Y. R. Lee, C. C. Chou, Y. J. Lee, L. D. Wang, and S. M. Lin

Articles you may be interested in

Photodissociation of 1,2-$C_2H_2Br_2$ at 248 nm: Competition between three-body formation Br+Br+C_2H_2 and molecular Br_2 elimination

Y. R. Lee, C. C. Chou, Y. J. Lee, L. D. Wang, and S. M. Lin[a)]

Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei, Taiwan
and Department of Chemistry, National Taiwan University, P.O. Box 23-166, Taipei, Taiwan

The photodissociation of 1,2-$C_2H_2Br_2$ at 248 nm has been studied by product translational spectroscopy. The results show that the molecule dissociates exclusively into the products (1) Br_2+C_2H_2 and (2) Br (fast)+Br (slow)+C_2H_2 with a branching ratio ~0.2:0.8. While the cleavages of the C–Br bonds are not symmetric, producing the Br atoms at unequal velocities, the anisotropy of the products indicates that both reactions occur in a fraction of a rotational period. Following an asynchronous concerted reaction, the triple products were simulated with the $P(E_t)$ distributions coupled by asymmetric angular distributions. A mechanism consistent with the measured results is proposed that the Br_2 elimination is a result of a fast intersystem crossing from the $\pi\pi^*$ pumped state while the triple products occur via a simultaneous asymmetric scission of the C–Br bonds along the $n\sigma^*$ state. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1387476]

I. INTRODUCTION

The UV photodissociation of vinyl chloride and its derivatives has been a focus of attention for many years.[1] Considerable progress in finding the mechanistic and dynamic details has been made for a total of five possible dissociation channels. A fast, anisotropic Cl product was explained to predissociate from the excited potential energy surface while the remaining products HCl, slow Cl, H, and H_2 were considered to originate from the ground electronic state after internal conversion from the $\pi\pi^*$ state. In the 193 nm photolysis of dichloroethylenes, however, no Cl_2 elimination could be observed.[2] According to *ab initio* calculations, this is a difficult process with a large energy barrier.[3,4] While the chloroethylenes have been extensively studied, there are only a few papers concerning the bromides. Wodtke *et al.*[5] reported that upon excitation at 193 nm, vinyl bromide underwent the competing dissociation into the products Br and HBr. From the maximum release of product translational energy, an upper limit of 77 ± 3 kcal/mol was determined for the C–Br bond energy. Using photofragment ion imaging, Katayanagi *et al.*[6] showed that the Br atom was mainly produced in the ground $^2P_{3/2}$ state with anisotropy parameter $\beta = 1.3$. This fast component was ascribed from surface crossing between the $\pi\pi^*$ pumped state and the $n\sigma^*$ or $\pi\sigma^*$ state. In addition, a low translational energy component of the Br atom was observed and explained to originate from the ground state molecule. The results of classical trajectory calculations by Raff and co-workers[7] indicated that several excited singlet and triplet states were involved in the Br atom production. Although Br elimination from the ground electronic state was possible, it was an order of magnitude smaller than the three-centered HBr elimination.[8,9]

The present work was undertaken to investigate the photodissociation of 1,2-$C_2H_2Br_2$ at 248 nm by product translational spectroscopy (PTS). This molecule has an absorption continuum around ~210 nm, which was primarily assigned as a $\pi^*\leftarrow\pi$ transition.[10,11] Our interest in this work is to examine how the molecule behaves when an additional Br atom is present. Surprisingly, we observed the three-body formation of Br (fast)+Br (slow)+C_2H_2 rather than a simple C–Br bond rupture. The product anisotropy indicates that both Br fragments were produced in a fraction of rotational period. In addition, a significant amount of the Br_2 product was measured.

In the photodissociation of isolated molecules, most experimental data involve pairs of products. Although dissociation into three fragments seldom happens, it can occur when the molecule is photoexcited with sufficient energy. In this case, a distinction must be made whether it proceeds by a sequential (stepwise) reaction or a synchronous concerted reaction.[12] In a sequential reaction, three fragments are produced consecutively when one of the binary products further dissociates into a pair of fragments. Because of the prolonged reaction time, these secondary products usually show no angular preference with respect to polarized laser light. In contrast, a synchronous concerted reaction is defined when three fragments occur simultaneously. Because each fragment can have a wide range of momentum for a given kinetic energy release, a full analysis in velocity space is normally required.[13] An asynchronous concerted reaction is another class of interest in the three-body formation. This was shown by North *et al.*[14] in the photolysis of azomethane ($CH_3N_2CH_3$) at 351 nm. It differs from a synchronous concerted reaction in that the two CH_3 fragments were produced at unequal velocities. Because the cleavages of the two C–N bonds are not symmetric, a satisfactory fit to the product time-of-flight (TOF) spectra was derived with product translational energy distributions $P(E_t)$ strongly coupled by asymmetric angular distributions.

