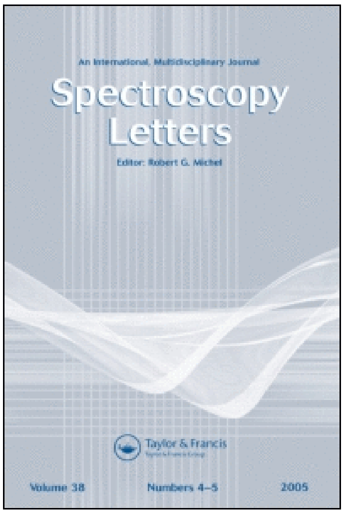

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Spectroscopy and Kinetics of HgBr (B-X) Formation Due to Collisions of Helium Ions with Methyl Mercury Bromide Molecules

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Spectroscopy and Kinetics of HgBr (B-X) Formation due to collisions of Helium Ions with Methyl Mercury Bromide Molecules

Key Words: HgBr laser, Ion-molecule reactions, He^+ and He_2^+ ions, CH_3HgBr, Molecular bands, Atomic lines.

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Abstract

Emission resulting from collisions of 100-1000 eV He^+/He_2^+ ions with CH_3HgBr molecules has been characterized in the 244-580 nm region. Emission bands due to HgBr (B-X), CH(A-X), and CH(B-X) transitions were observed besides atomic mercury lines. Emission cross-sections as a function of energy of helium ions for the strongest band of HgBr radical at 502 nm corresponding to the transition ($v' = 0$ - $v'' = 22$) were determined.

INTRODUCTION

Laser action has been demonstrated from low-lying vibrational levels of the electronically excited B-state to the high vibrational levels of ground state of the HgBr radical, i.e. (B, v′ = 0 - X, v″ = 22) by using different excitation techniques.[1-7] The efficiency of mercury bromide lasers has been observed to improve significantly in the presence of buffer gases such as N_2, Ar, He, etc. in the discharge medium.[8] In a discharge medium containing these gases with $HgBr_2$ vapor, a number of processes such as excitation, ionization, dissociation, etc. may take place giving rise to the formation of excited as well as ionized species. Based on this information, a large number of He^+ and He_2^+ ions are expected to be produced in a discharge medium containing He gas with $HgBr_2$ vapor.[9] The formation of excited states of mercury atom has been observed in the past[10] during collisions involving He (2^3S) and $HgBr_2$ molecules with no emission from the HgBr (B-X) transition. Also, formation of ionized species such as Hg^+ and $HgBr^+$ has been observed by Johnsen and Biondi[11] during dissociative charge transfer processes involving collisions of He^+ ions with $HgBr_2$ molecules at thermal energy. In this paper, observations are reported, for the first time, on the formation of excited state species such as HgBr (B), CH(A), CH(B) and Hg^* during collisions of He^+ and He_2^+ ions with CH_3HgBr molecules at various laboratory kinetic energies of the projectile ions. It is advantageous that CH_3HgBr has a much higher vapor pressure than $HgBr_2$ at low temperatures. Emission cross-sections have also been determined of the strongest band of the HgBr (B-X) transition corresponding to 502 nm at various kinetic energies of He^+ and He_2^+ ions.

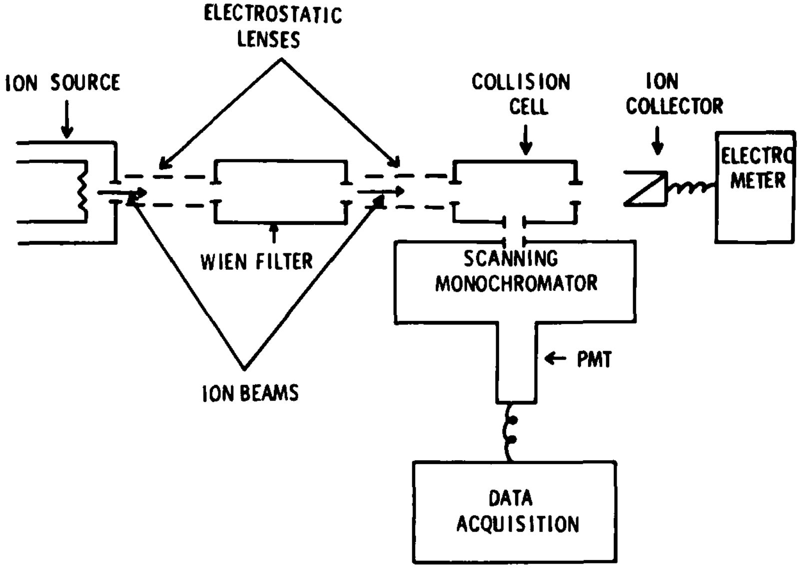

Fig. 1 Schematic diagram of the experimental setup.

