

Experimental and quantum-chemical studies on photoionization and dissociative photoionization of CH₂Br₂

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Experimental and quantum-chemical studies on photoionization and dissociative photoionization of CH_2Br_2

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The dissociative photoionization of CH_2Br_2 in a region $\sim 10\text{--}24$ eV was investigated with photoionization mass spectroscopy using a synchrotron radiation source. An adiabatic ionization energy of 10.25 eV determined for CH_2Br_2 agrees satisfactorily with predictions of 10.26 and 10.25 eV with G2 and G3 methods, respectively. Observed major fragment ions CH_2Br^+ , CHBr^+ , and CBr^+ show appearance energies at 11.22, 12.59, and 15.42 eV, respectively; minor fragment ions CHBr_2^+ , Br^+ , and CH_2^+ appear at 12.64, 15.31, and 16.80 eV, respectively. Energies for formation of observed fragment ions and their neutral counterparts upon ionization of CH_2Br_2 are computed with G2 and G3 methods. Dissociative photoionization channels associated with six observed fragment ions are proposed based on comparison of determined appearance energies and predicted energies. An upper limit of $\Delta H_{f,298}^0(\text{CHBr}^+) \leq 300.7 \pm 1.5$ kcal mol⁻¹ is derived experimentally; the adiabatic ionization energy of CHBr is thus derived to be $\leq 9.17 \pm 0.23$ eV. Literature values for $\Delta H_{f,298}^0(\text{CBr}^+) = 362.5$ kcal mol⁻¹ and ionization energy of 10.43 eV for CBr are revised to be less than 332 kcal mol⁻¹ and 9.11 eV, respectively. Also based on a new experimental ionization energy, $\Delta H_{f,298}^0(\text{CH}_2\text{Br}_2^+)$ is revised to be 236.4 ± 1.5 kcal mol⁻¹. © 2004 American Institute of Physics. [DOI: 10.1063/1.1641010]

I. INTRODUCTION

Photoexcitation and photoionization of bromine-containing molecules hold fundamental interest in dissociation dynamics.¹⁻⁴ The catalytic depletion of stratospheric ozone by Br atoms has been characterized.^{5,6} Dibromomethane (CH_2Br_2) is an important substance that contains bromine and destroys ozone because it contributes up to 20% of Br atoms released into the upper troposphere.⁷⁻¹⁰ It has wide use as a reagent for cyclopropanation,¹¹ but the main anthropogenic sources of CH_2Br_2 originate from its use in fire extinguishers and as a fumigant.⁹ Ultraviolet absorption spectra^{5,12} and photoelectron spectra¹³⁻¹⁵ of CH_2Br_2 are well characterized, but only limited experimental work on the dissociative photoionization properties of CH_2Br_2 and the corresponding thermochemical data for associated fragments are reported in the literature.^{1-3,16-21}

The ionization energy (IE) of CH_2Br_2 was determined to be 10.24 ± 0.02 eV by Ma *et al.*² from a small step in the photoionization efficiency (PIE) curve; this value is significantly smaller than values derived from previous experi-

ments using electron impact (EI) and photoionization (PI) techniques: 10.5,²² 10.52,¹ and 10.49 eV.¹⁶ Reported appearance energies (AE) of the principal ions CH_2Br^+ are scattered, ranging from 10.93 to 11.35 eV;^{1,2,20,22,23} Ma *et al.*² indicated that signals of CH_2Br^+ near the threshold suffered from interference by signals resulting from an ion-pair process. AE of other fragment ions were determined with EI, but associated dissociation processes were not discussed.^{22,24,25} Recently, Huang *et al.*³ investigated photodissociation of CH_2Br_2^+ at 355 nm with ion-velocity imaging and time-of-flight mass spectroscopy; they determined a branching ratio of 2.2:1.0 between dissociation channels $\text{CH}_2\text{Br}^+ + \text{Br}^*(^2P_{1/2})$ and $\text{CH}_2\text{Br}^+ + \text{Br}(^2P_{3/2})$, and their results confirm the assumptions made on the electronic states of CH_2Br_2^+ in its ultraviolet absorption spectrum.²¹

The aim of this work is to determine the ionization energy of CH_2Br_2 and to investigate its dissociative photoionization. We measured photoionization efficiency spectra of various fragment ions and undertook associated theoretical calculations with both GAUSSIAN-2^{26,27} and GAUSSIAN-3^{28,29} methods. Combining experimental and calculation results, we establish dissociative photoionization channels of CH_2Br_2 and discuss plausible dissociation mechanisms. Predicted enthalpies of formation and ionization energies at G2

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and G3 levels enable an assessment of accuracies of both methods for bromine-containing species.