[a)]Author to whom correspondence should be addressed. Electronic mail: smlin@po.iams.sinica.edu.tw

II. EXPERIMENT

The PTS apparatus used in the present experiment is a rotating source molecular beam machine that has been previously described elsewhere.[15,16] A continuous reactant beam was prepared by bubbling helium through a liquid sample maintained at $-10\,°C$ and expanded into the vacuum chamber from a preheated oven at $190\,°C$. Commercially available $1,2\text{-}C_2H_2Br_2$ (Fluka, a mixture of cis and trans isomers with a stated purity of 98%) was used without further purification. As described in the appendix, the cis isomer in the mixture was 66% (by wt). The most probable beam velocity was measured at 1.3×10^5 cm/s with a spread of ~8% in full width at half maximum.

A Lambda Physik EMG 103 MSC Excimer laser operating on the KrF transition (248 nm) crossed the molecular beam at the interaction region. The dissociation products after traveling a flight path of 365 mm from the reaction zone were measured with a detector consisting of a 200 eV electron impact ionizer, quadrupole mass filter, and Daly type ion counter. The ion flight time constant in the detector was determined as 2.9 μs per amu$^{1/2}$.

For the polarization measurements, the laser beam was linearly polarized with a stacked pile of fused-silica plates at the Brewster angle followed by a half-wave retarder. In the present study, the polarized TOF were collected with the electric field vector ε either parallel ($\varepsilon_{\parallel}$) or perpendicular ($\varepsilon_{\perp}$) to the detection axis.

FIG. 1. The experimental evidence for the Br_2 elimination.

III. RESULTS AND ANALYSIS

In the present study, unpolarized TOF spectra of $m/e^+ = 158\,(Br_2^+)$, $79\,(Br^+)$, and $26\,(C_2H_2^+)$ were collected mostly at a 20° beam angle. Within the limits of apparatus sensitivity, neither $m/e^+=105\,(C_2H_2Br^+)$ nor $80\,(HBr^+)$ was observed.

These unpolarized spectra were simulated by a forward convolution method for the determination of product translational energy distribution $P(E_t)$.[17] Figure 1 shows the Br_2^+ spectra taken with the laser output energy at ~100 mJ/pulse and ~25 mJ/pulse. The circles are experimental data while the solid curve was derived according to reaction (1),

$$C_2H_2Br_2 \rightarrow Br_2 + C_2H_2. \tag{1}$$

The corresponding $P(E_t)$ distribution of Fig. 2 peaked at 27 kcal/mol with a rather narrow breadth.

