the dissociation barrier, such that the subsequent Br fragments may carry more translational energy to blue-shift the peak. Such blue-shift phenomena were also found in o- and p-dibromobenzene. The results may provide support to the mechanisms proposed for dibromobenzenes, in which both dissociation pathways are bound to a barrier, but the fast one surpasses the smaller barrier.

The shift of the peak position to the higher kinetic energy side with an increase of the laser energy could not be caused significantly by Coulombic repulsion. If excess  $Br^+$  ions are produced, the resultant Coulombic repulsion may force the fragment image towards elliptical distortion along the dissociation direction. However, in this work the images remain circularly symmetric even at the larger energy of 200 µJ (Figure 2). The ion numbers passing over the threshold level were carefully controlled to prevent interference from the Coulombic repulsion. To verify this point, a chemical analogue is dissociated for comparison. Bromofluorobenzenes may similarly undergo Br fragmentation via two dissociation channels upon irradiation

at 266 nm.<sup>[25]</sup> When the laser energy was increased up to 200  $\mu J$  (for o-bromofluorobenzene), the lower-speed component of the Br fragment shifted to the side of higher kinetic energy, whereas the higher-speed component remained invariant.

### 2.4. Comparison with Bromobenzene and Bromofluorobenzenes

By using PTS to study the Br fragmentation of bromobenzene at 266 nm, Han's research group<sup>[15]</sup> earlier proposed qualitatively two possible dissociation mechanisms. One is through fast predissociation; the parent molecules are excited to a bound singlet state, followed by rapidly crossing to a repulsive triplet state. In a later work, Davidsson and co-workers<sup>[10,12]</sup> proposed that only one dissociation channel is caused by predissociation via ISC, consistent with the ab initio calculations and Han's work.<sup>[1,15,34,35]</sup> Increasing the number of the Br substitution stabilizes the repulsive excited states and enhances the spin–orbit coupling to facilitate the predissociation mechanism. There are more repulsive states that cross the bound singlet state of dibromobenzenes near the excitation energy at 266 nm which lead to additional dissociation routes.

In the photodissociation of o-, m-, and p-bromofluorobenzene at about 266 nm,  $Br({}^{2}P_{3/2})$  was found to be the primary product through two dissociation channels by using a velocity imaging technique.<sup>[25]</sup> The fast route with a positive anisotropy parameter might be attributed to a direct dissociation, whereas the slow one with the anisotropy parameter close to zero is initiated from the lowest excited singlet state coupled to a repulsive triplet state. In this work, the molecular dissociations at 266 nm are all characterized by one fast and other slow channels, consistent with those found in bromofluorobenzenes. The former exhibits a constant ratio of  $\Phi(Br)$  between these two dissociation channels, whereas the latter shows the dependence of  $\Phi(Br)$  on the Br-substituted position. The proposed slow dissociation mechanisms in both cases are similar, but the fast dissociation channels are different. The laser energy dependences of the Br speed distributions for m-dibromobenzene and *m*-bromofluorobenzene are compared in Figure 7. The higher-speed component for the latter molecule appears insensitive to the laser energy variation. Furthermore, the  $f_{\rm T}$ values for the fast channel obtained in bromofluorobenzenes are between 61 and 71%, comparable to those found in the alkyl halides.<sup>[25]</sup> In contrast, the  $f_{T}$  obtained in this work lies between 29 and 40%, and is less likely to stem from a process of direct dissociation.

### 3. Conclusions

The photodissociation of o-, m-, and p-dibromobenzene at about 266 nm is investigated, which gives rise to the primary  $Br({}^{2}P_{3/2})$  product through two dissociation channels. One channel is initiated from the lowest excited singlet state coupled to a repulsive triplet state, while the other is attributed to a bound triplet state. Both channels are bound to an individual barrier. As compared to the present work, the fast channels in

the photodissociation of bromofluorobenzenes are governed by direct dissociation that leads to relatively larger fractions of the translational energy release. The anisotropy parameters determined herein are consistent with observation of the dissociation lifetimes by femtosecond laser spectroscopy. The guantum yields of these two dissociation channels remain almost constant. As a whole, increasing the number of halogen substitutions on the phenyl ring complicates the behavior of halogen-atom dissociation. Given a photolyzing laser wavelength, these channels rely on the halogen type, molecular symmetry, and substituent position, which affect the relative stability and coupling strength of the potential surfaces involved. Therefore, information on ab initio potential energy calculations is required for understanding how the dissociation pathways proceed. Further systematic investigation in this field should be worthwhile.

### Acknowledgements

This work is supported by the National Taiwan University, Ministry of Education, and National Science Council of Taiwan, Republic of China, under contract no. NSC 96-2113-M-002-027.