II. EXPERIMENT

We performed photoionization mass-spectrometric measurements with a molecular beam/quadrupole mass spectrometer system on the 1-m Seya-Namioka beamline at the National Synchrotron Radiation Research Center in Taiwan. The apparatus is described in detail elsewhere.³⁰ Briefly, a mixture of CH₂Br₂ and He (or Ar) at a total pressure \sim 300 Torr and with a seed ratio of \sim 10% was expanded through a nozzle and two skimmers to form a molecular beam. The cooled CH₂Br₂ molecules were ionized with monochromatic vacuum ultraviolet radiation at a right angle in the ionization chamber. Produced ions were mass-analyzed and detected with a quadrupole mass spectrometer mounted in a direction perpendicular to the plane defined by molecular and photon beams; an electron multiplier (channeltron) operated in pulse-counting mode served as a detector for ion collection.

The PIE curves in a region \sim 10–24 eV were measured and normalized with respect to the photon flux. With a grating monochromator (1200 grooves mm⁻¹; slit width 0.15 mm), the photon resolution is 30 meV and the photon flux is $>10^9$ photons s⁻¹. The wavelength of the monochromator was calibrated with the photoionization spectra of Ar and He. CH₂Br₂ (Merck, >99%) was degassed with several freeze-pump-thaw cycles before use.

III. THEORETICAL CALCULATIONS

Energies of CH₂Br₂, CH₂Br₂⁺ and fragment species at their equilibrium geometries were calculated with G2 and G3 methods using GAUSSIAN 98 program.³¹ Because basis sets for bromine-containing species are lacking from standard G3 calculations, we employed basis sets reported by Curtiss.³² We describe briefly the G2 and G3 procedures to compute total energies of molecules at their equilibrium geometries as follows. The equilibrium structure of each species was initially optimized at the HF/6-31G(*d*) level, to calculate its zero-point vibrational energy, and then fully optimized at the MP2(full)/6-31G(*d*) level for further calculations. To calculate a G2 energy, calculations of single-point energies were carried out at the levels of MP4/6-311G(*d,p*), MP4/6-311+G(*d,p*), MP4/6-311G(2*df,p*), QCSID(T)/6-311G(*d,p*), and MP2/6-311+G(3*df,2p*), including corrections of a higher-level energy and zero-point vibrational energy. To calculate a G3 energy, we performed calculations of single-point energies at the levels of MP4/6-31G(*d*), QCSID(T)/6-31G(*d*), MP4/6-31+G(*d*), MP4/6-31G(2*df,p*), and MP2(full)/G3 large; G3 large is a modification of the MP2/6-311+G(3*df,2p*) basis set. Additional energies include a spin-orbit correction for atomic species, higher-level corrections for atoms and molecules, and a zero-point vibrational energy. Enthalpies of formation at temperature *T* K ($\Delta H_{f,T}^0$) were obtained from calculated enthalpy changes for their equations of formation and experimental $\Delta H_{f,T}^0$ for isolated atoms C, H, and Br.³³

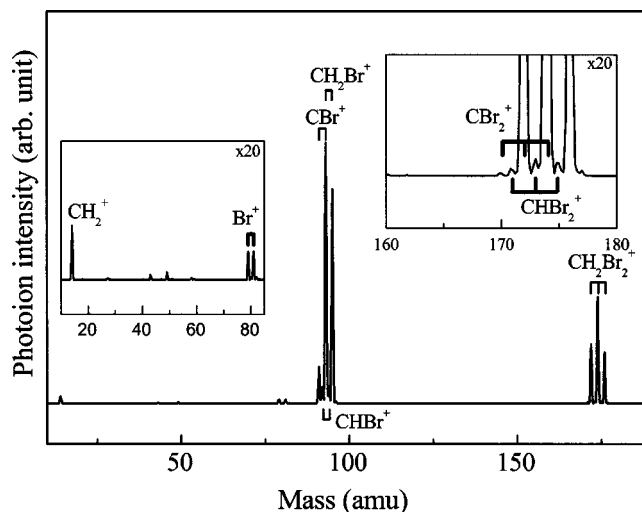


FIG. 1. Mass spectra of CH₂Br₂ excited at 60 nm (20.66 eV). Weak signals of CHBr₂⁺, CBr₂⁺, Br⁺, and CH₂⁺ are shown in two insets on an expanded scale.

IV. RESULTS AND DISCUSSION

A. Results of experiments

Figure 1 shows a mass spectrum of CH₂Br₂/He excited at 60 nm (20.66 eV) and with steps of 0.2 amu. In this spectrum, three major fragment ions CH₂Br₂⁺, CHBr₂⁺, and CBr₂⁺, and four minor fragment ions CHBr₂⁺, CBr₂⁺, Br⁺, and CH₂⁺ were observed; their bromine isotopic variants (abundances ⁷⁹Br=50.69%, ⁸¹Br=49.31%)³⁴ are marked as pairs in the figure. As no signal at mass greater than that of CH₂Br₂⁺ was detected at various excitation wavelengths, we deduced that all observed fragment ions originated from dissociation of CH₂Br₂⁺; the largest *m/z* value of our mass spectrometer is 280. Minute signals in the region 40–50 amu result from impurities in the sample.