We then proceeded to analyze the coproduct C_2H_2 of reaction (1) with this $P(E_t)$ distribution. As shown by the dashed curve in Fig. 3(a), it only accounted for the fast $C_2H_2^+$ ions. In search of the precursor for the unfit $C_2H_2^+$ signal, we looked into the unpolarized Br^+ spectrum of Fig. 3(b) for the possible coproduct. This spectrum consists of three components. Apart from the slow signal (dashed curve) cracked from the Br_2 product by a 200 eV electron impact ionizer, there are two fast Br^+ ion components. Since these fast Br^+ ions and the unfit $C_2H_2^+$ signal are separated by more than ~50 μs in the appearance time, their precursors must be totally different. Hence, a possible involvement of
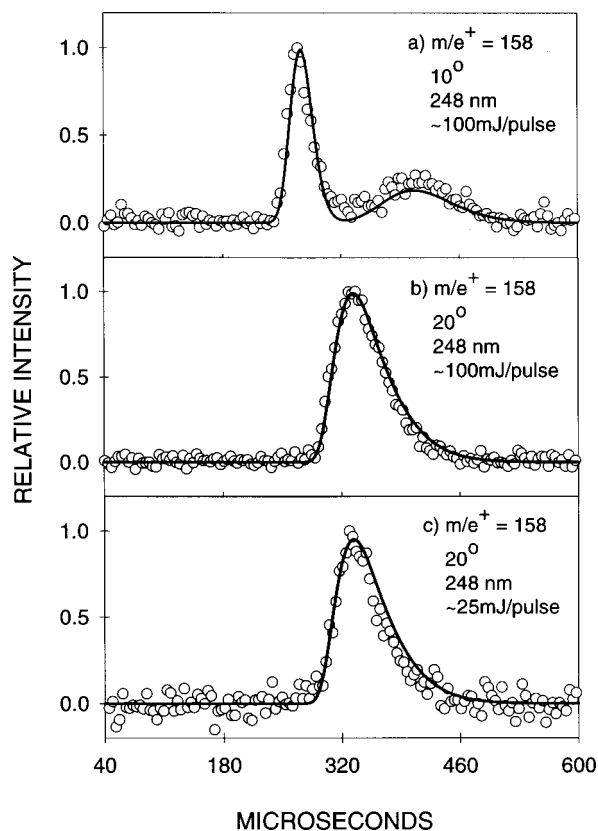
triple products $Br(fast)+Br(slow)+C_2H_2$ should be considered. Consequently, we looked into the polarized spectra of Fig. 4 for more information.

These polarized spectra were measured with a laser output energy of ~20 mJ/pulse at which no saturation was experimentally verified. Close inspection of these spectra shows that the intensity of the relevant ions including the Br_2^+ signal of Fig. 4(c) enhanced (open circles) when the electric field vector of polarized laser light was set parallel to the detection axis, $\varepsilon = \varepsilon_{\parallel}$. Thus, we expect that reaction (1) and the reaction channel for the triple products occurred in a fraction of rotational period.[18,19] More importantly, since the first Br^+ component at ~200 μs has a stronger polarization
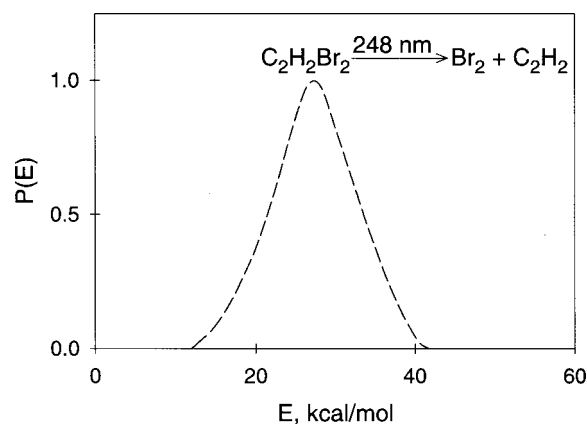

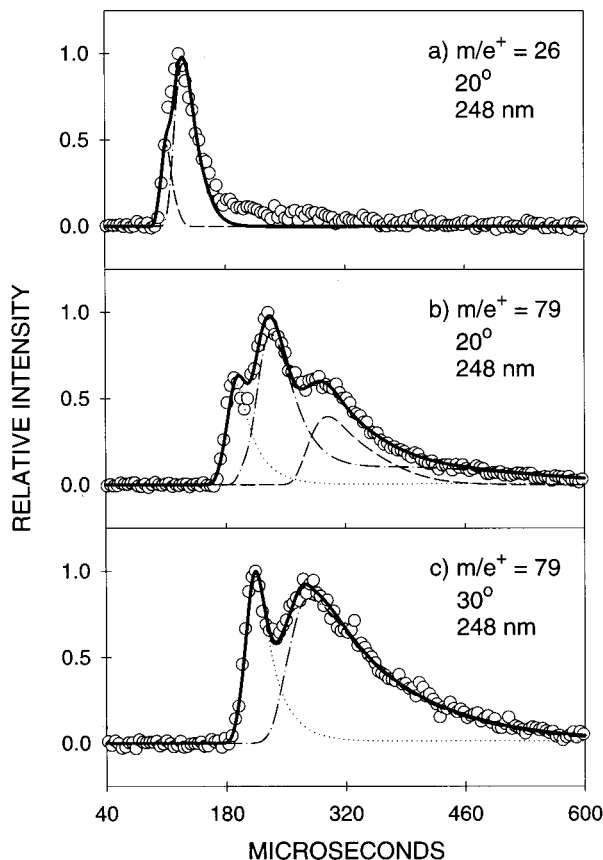FIG. 2. The $P(E_t)$ distribution for the Br_2 elimination of reaction (1).