EXPERIMENTAL

The experimental results reported here are obtained by directing a mass selected ion beam of He^+/He_2 at a desired kinetic energy into a collision cell containing CH_3HgBr vapor. Fig. 1 shows the schematic diagram of the experimental setup used in the present study. The He^+ and He_2^+ ions were generated in a low voltage d.c. discharge by flowing He gas through it controlled by a precision leak valve (Grainville Philips model 328), extracted from a hole in the anode and then accelerated to an energy of about 1 keV before entering into a high resolution Wien velocity filter[12] (Resolution: $M/\Delta M = 400$). The desired mass-selected ions were deaccelerated by a set of electrostatic lenses into the collision cell which was made of copper. The collision cell has a slot (2 cm x 2 mm) parallel to the ion beam for monitoring the light resulting from the ion-molecule reactions. The methyl mercury bromide vapor was generated by heating CH_3HgBr salt kept in a container underneath collision cell. The temperatures of the collision cell and the container were measured by a calibrated thermocouple (k-type, Keithley Instruments) and displayed on a digital thermometer. Ions were collected on a Faraday cup connected to a very sensitive electrometer (Keithley Instruments Model 610C) to measure ion currents. These ion currents were observed to be in the range of 1nA to 1μA in the kinetic energy range of 100 - 1000 eV. The ion source, Wien velocity filter, collision cell, CH_3HgBr vapor generator, and Faraday cup were all housed in a stainless steel chamber. The chamber was evacuated by two mechanical pumps (Edwards Model E2M12, 30 CFM) and a cryo pump (CTI model Cryo Torr - 8) to a base pressure of 10^{-7} Torr. The light emitted from the collision cell as a result of ion-molecule reactions involving collisions of helium ions with CH_3HgBr molecules was dispersed by a 0.2m scanning monochromator with 1200 lines/mm grating (McPherson model 275 attached to a scanner model 789) and detected by a cooled (-25°C) photomultiplier tube (PMT) (EMI GenCom model 9863 QB/5). The output of the PMT was amplified and displayed on a photon counter (EMI GenCom model AD-100 amplifier and C-10 counter). The output signal from the photon counter was fed to a multichannel analyzer (MCA)

(Norland Corporation model 5608) for storage and plotting data on a printer (Epson model LX-800).

RESULTS AND DISCUSSION

The emission bands due to HgBr (B-X), CH(A-X) (Q heads of (0,0) and (0, 1) bands at 431.4 and 489.0 nm, respectively), CH(B-X) (Q head of (0, 0) band at 388.9 nm) transitions and atomic mercury lines at 546, 435.8, 404.6, 365 and 312.56 nm due to the transitions $Hg(7^3S_1-6^3P_{0,1,2})$ and $Hg(6^3D_{1,2,3}-6^3P_{0,1,2})$ according to the electric dipole selection rule $\Delta J = 0, \pm 1$ were observed during collisions of He^+ and He_2^+ ions with CH_3HgBr molecules. These observations were, however, limited in the kinetic energy range of 100 -1000 eV because of low ion currents at energies below 100 eV and high vapor pressure of CH_3HgBr causes severe attenuation of the ion beam when passed through the vapor. Fig. 2 shows the emission spectra observed during collisions of He^+ and He_2^+ ions with CH_3HgBr molecules at a kinetic energy (lab.) of 700 eV. It is known that the ionization potential[13] of CH_3HgBr (10.16 eV) is lower than that of $HgBr_2$ (10.62 eV) and, therefore, a large number of ionized species such as CH_3HgBr^+, $HgBr^+$, Hg^+, CH_3^+, CH_2^+, CH^+, etc. are expected to be formed during collisions of He^+ and He_2^+ ions with CH_3HgBr molecules. Based on expected ionized and emitted species observed in the present study, the following set of reactions may be responsible for the observation of emission bands of HgBr radical and atomic mercury lines.