PIE curves of CH₂Br₂⁺ and fragment ions were recorded at steps of 0.2 nm and normalized with respect to the photon flux. Figure 2 shows PIE curves of CH₂⁷⁹Br₂⁺ and major fragment ions CH₂⁸¹Br⁺, CH⁷⁹Br⁺, and C⁷⁹Br⁺ from their respective appearance onsets to 24 eV; the PIE curve of CH₂⁸¹Br⁺ was employed because signals of CH₂⁷⁹Br⁺ overlap with those of C⁸¹Br⁺. As shown in Fig. 2, the major dissociation channel CH₂Br₂⁺ → CH₂Br₂⁺ + Br requires the least energy. That decrease of CH₂Br₂⁺ and CH₂Br₂ is accompanied by the increase of CBr₂⁺ which implies consecutive dissociation of CH₂Br₂⁺ into the high energy fragment ion CBr₂⁺. PIE curves of minor fragment ions CHBr₂⁺, Br⁺, and CH₂⁺ are shown in Fig. 3; the proportions of these fragment ions are less than 2%.

AE of major fragment ion CBr₂⁺ and minor fragment ions CHBr₂⁺, Br⁺, and CH₂⁺ were determined directly from threshold regions of their low-resolution PIE curves because their small signals preclude recording of high-resolution PIE curves. The PIE curves near the threshold regions of CH₂Br₂⁺, CH₂Br₂⁺, and CHBr₂⁺, measured with steps of 0.05 nm and shown in Figs. 4(a)–4(c), serve to determine the AE of each fragment ion. As seen with an expanded scale in Fig. 4(a), the ion signal of CH₂Br₂⁺ rises in a small step-like

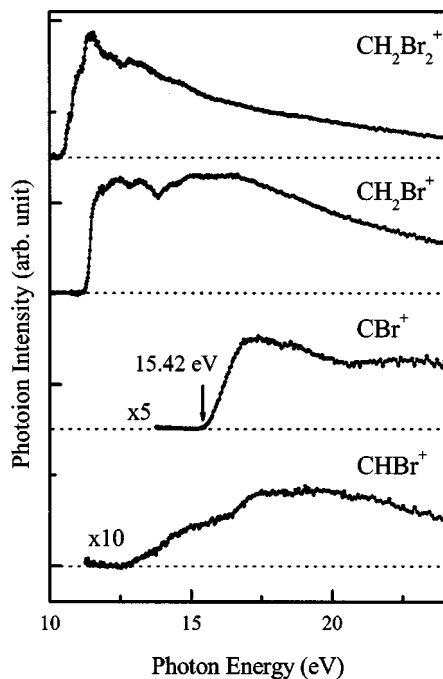


FIG. 2. Photoionization efficiency curves of CH_2Br_2 and three major fragment ions CH_2Br^+ , CBr^+ , and CHBr^+ .

feature near the ionization threshold; we thus assigned the first small step feature observed at 10.25 ± 0.02 eV to be the IE of CH_2Br_2 . Two additional big steps marked at 10.60 and 10.80 eV in Fig. 4(a) correspond to vertical transition energies of photoelectron bands associated with ionization of a lone-pair electron of Br.¹⁵ For fragment ion CH_2Br^+ , the PIE curve in Fig. 4(b) shows a short region of gradually rising slope near the threshold before a rapid increase; AE of 11.22 ± 0.02 eV was determined from the midpoint of two inter-

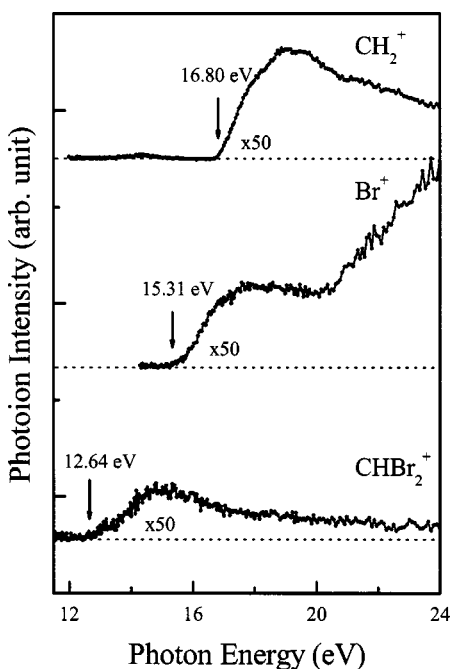


FIG. 3. Photoionization efficiency curves of three minor fragment ions CH_2^+ , Br^+ , and CHBr_2^+ .