FIG. 3. Unpolarized spectra of (a) C$_2$H$_2^+$ at 20°, (b) Br$^+$ at 20°, and (c) Br$^+$ at 30° taken at 248 nm with a laser energy of $\sim$100 mJ/pulse. The simulated curves are: -- for C$_2$H$_2$+Br$_2$ of reaction (1), $\cdots$ for the Br product of reaction (2a), and -$\cdot$- for C$_2$H$_2$+Br of reaction (2b).

FIG. 4. Polarized TOF of (a) C$_2$H$_2^+$, (b) Br$^+$, and (c) Br$_2^+$ collected at a 20° beam angle with a laser energy of $\sim$20 mJ/pulse. These spectra were measured with $\varepsilon = \varepsilon_\parallel$ (open circles) and $\varepsilon = \varepsilon_\perp$ (solid circles) to the detection axis. Each spectrum was measured with 100 000 laser shots.

effect than the second one at $\sim$250 μs, their precursors must be produced at different stages. Thus, we used an asynchronous concerted reaction model[14] for subsequent simulation of Fig. 3. This was performed by assuming that the first Br$^+$ ion peak was cracked from the Br atom of reaction (2a),

$$C_2H_2Br_2 \rightarrow Br\,(fast) + C_2H_2Br, \qquad (2a)$$
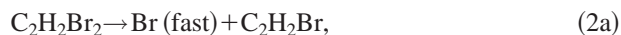
and the slow Br$^+$ signal and the unfit C$_2$H$_2^+$ ion were due to a rapid dissociation of unstable C$_2$H$_2$Br,

$$C_2H_2Br_2 \rightarrow Br(slow) + C_2H_2. \qquad (2b)$$
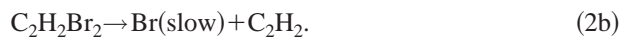
Using the standard forward convolution method,[17] reaction (2a) was calculated and shown by the dotted curves in Figs. 3(b)–3(c). The resultant P(E$_t$) distribution (dotted curve) of Fig. 5(a) yielded an average translational energy $\langle E_t \rangle = 19$ kcal/mol. The simulation of reaction (2b) was more complicated by incorporating asymmetric angular distribution with respect to the recoil direction of the nascent product C$_2$H$_2$Br with an assumed P(E$_t$) distribution. The computation was iterated until a satisfactory fit was obtained. The results are shown by the dashed-dot curves in Figs. 3 and 5. The asymmetric angular distributions of Fig. 5(b) indicates that the slow recoil Br atom and C$_2$H$_2$ are produced in a limited range of angles. This is in agreement with the prediction from the measured anisotropy. As shown in Fig. 3, the overall fit is acceptable except the slowly decaying C$_2$H$_2^+$ signal from $\sim$200 μ's to 400 μs over which the calculated

values are smaller than the measured data. The discrepancy was ignored in the present study because the measured signals were likely due to the thermalized C$_2$H$_2$ fragment bouncing off various surfaces in the detection chamber.[17]

With the derived center-of-mass (c.m.) distributions of Fig. 5, we proceeded to deconvolute the Br$^+$ spectrum to determine whether it was free from the second photon effect. In particular, we must assure that reaction (2b) was not due to the absorption of additional photons by the C$_2$H$_2$Br radical. This is shown in Fig. 6 with a log-log plot for the integrated ion counts vs. the laser output energies of 120, 40, 24, and 12 mJ/pulse. The results clearly indicate that both the fast and the slow Br$^+$ signals were collected in a single photon absorption process.