**Keywords:** bromine · laser spectroscopy · photochemistry · resonance-enhanced multiphoton ionization · velocity imaging

- [1] Y. J. Liu, P. Persson, H. O. Karlsson, S. Lunell, M. Kadi, D. Karlsson, J. Davidsson, J. Chem. Phys. 2004, 120, 6502–6509.
- [2] A. Freedman, S. C. Yang, M. Kawasaki, R. Bersohn, J. Chem. Phys. 1980, 72, 1028–1033.
- [3] T. Ichimura, Y. Mori, H. Shinohara, N. Nishi, Chem. Phys. Lett. 1986, 125, 263–266.
- [4] H. J. Hwang, M. A. El-Sayed, J. Chem. Phys. 1992, 96, 856-858.
- [5] X. P. Zhang, Z. R. Wei, Y. Tang, T. J. Chao, B. Zhang, K. C. Lin, *ChemPhys-Chem* 2008, 9, 1130–1136.
- [6] T. Ichimura, Y. Mori, H. Shinohara, N. Nishi, J. Chem. Phys. 1997, 107, 835–842.
- [7] K. L. Han, G. Z. He, J. Photochem. Photobiol. C 2007, 8, 55-66.
- [8] M. Kadi, J. Davidsson, Chem. Phys. Lett. 2003, 378, 172-177.
- [9] M. Kadi, E. Ivarsson, J. Davidsson, Chem. Phys. Lett. 2004, 384, 35–39.
- [10] O. A. Borg, Y. J. Liu, P. Persson, S. Lunell, D. Karlsson, M. Kadi, J. Davidsson, J. Phys. Chem. A 2006, 110, 7045–7056.
- [11] P. Y. Cheng, D. Zhong, A. H. Zewail, Chem. Phys. Lett. 1995, 237, 399– 405.
- [12] M. Kadi, J. Davidsson, A. N. Tarnovsky, M. Rasmusson, E. Akesson, Chem. Phys. Lett. 2001, 350, 93–98.
- [13] M. Dzvonik, S. Yang, R. Bersohn, J. Chem. Phys. 1974, 61, 4408-4421.
- [14] J. A. Griffiths, K. Junk, M. A. El-Sayed, J. Phys. Chem. 1996, 100, 7989-
- 7996. [15] H. Zhang, R. S. Zhu, G. J. Wang, K. L. Han, G. Z. He, N. Q. Lou, *J. Chem. Phys.* **1999**, *110*, 2922–2927.
- [16] X. B. Gu, G. J. Wang, J. H. Huang, K. L. Han, G. Z. He, N. Q. Lou, J. Phys. Chem. A 2001, 105, 354–362.
- [17] T. Ichimura, Y. Mori, H. Shinohara, N. Nishi, Chem. Phys. 1994, 189, 117– 125.
- [18] J. E. Freitas, H. J. Hwang, M. A. El-Sayed, J. Phys. Chem. 1995, 99, 7395– 7406.
- [19] R. S. Zhu, H. Zhang, G. J. Wang, X. B. Gu, K. L. Han, G. Z. He, N. Q. Lou, *Chem. Phys.* **1999**, 248, 285–292.
- [20] S. Unny, Y. Du, L. Zhu, K. Truhins, R. J. Gordon, A. Sugita, M. Kawasaki, Y. Matsumi, R. Delmdahl, D. H. Parker, A. Berces, *J. Phys. Chem. A* 2001, 105, 2270–2280.

- [21] M. D. Poulsen, E. Skovsen, H. Stapelfeldt, J. Chem. Phys. 2002, 117, 2097–2102.
- [22] E. Péronne, M. D. Poulsen, H. Stapelfeldt, C. Z. Bisgaard, E. Hamilton, T. Seideman, Phys. Rev. A 2004, 70, 063410–9.
- [23] D. W. Chandler, P. L. Houston, J. Chem. Phys. 1987, 87, 1445-1447.
- [24] D. H. Parker, A. T. J. B. Eppink, J. Chem. Phys. 1997, 107, 2357–2362.
- [25] Y. Tang, W. B. Lee, B. Zhang, K. C. Lin, J. Phys. Chem. A 2008, 112, 1421– 1429.
- [26] Y. Tang, W. B. Lee, Z. Hu, B. Zhang, K. C. Lin, J. Chem. Phys. 2007, 126, 064302–8.
- [27] R. N. Zare, D. R. Herschbach, Proc. IEEE 1963, 51, 173-182.
- [28] R. N. Zare, Mol. Photochem. 1972, 4, 1.
- [29] Z. Hu, W. B. Lee, X. P. Zhang, P. Y. Wei, K. C. Lin, ChemPhysChem 2008, 9, 422–430.

- [30] S. A. Peebles, P. A. Peebles, J. Mol. Struct. 2003, 657, 107-116.
- [31] R. D. Levine, R. B. Bernstein, Molecular Reaction Dynamics and Chemical Reactivity, Oxford University Press, New York, 1987, p. 284.
- [32] A. V. Korshunov, V. E. Volkov, Zh. Strukt. Khim. 1961, 2, 151–157.
- [33] O. A. Borg, Chem. Phys. Lett. 2007, 436, 57-62.
- [34] Y. J. Liu, P. Persson, S. Lunell, J. Phys. Chem. A 2004, 108, 2339-2345.
- [35] M. Rasmusson, R. Lindh, N. Lascoux, A. N. Tarnovsky, M. Kadi, O. Kuhn, V. Sundstrom, E. Akesson, *Chem. Phys. Lett.* **2003**, *367*, 759–766.

Received: March 26, 2008 Revised: May 27, 2008 Published online on July 15, 2008