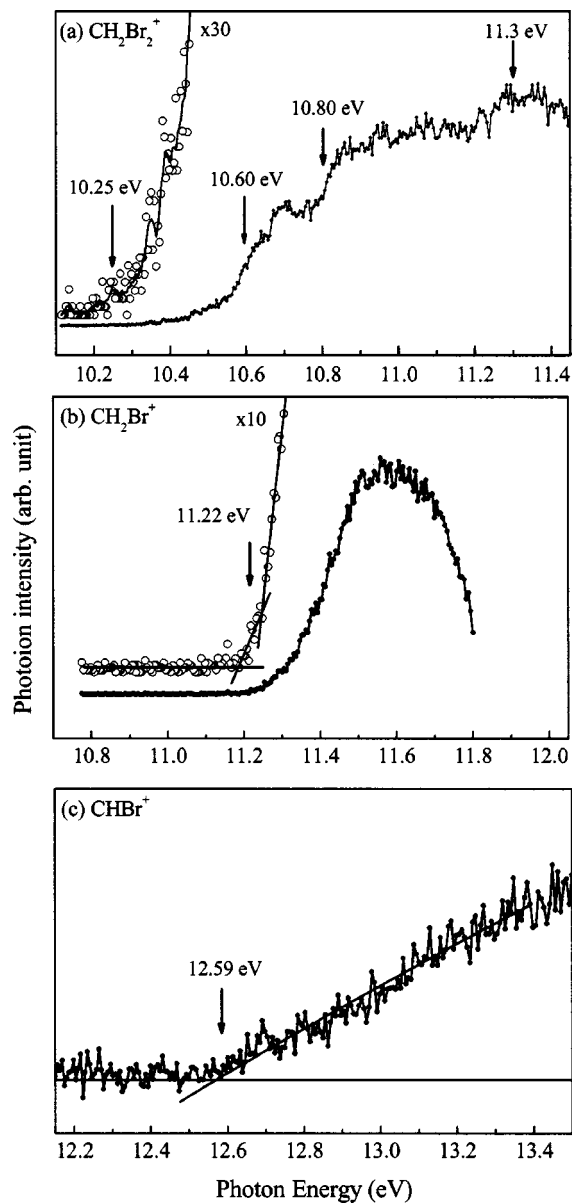


FIG. 4. Photoionization efficiency curves of CH_2Br_2 and fragment ions CH_2Br^+ and CHBr^+ , with their fitted lines near the threshold region.

sects among the base line and two fitted slopes. An AE value of 12.59 ± 0.02 eV for CHBr^+ was determined from the intersection of the base line and the linearly rising line, as shown in Fig. 4(c). We exclude effects of thermal energy and collisions from our IE and AE values because CH_2Br_2 was cooled under supersonic conditions.

Table I lists IE of CH_2Br_2 and AE values of observed fragment ions determined in this work to compare with literature values; relative intensities of CH_2Br_2^+ and fragment ions measured at 60 nm are also listed. An IE = 10.25 eV determined in this work agrees with a value of 10.24 ± 0.02 eV determined by Ma *et al.*² Previous values of 10.5,¹ 10.52,¹ and 10.49 eV¹⁶ might result from overestimated hot-band effects; such effects and interference from ion-molecule reactions are negligible under supersonic expansion conditions in our and in Ma's experiments. Our AE value of 11.22 eV for CH_2Br^+ agrees with the onset of the third ionic state

TABLE I. Comparison of reported AE of parent and fragment ions of CH₂Br₂, and their relative intensities measured at 60 nm.

Species	Relative Intensity	AE/eV			
		This work (PI)	Literature	Method	Ref.
CH ₂ Br ₂ ⁺	50	10.25±0.02	10.24±0.02	PI	2
			10.5±0.1	EI	22
			10.52±0.05	PI	1
			10.49±0.02	PI	16
CH ₂ Br ⁺	100	11.22±0.02	11.27	PI	2
			11.29	EI	20
			11.1±0.2	EI	22
			11.35±0.02	PI	1
			10.93±0.04	EI	23
CHBr ⁺	7.7	12.59±0.02	16.0±0.5	EI	22
CHBr ₂ ⁺	<1	12.64±0.08			
Br ⁺	1.8	15.31±0.08	15.5±0.1	EI	24
			16.0	EI	25
CBr ⁺	18	15.42±0.08	19.6±0.3	EI	22
			17.1±0.3	EI	22
CH ₂ ⁺	1.7	16.80±0.04			

of CH₂Br₂⁺, shown in Fig. 4(a), and a band at 11.3 eV in the photoelectron spectrum.¹⁵ Ma *et al.*² were unable to determine an accurate AE for CH₂Br⁺ due to severe interference of spike-like signals that they attributed to formation of an ion pair (CH₂Br⁺, Br⁻) in the region ~10.88–11.27 eV. In contrast, as shown in Fig. 4(b), only a slow rising onset of CH₂Br⁺ was observed in the region ~11.19–11.23 eV. This result is similar to an observation of a small rising onset of CH₂Cl⁺ in the dissociation of CH₂Cl₂⁺; ³⁵ the reason of the discrepancy between our results and those of Ma *et al.* is unclear. Considering the quality of our data, our value of 11.22 eV is expected to be more accurate than existing literature values. AE values of 12.59, 15.31, 15.42, and 16.80 eV for CHBr⁺, Br⁺, CBr⁺, and CH₂⁺, respectively, determined with the PI method are reported for the first time; these values are smaller than values derived with the EI method by 0.2–4.2 eV.^{22,24,25} The AE value of 12.64 eV for CHBr₂⁺ is new.