We now returned to the polarized TOF of Fig. 4 for the determination of anisotropy parameter β. This parameter is a function of the angle between the c.m. recoil velocity of the products and the transition dipole moment in the conventional expression, ^{18}I(θ) $\sim 1 + \beta P_2(\theta)$, where θ is the angle between the electric field vector ε and the product recoil direction, and P$_2$ is the second degree Legendre polynomial. In the limit of instantaneous dissociation, β equals 2 if they are parallel and -1 if perpendicular. Because we measured the polarized spectra with the electric vector ε relative to the detection axis, an offset angle should account for the difference in the fragmentation between the c.m. and laboratory coordinates. The results are shown in Fig. 7 with the open circles for $\varepsilon = \varepsilon_\parallel$ and the solid ones for $\varepsilon = \varepsilon_\perp$. The fast and
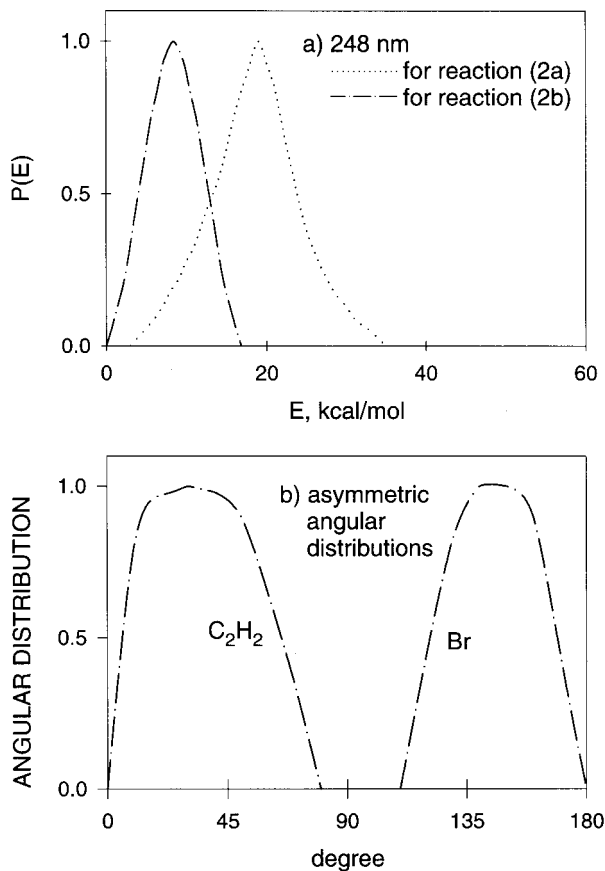
FIG. 5. The c.m. distributions for the asynchronous three-body formation of Br (fast)+Br (slow)+C_2H_2 in the 248 nm photolysis. (a) The $P(E_t)$ curves, $\cdots$ and $-\cdot\cdot-$, were derived for reactions (2a) and (2b), respectively. (b) Asymmetric angular distributions were calculated for reaction (2b) with respective to the recoil direction of the nascent fragment C_2H_2Br.

slow Br^+ ions in Figs. 7(b)–7(c) were obtained from Fig. 4(b) after deconvoluting in accord with reactions (2a) and (2b). The best fit led to $\beta = -0.5$, 1.5, and 0.4 for reactions (1), (2a), and (2b) in sequence. If the $C_2H_2^+$ spectrum of Fig. 4(a) was used, we obtained $\beta = 0.6$ for reaction (2b).
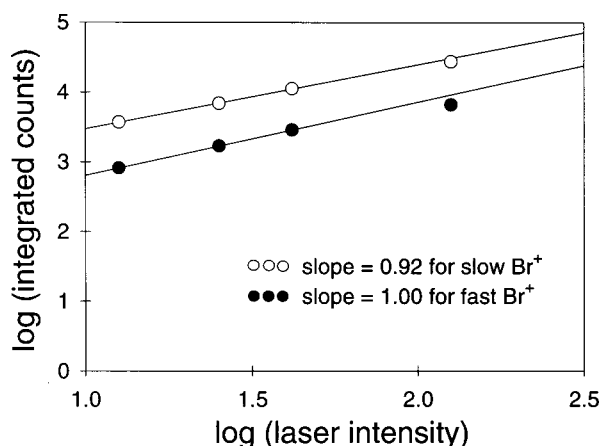