B. Results of calculations

Geometries of CH₂Br₂, CHBr₂, CH₂Br, CHBr, CBr, HBr, Br₂, and their corresponding ions were optimized at the MP2(full)/6-31G* level. Predicted structural parameters for CH₂Br₂ and CH₂Br₂⁺ agree with previous experimental values³⁶ of CH₂Br₂ and theoretical predictions of CH₂Br₂⁺ at the B3LYP/6-311++G(3df,3pd)³⁷ and 6-311G(d,p)³ levels except that angle ∠BrCBr=91.3° predicted for CH₂Br₂⁺ is smaller than literature values of 94.0° and 94.6°. A significant decrease of ∠BrCBr from 112.7° to 91.3° is a major structural alteration of CH₂Br₂ upon ionization; other minor alterations arise for angles ∠HCB and ∠HCH, both being less than 5°. An altered conformation upon ionization is consistent with an observation of a small rising onset of CH₂Br₂⁺ in Fig. 4(a).

Predicted structural parameters for CH₂Br, CHBr, CBr, HBr, Br₂, and their corresponding ions agree with calculations performed at various levels and experimental values in the literature.^{37–40} Paddison and Tschuikow-Roux have pre-

dicted the structure of CHBr₂ at the MP2/6-31G* level,⁴¹ the same level employed in G2 and G3 methods. The structure of CHBr₂⁺ is unreported in the literature, either experimentally or theoretically. The predicted structure of CHBr₂⁺ is planar with C_{2v} symmetry, similar to CH₂Br⁺. Our predictions for CHBr₂⁺ are lengths of 1.779 and 1.091 Å for C–Br and C–H bonds, respectively, and angles ∠HCB=117.9° and ∠BrCBr=124.3°.

Table II lists total energies E_0 and enthalpies H_{298} calculated with G2 and G3 methods for species involved in this work; symmetries and electronic states are also indicated. The spin-orbit correction is excluded in G2 theory, but found to be important for molecules containing third-row atoms, particularly those with degenerate states.²⁷ Consequently, E_0 (G2) energies with spin-orbit corrections taken from the literature for Br(³P), Br⁺(²P), Br₂⁺(²Π_g), and HBr⁺(²Π) are listed in parentheses for comparison.²⁷ A spin-orbit correction for CBr(²Π) is unavailable in the literature. The G3 method includes experimental spin-orbit corrections for atomic species; E_0 (G3) energies incorporated with available molecular spin-orbit corrections are also listed in parentheses.²⁹

Table III lists experimental AE values of fragment ions and reaction energies ΔE calculated for possible dissociative photoionization channels for six fragment ions. Theoretical values ΔE (G2) and ΔE (G3) are calculated from E_0 (G2) and E_0 (G3) energies listed in Table II; ΔE (G2) including spin-orbit corrections of Br and Br⁺ are listed in parentheses. Calculated reaction energies take into account neither a possible reaction barrier nor electronic excitation of products.

The experimental AE=11.22 eV for channel CH₂Br₂ → CH₂Br⁺ + Br differs from ΔE (G2)=11.44 eV and ΔE (G3)=11.39 eV by 0.22 and 0.17 eV, respectively; the discrepancies are greater than typical errors of 0.15 eV reported for sulfur- and chlorine-containing species and oxides.^{42,43} In contrast, the spin-orbit corrected ΔE (G2) of 11.28 eV agrees satisfactorily with the experimental AE, sig-

TABLE II. Energies (E_0) and enthalpies (H_{298}) in Hartree calculated with G2 and G3 methods for species involved in ionization and dissociative photoionization of CH_2Br_2 .