FIG. 6. A linear least-square fit for the fast and slow Br^+ signals collected at four laser energies of 12, 24, 40, and 120 mJ/pulse. They were obtained after deconvoluting with reactions (2a) and (2b). The slopes were calculated for the first three laser energies with a standard deviation of ± 0.01.
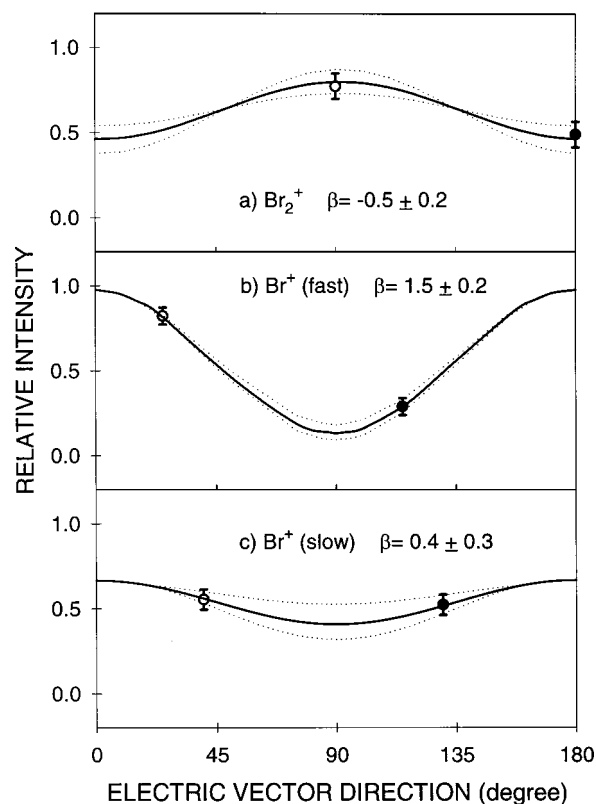

FIG. 7. Polarization dependence of (a) Br_2^+, (b) the fast Br^+ ion peak, and (c) the second Br^+ peak at 248 nm. The data are the integrated ion counts of Figs. 4(b) and 4(c) with the open circles for $\varepsilon = \varepsilon_\parallel$ and the solid circles for $\varepsilon = \varepsilon_\perp$. The solid lines represent the best fit to the data with the dotted curves indicating the limits of uncertainty.

Using the standard procedure[20] and the correction factor[21] of $1 + \beta/4$, the branching ratio for reaction (1)/(2) was determined at 0.2:0.8. This is calculated from the spectra collected at the laser energy of 100 mJ pulse and at a 20° beam angle.

IV. DISCUSSION

A. The triple products of Br (fast)+Br (slow)+C_2H_2

We started the discussion by examining the thermochemistry of reactions (2a) and (2b). With estimated enthalpy of formation $\Delta_f H^0 = 25$ kcal/mol for 1,2-$C_2H_2Br_2$,[22] these reactions are endothermic by a total amount of 83 kcal/mol. If we neglect the internal energy of the reactant, it yields a total available energy of 32 kcal/mol for reactions (2a) and (2b) upon excitation at 248 nm.[23] After subtracting from $\langle E_t \rangle = 19$ and 8 kcal/mol, we obtained ~ 5 kcal/mol for the product internal excitation energy. From the energy considerations, we then predict that only the ground state Br ($^2P_{3/2}$) atom was produced. Because reaction (2a) was measured with a maximum kinetic energy release $E_{max} = 35$ kcal/mol, we placed an upper limit of 80 kcal/mol for the C–Br bond energy of the reactant molecule. This value is in agreement with the bond dissociation energy $\leqslant 83.8$ kcal/mol determined from the experimental activation energy for dissociative thermal electron attachment.[24] It follows that the C–Br bond energy of the β-bromovinyl radical $\cdot$CH=CHBr

should be very weak ~3 kcal/mol compared to ~11 kcal/mol for the C–Cl bond energy of $\cdot$CH=CHCl[1,2] and ~45 kcal/mol for the C–F bond energy of CH=CHF.[25]

The observation of three-body formation is quite unexpected in the present study, not only because of its high reaction yield, but because it proceeded by asynchronous concerted reactions (2a) and (2b). It differs from the sequential C–Cl bond ruptures of dichloroethylenes[2] with anisotropy parameter $\beta = 0.4$ derived for reaction (2b) relative to $\beta = 1.5$ for reaction (2a). These polarized data indicate that reaction (2b) should occur very rapidly after reaction (2a) so that product TOF spectra could be simulated only when the $P(F_t)$ distributions were coupled by asymmetric angular distributions. If we assume that reaction (2a) is to originate from the $n\sigma^*$ or $\pi\sigma^*$ state as the C–Br bond rupture of vinyl bromide,[6,7] a simultaneous elongation of the second C–Br bond was then expected to proceed when the critical length for the first C–Br bond cleavage was reached. This is feasible for the bromovinyl radical with a weak C–Br bond strength and the cleavage of the second C–Br bond can be immediately driven by the unpaired electrons to form the C–C triple bond. This explains why no trace amount of $C_2H_2Br^+$ could be measured in the present study. Therefore, no energy barrier is expected for reaction (2b). This is compatible with a negative temperature-dependent rate constant derived for the addition of Br atom to acetylene at high-pressure limit.[26]