Species	Symmetry	G2 ^a		G3 ^a	
		E_0	H_{298}	E_0	H_{298}
CH_2Br_2	$C_{2v}(^1A_1)$	-5184.369 89	-5184.365 05	-5186.382 06	-5186.377 22
CH_2Br_2^+	$C_{2v}(^2B_2)$	-5183.992 74	-5183.987 79	-5186.005 47	-5186.000 52
CHBr_2	$C_s(^2A')$	-5183.715 31	-5183.710 39	-5185.728 66	-5185.723 74
CHBr_2^+	$C_{2v}(^1A_1)$	-5183.421 32	-5183.416 70	-5185.431 51	-5185.426 89
CH_2Br	$C_s(^2A')$	-2611.730 32	-2611.726 07	-2612.760 82	-2612.756 57
CH_2Br^+	$C_{2v}(^1A_1)$	-2611.418 99	-2611.415 05	-2612.445 88	-2612.441 94
CHBr	$C_s(^1A')$	-2611.073 70	-2611.069 74	-2612.100 50	-2612.096 54
CHBr^+	$C_s(^2A')$	-2610.742 19	-2610.738 28	-2611.769 72	-2611.765 81
CH_2^+	$C_{2v}(^2A_1)$	-38.690 06	-38.686 24	-38.736 15	-38.732 33
CBr	$C_{\infty v}(^2\Pi)$	-2610.444 62	-2610.441 17	-2611.472 44	-2611.468 99
CBr^+	$C_{\infty v}(^1\Sigma)$	-2610.130 51	-2610.127 16	-2611.154 58	-2611.151 23
HBr	$C_{\infty v}(^1\Sigma)$	-2573.173 19	-2573.169 89	-2574.156 56	-2574.153 26
HBr^+	$C_{\infty v}(^2\Pi)$	-2572.741 45	-2572.738 14	-2573.723 31	-2573.720 00
		(-2572.747 7)	(-2572.744 4)	(-2573.729 37)	(-2573.726 07)
Br_2	$D_{\infty h}(^1\Sigma_g)$	-5145.141 30	-5145.137 60	-5147.107 46	-5147.103 76
Br_2^+	$D_{\infty h}(^2\Pi_g)$	-5144.749 42	-5144.745 79	-5146.714 14	-5146.710 51
		(-5144.755 97)	(-5144.752 34)	(-5146.720 56)	(-5146.716 93)
H_2	$D_{\infty h}(^1\Sigma_g)$	-1.166 36	-1.163 05	-1.167 37	-1.164 06
Br	(^2P)	-2572.530 58	-2572.528 22	-2573.517 47	-2573.515 11
		(-2572.536 36)	(-2572.534)		
Br^+	(^3P)	-2572.099 02	-2572.096 66	-2573.084 05	-2573.081 69
		(-2572.105 79)	(-2572.103 43)		
C	(^3P)	-37.784 30	-37.781 94	-37.827 72	-37.825 36
C^+	(^2P)	-37.373 45	-37.371 09	-37.415 71	-37.413 35
H	(^2S)	-0.5	-0.497 64	-0.501 00	-0.498 64

^a E_0 and H_{298} with spin-orbit corrections taken from Refs. 27 and 29 for G2 and G3 calculations, respectively, are listed in parentheses.

nifying the importance of this spin-orbit effect on energies of bromine-containing species.

Two possible channels are involved in formation of CHBr^+ . Channel $\text{CH}_2\text{Br}_2 \rightarrow \text{CHBr}^+ + \text{H} + \text{Br}$ is unlikely near the observed threshold because a predicted energy of 16.2 eV is much greater than the experimental AE=12.59 eV. Channel $\text{CH}_2\text{Br}_2 \rightarrow \text{CHBr}^+ + \text{HBr}$ involves a significant structural change and is expected to have a barrier for dissociation; the barrier and reverse barrier for HX loss is a common and well-known phenomenon in alkyl halide mass spectrometry. The experimental AE=12.59 eV for this channel is slightly greater than $\Delta E(\text{G2})=12.37$ eV and $\Delta E(\text{G3})=12.40$ eV.

TABLE III. Experimental appearance energies (AE/eV) of fragment ions and calculated reaction energies ($\Delta E/\text{eV}$) for various dissociative photoionization channels of CH_2Br_2 .

Fragment ions	Proposed neutral	AE (expt.)	$\Delta E(\text{G2})^a$	$\Delta E(\text{G3})$
CH_2Br^+	Br	11.22	11.44 (11.28)	11.39
CHBr^+	HBr	12.59	12.37	12.40
	H+Br		16.25 (16.09)	16.16
CHBr_2^+	H	12.64	12.21	12.23
Br^+	CH_2Br	15.31	14.71 (14.53)	14.62
CBr^+	$\text{H}_2 + \text{Br}$	15.42	14.76 (14.60)	14.77
	HBr+H		15.41	15.51
CH_2^+	Br+Br	16.80	16.84 (16.52)	16.63
	Br_2		14.65	14.65

^a $\Delta E(\text{G2})$ values with spin-orbit corrections of Br and Br^+ are listed in parentheses.

This result indicates that a small reaction barrier exists for dissociation, similar to the case $\text{CH}_2\text{Cl}_2 \rightarrow \text{CHCl}^+ + \text{HCl}$ for which a theoretical prediction of reaction energy is smaller than the experimental AE value.³⁵

The experimental AE=12.64 eV for channel $\text{CH}_2\text{Br}_2 \rightarrow \text{CHBr}_2^+ + \text{H}$ differs from $\Delta E(\text{G2})=12.21$ eV and $\Delta E(\text{G3})=12.23$ eV by 0.43 and 0.41 eV, respectively; the large discrepancy might result from poor detectivity of small signals of CHBr_2^+ or excess energies required in dissociation due to competition with other dissociation channels at smaller energies. Discrepancies between experimental AE and predicted values at greater energies are expected to be generally large because of the possible presence of kinetic shifts and reverse activation barriers. Channel $\text{CH}_2\text{Br}_2 \rightarrow \text{Br}^+ + \text{CH}_2\text{Br}$ is proposed on the basis of energy consideration; the experimental AE=15.31 eV is consistent with a previous experimental value of 15.5 ± 0.1 eV,²⁴ but is much greater than $\Delta E(\text{G2})=14.71$ eV, spin-orbit corrected $\Delta E(\text{G2})=14.53$ eV, and $\Delta E(\text{G3})=14.62$ eV. To form CBr^+ , channels $\text{CH}_2\text{Br}_2 \rightarrow \text{CBr}^+ + \text{H}_2 + \text{Br}$ and $\text{CBr}^+ + \text{HBr} + \text{H}$ are energetically accessible based on comparison of the experimental AE=15.42 eV with predicted values, $\Delta E(\text{G2})=14.76$ eV and $\Delta E(\text{G3})=14.77$ eV for the former channel, and $\Delta E(\text{G2})=15.41$ eV and $\Delta E(\text{G3})=15.51$ eV for the latter channel. The former channel is more favorable because of smaller predicted ΔE values and an observation of competition between CH_2Br^+ and CBr^+ in Fig. 2. A similar channel $\text{CH}_2\text{Cl}_2 \rightarrow \text{CCl}^+ + \text{H}_2 + \text{Cl}$ was observed in photoionization