B. The molecular elimination of Br_2

The Br_2 elimination is another important dissociation channel detected in the present study. To our knowledge, such a molecular elimination is without precedent for this class of molecules.[2,27]

The Br_2 elimination of reaction (1) was measured with anisotropy parameter $\beta = -0.5$ and a Gaussian-like $P(E_t)$ distribution of Fig. 2. These experimental results strongly suggest that it cannot occur from the ground state potential energy surface. Hence dissociation through the excited state must be sought. With $E_{avl} = 79$ kcal/mol for reaction (1), the products were internally excited by 52 kcal/mol, which is in excess of 45 kcal/mol for the dissociation energy of the ground state Br_2 molecule. If the coproduct C_2H_2 was not much excited, this amount of internal excitation is sufficient for Br_2 to be formed in the triplet A $^3\Pi(1_u)$ or B $^3\Pi(0_u^+)$ state.[28] If this truly happened, reaction (1) could arise most likely from an excited triplet state after a fast intersystem crossing from the $\pi\pi^*$ state. For the Br atom with a large spin-orbit interaction, this crossing rate can be strongly enhanced and has been used to account for the difference in the photolysis of bromo and chloropropynes.[29,30] Furthermore, if we assume that the geometry of the ground state molecule was not largely distorted upon excitation,[31] the Br_2 elimination could arise most likely from the cis isomer in the reactant beam. In contrast, the triple products may be produced from both isomers. Then a negative β for reaction (1) as opposed to a positive β for reaction (2a) implies that the transition dipole moment must lie in the molecular plane close to the C=C bond direction if they were treated from

the same $\pi^* \leftarrow \pi$ transition. However, this does not mean that a $\sigma^*(C-Br) \leftarrow n$ (Br) transition is totally absent in the 248 nm photoexcitation.[32]

V. CONCLUSION

In the present study, we have examined the photodissociation of 1,2-$C_2H_2Br_2$ at 248 nm by product translational spectroscopy. The results indicate that the molecule dissociates predominantly into the triple products Br (fast)+Br (slow)+C_2H_2 by an asynchronous concerted reaction. From the measured anisotropy of the products, the molecule was considered to dissociate from the repulsive $n\sigma^*$ state. Because of the weakness of the C–Br bond strength in the intermediate, a simultaneous asymmetric scission of the second C–Br bond was proposed for the slow Br atom. The Br_2 elimination is another important reaction channel measured in the present study. From the Gaussian-like $P(E_t)$ distribution and the anisotropy of the products, it was explained to arise from the excited triplet state by a fast intersystem crossing from the $\pi\pi^*$ pumped state. This is supported from energy considerations the triplet state A $^3\Pi(1_u)$ or B $^3\Pi(0_u^+)$ was accessible to the Br_2 product.

APPENDIX: THE CONCENTRATION OF THE CIS AND TRANS ISOMERS IN THE REAGENT

A carbon-13 with proton coupling NMR spectrum was measured at 25 °C (Bruker MSL-500P). Tetramethyl silane was used as a standard reference for ^{13}C chemical shift δ. The shift δ for the cis and the trans isomers was identified at -115.1 and -108.1 ppm, respectively. It yielded an intensity ratio of 0.66:0.34 for the cis/trans isomers. It should be noted that this ratio may change in the gas phase since the latter has a slightly higher vapor pressure than the former at the operating temperature -10 °C.[33]

[1] D. A. Blank, W. Sun, A. G. Suits, Y. T. Lee, S. W. North, and G. E. Hall, J. Chem. Phys. **108**, 5414 (1998), and references therein.

[2] K. Sato, S. Tsunashima, T. Takayanagi, G. Fujisawa, and A. Yokoyama, J. Chem. Phys. **106**, 10123 (1997).

[3] J. Riehl, D. G. Musaev, and K. Morokuma, J. Chem. Phys. **101**, 5942 (1994).