TABLE IV. Observed and calculated enthalpies of formation at 298 K ($\Delta H_{f,298}^0$ /kcal mol⁻¹) and ionization energies (IE/eV) of CH_xBr_y and CH_xBr_y⁺.

Species	$\Delta H_{f,298}^0$ ^a				IE			
	G2 ^b	G3	Expt.	Ref.	G2	G3	Expt.	Ref.
CH ₂ Br ₂	-4.6(2.8)	-0.1	0±1	33	10.26	10.25	10.24±0.02 10.25±0.02	2 This work
CH ₂ Br ₂ ⁺	232.3(239.5)	236.3	242 236.4±1.5	33 This work				
CHBr ₂	42.0(49.2)	45.0	45.0±2.2	44	8.00	8.09	8.13±0.16 8.30±0.03	34 34
CHBr ₂ ⁺	226.3(233.5)	231.3	224	33				
CH ₂ Br	38.3(41.9)	39.4	40.4±1.0	44	8.47	8.57	8.61±0.01	2
CH ₂ Br ⁺	233.5(237.1)	236.9	234±0.4 233.1±1.5	2 This work				
CHBr	85.8(89.4)	88.6	89.2±4.3	18	9.02	9.00	9.17±0.23	This work
CHBr ⁺	293.8(297.4)	296.1	≤300.7±1.5	This work				
CBr	115.8(119.5)	117.4	122±15	33	8.55	8.65	10.43±0.02 ≤9.11±0.78	39 This work
CBr ⁺	312.9(316.5)	316.8	362.5 ≤332±3	33 This work				

^a $\Delta H_{f,298}^0$ for all species were calculated using experimental literature $\Delta H_{f,298}^0$ values of 171.3 (C), 431.0 (C⁺), 52.1 (H), 365.7 (H⁺), 26.74 (Br), and 299.2 (Br⁺) kcal mol⁻¹.

^b $\Delta H_{f,298}^0$ values calculated with spin-orbit corrections of Br and Br⁺ taken from Ref. 27 are listed in parentheses.

of CH₂Cl₂.³⁵ Two channels CH₂Br₂→CH₂⁺+Br+Br and CH₂⁺+Br₂ are possible for formation of CH₂⁺, but the former is more likely because the predicted energy of 14.65 eV compared with 16.6 eV for the other channel is much smaller than the experimental AE=16.80 eV.

C. Enthalpies of formation and ionization energies

Experimental $\Delta H_{f,298}^0$ values of CH₂Br₂ are scattered, 1.4±1.2, 2.39±3.59, -2.65±1.2, and -3.53±0.8 kcal mol⁻¹;⁴¹ we used a value of 0±1 kcal mol⁻¹ recommended in JANAF tables.³³ Based on our experimental IE=10.25±0.02 eV and $\Delta H_{f,298}^0$ (CH₂Br₂)=0±1 kcal mol⁻¹, we obtained $\Delta H_{f,298}^0$ (CH₂Br₂⁺)=236.4±1.5 kcal mol⁻¹; this value is slightly smaller than a literature value of 242 kcal mol⁻¹. Enthalpies of formation $\Delta H_{f,0}^0$ of ions are derived from observed AE and $\Delta H_{f,0}^0$ of associated neutral species; values of $\Delta H_{f,298}^0$ are converted from $\Delta H_{f,0}^0$ based on vibrational frequencies of calculations. $\Delta H_{f,298}^0$ (CH₂Br⁺)=233.1±1.5 kcal mol⁻¹ is derived with $\Delta H_{f,0}^0$ (Br)=28.2 kcal mol⁻¹, $\Delta H_{f,0}^0$ (CH₂Br₂)=5.2±1.0 kcal mol⁻¹, and the experimental AE=11.22 eV; this value is consistent with a literature value of 234±0.4 kcal mol⁻¹. For CHBr⁺ and CBr⁺, we can derive only upper limits for $\Delta H_{f,298}^0$ because there is no information on barriers of dissociation. $\Delta H_{f,298}^0$ (CHBr)≤300.7±1.5 kcal mol⁻¹ is derived from our experimental AE=12.59 eV and $\Delta H_{f,0}^0$ (HBr)=-6.8 kcal mol⁻¹ converted from $\Delta H_{f,298}^0$ (HBr)=-8.67±0.04 kcal mol⁻¹,³³ this value is consistent with predictions of a spin-orbit corrected value of 297.4 and 296.1 kcal mol⁻¹ with G2 and G3 methods, respectively. $\Delta H_{f,298}^0$ ≤332±3 kcal mol⁻¹ derived for CBr⁺ is much smaller than the literature value of 362.5 kcal mol⁻¹, but closer to predictions of 316.5 and 316.8 kcal mol⁻¹ with the G2 and G3 methods, respectively; the literature value is inaccurate.