[4] S. M. Resende and W. B. De Almeida, Chem. Phys. **238**, 11 (1998).

[5] A. M. Wodtke, E. J. Hintsa, J. Somorjai, and Y. T. Lee, Isr. J. Chem. **29**, 383 (1989).

[6] H. Katayanagi, N. Yonekuira, and T. Suzuki, Chem. Phys. **231**, 345 (1998).

[7] G. J. Mains, L. M. Raff, and S. A. Abrash, J. Phys. Chem. **99**, 3532 (1995).

[8] S. A. Abrash, R. W. Zehner, G. J. Mains, and L. M. Raff, J. Phys. Chem. **99**, 2959 (1995).

[9] R. D. Kay and L. M. Raff, J. Phys. Chem. A **101**, 1007 (1997).

[10] J. Schander and B. R. Russell, J. Am. Chem. Soc. **98**, 6900 (1976).

[11] K. Wittel, W. S. Felps, L. Klasinc, and S. P. McGlynn, J. Chem. Phys. **65**, 3698 (1976).

[12] C. E. M. Strauss and P. L. Houston, J. Phys. Chem. **94**, 8751 (1990).

[13] X. Zhao, W. B. Miller, E. J. Hintsa, and Y. T. Lee, J. Chem. Phys. **90**, 5527 (1989).

[14] S. W. North, C. A. Longfellow, and Y. T. Lee, J. Chem. Phys. **99**, 4423 (1993).

[15] A. M. Wodtke and Y. T. Lee, J. Phys. Chem. **89**, 4744 (1985).

[16] Y. R. Lee, C. L. Chiu, and S. M. Lin, J. Chem. Phys. **100**, 7376 (1994).

[17] R. K. Sparks, K. Shobatake, L. R. Carlson, and Y. T. Lee, J. Chem. Phys. **75**, 3838 (1981).

[18] R. N. Zare, Mol. Photochem. **4**, 1 (1972).

[19] C. Jonah, J. Chem. Phys. **55**, 1915 (1971).

[20] L. J. Butler, E. J. Hintsa, S. F. Shane, and Y. T. Lee, J. Chem. Phys. **86**, 2051 (1987).

[21] D. Krajnovich, F. Huisken, Z. Zhang, Y. R. Shen, and Y. T. Lee, J. Chem. Phys. **77**, 5977 (1982).

[22] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levine, and W. G. Mallard, J. Phys. Chem. Ref. Data Suppl. **17**, 1 (1988).

[23] An amount of ~5.1 kcal/mol will be added to the excess energy if we assume no vibrational relaxation in the nozzle beam expansion. It was calculated from the fundamental frequencies listed for the cis isomer in J. M. Dowling, P. G. Puranik, A. G. Meister, and S. I. Miller, J. Chem. Phys. **26**, 233 (1957).

[24] E. C. M. Chen, K. Albyn, L. Dussack, and W. E. Wentworth, J. Phys. Chem. **93**, 6827 (1989).

[25] M. R. Zachariah, P. R. Westmoreland, D. R. Burgess, Jr., W. Tsang, and C. F. Melius, J. Phys. Chem. **100**, 8737 (1996).

[26] I. Barnes, V. Bastian, K. H. Becker, R. Overath, and Z. Tong, Int. J. Chem. Kinet. **21**, 499 (1989).

[27] B. A. Balko, J. Zhang, and Y. T. Lee, J. Phys. Chem. A **101**, 6611 (1997).

[28] G. Herzberg, ''Molecular Spectra and Molecular Structure,'' *Spectra of Diatomic Molecules*, Vol. 1 (Van Nostrand, Princeton, 1950).

[29] M. Kawasaki, K. Kasatani, H. Sato, H. Shinohara, and N. Nishi, Chem. Phys. **88**, 135 (1984).

[30] Y. R. Lee and S. M. Lin, J. Chem. Phys. **108**, 134 (1998).

[31] P. Scharfenberg and I. Hargittai, J. Mol. Struct. **112**, 71 (1984).

[32] L. T. Molina, M. J. Molina, and F. S. Rowland, J. Phys. Chem. **86**, 2672 (1982).

[33] R. M. Noyes, W. A. Noyes, and H. Steinmetz, J. Am. Chem. Soc. **72**, 33 (1950).