Assessment of accuracies of predicted thermochemical properties with G2 and G3 methods in the literature focus mainly on molecules containing atoms in the first and second rows; comparisons for species containing third-row atoms are sparse.²⁶⁻²⁹ Predictions of accurate enthalpies of formation and IE for polyatomic species containing third-row atoms are more challenging because of increased configuration interaction and spin-orbit effects.

Table IV compares experimental^{2,18,33,34,44} and calculated $\Delta H_{f,298}^0$ and IE for bromine-containing species involved in this work; $\Delta H_{f,298}^0$ calculated with a spin-orbit correction of Br taken into account are listed in parentheses. According to Table IV, predicted $\Delta H_{f,298}^0$ at the G2 level with spin-orbit correction and those at the G3 level agree with experimental values within 5 kcal mol⁻¹ except for CHBr₂⁺ and CBr⁺; a larger discrepancy for CBr⁺ might reflect experimental uncertainties described previously. Predicted $\Delta H_{f,298}^0$ values at the G3 level are typically closer to experimental values than those at the G2 level.

Also seen in Table IV, predicted values IE(G2)=10.26 eV and IE(G3)=10.25 eV for CH₂Br₂ agree with the experimental IE=10.25 eV determined in this work and 10.24 eV determined by Ma *et al.*² Predictions of IE(G2)=8.00 eV and IE(G3)=8.09 eV for CHBr₂ are smaller than the quoted value of 8.30 eV estimated from the photoelectron threshold, but are consistent with a value of 8.13±0.16 eV determined by EI.³⁴ Predicted IE(G2)=8.47 eV and IE(G3)=8.57 eV for CH₂Br differ from the experimental IE=8.61 eV by only 0.14 and 0.04 eV, respectively.² No experimental IE of CHBr is available in the literature, but predicted IE(G2)=9.02 eV and IE(G3)=9.00 eV are consistent with an upper limit of 9.17±0.23 derived from our experimental $\Delta H_{f,298}^0$ (CHBr⁺) and literature $\Delta H_{f,298}^0$ (CHBr)=89.2±4.3 kcal mol⁻¹. For CBr, predicted IE(G2)=8.55 eV and IE(G3)=8.65 eV are

much smaller than the experimental $IE=10.43$ eV,³⁹ but closer to an upper limit of 9.11 eV derived from our experimental $\Delta H_{f,298}^0(\text{CBr}^+)$ and literature $\Delta H_{f,298}^0(\text{CBr})=122 \pm 15$ kcal mol⁻¹, a literature value of 10.43 eV of this IE must be erroneous.

IV. CONCLUSIONS

Dissociative photoionization of CH_2Br_2 to form fragment ions CH_2Br^+ , CHBr^+ , CHBr_2^+ , Br^+ , CBr^+ , and CH_2^+ was investigated with a molecular beam quadrupole mass spectroscopy system coupled to a synchrotron radiation source. The IE of CH_2Br_2 and AE of fragment ions were derived from their respective photoionization efficiency curves. Theoretical predictions of IE for CH_2Br_2 and of energies for formation of fragment ions were performed with G2 and G3 methods. An experimental $IE=10.25 \pm 0.02$ eV agrees satisfactorily with predicted G2 and G3 values of 10.26 and 10.25 eV, respectively. Dissociative photoionization channels associated with the six fragments ions are established based on comparisons of experimental AE and predicted reaction energies. New experimental values of $\Delta H_{f,298}^0(\text{CHBr}^+) \leq 300.7 \pm 1.5$ kcal mol⁻¹ and $IE(\text{CHBr}) \leq 9.17 \pm 0.23$ eV are consistent with predictions of $\Delta H_{f,298}^0 = 297.4$ and 296.1 kcal mol⁻¹ and $IE=9.02$ and 9.00 eV with G2 and G3 methods, respectively. $\Delta H_{f,298}^0(\text{CBr}^+) \leq 332 \pm 3$ kcal mol⁻¹ and $IE(\text{CBr}) \leq 9.11 \pm 0.78$ eV are revised from literature values of 362.5 kcal mol⁻¹ and 10.43 eV, respectively. $\Delta H_{f,298}^0(\text{CH}_2\text{Br}_2^+)$ is also revised to be 236.4 ± 1.5 kcal mol⁻¹ based on new experimental IE.

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