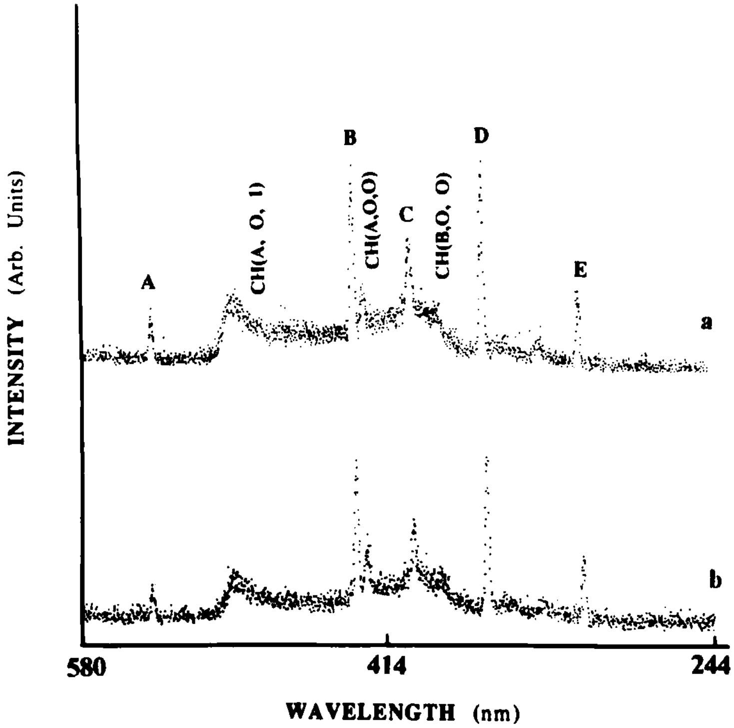

Fig. 2 Emission spectra observed due to collisions of (a) He_2^+ and (b) He^+ ions with CH_3HgBr (≈ 0.15 Torr) molecules at a laboratory kinetic energy of 700 eV.

A = $Hg(7^3S_1-6^3P_2)$, B = $Hg(7^3S_1-6^3P_1)$,

C = $Hg(7^3S_1-6^3P_0)$, D = $Hg(7^3D_3-6^3P_2)$,

E = $Hg(7^3D_2-6^3P_1)$.

A. Collision-induced dissociative charge transfer processes:

$He^+/He_2^+ + CH_3HgBr \rightarrow CH_3HgBr^+ + He/He_2 + \Delta E$ (14.43/12.06 eV) (1)

$He^+/He_2^+ + CH_3HgBr \rightarrow CH_3 + HgBr^+ + He/He_2 + \Delta E$ (9.84/7.47 eV) (2)

$He^+/He_2^+ + CH_3HgBr \rightarrow CH_3^+ + HgBr + He/He_2 + \Delta E$ (12.13/9.76 eV) (3)

$He^+/He_2^+ + CH_3HgBr \rightarrow CH_2^+ + H + HgBr + He/He_2 + \Delta E$ (6.63/4.26 eV) (4)

$He^+/He_2^+ + CH_3HgBr \rightarrow CH^+ + H_2 + HgBr + He/He_2 + \Delta E$ (6.39/4.02 eV) (5)

$He^+/He_2^+ + HgBr \rightarrow HgBr^+ + He/He_2 + \Delta E$ (12.50/10.13 eV) (6)

$He^+/He_2^+ + HgBr \rightarrow Hg + Br^+ + He/He_2 + \Delta E$ (12.07/9.70 eV) (7)

$He^+/He_2^+ + HgBr \rightarrow Hg^+ + Br + He/He_2 + \Delta E$ (13.44/11.07 eV) (8)

$He^+/He_2^+ + Hg \rightarrow Hg^+ + He/He_2 + \Delta E$ (14.15/11.78 eV) (9)

B. Collision-induced dissociative excitation processes.

$He^+/He_2^+ + CH_3HgBr \rightarrow CH_3HgBr^* + He^+/He_2^+ + \Delta E$ (≈ -6.70 eV) (10)

$He^+/He_2^+ + CH_3HgBr \rightarrow CH_3 + HgBr^* + He^+/He_2^+ + \Delta E$ (-5.58 eV) (11)

$He^+/He_2^+ + HgBr \rightarrow HgBr^* + He^+/He_2^+ + \Delta E$ (-2.92 eV) (12)

$He^+/He_2^+ + HgBr \rightarrow Hg + Br + He^+/He_2^+ + \Delta E$ (-0.71 eV) (13)

$He^+/He_2^+ + CH_3 \rightarrow CH + H_2 + He^+/He_2^+ + \Delta E$ (-4.9 eV) (14)

$He^+/He_2^+ + CH \rightarrow CH^* + He^+/He_2^+ + \Delta E$ (≈-3.0 eV) (15)

$He^+/He_2^+ + Hg \rightarrow Hg^* + He^+/He_2^+ + \Delta E$ (-4.86 eV) (16)

$He^+/He_2^+ + Hg^* \rightarrow Hg^{**} + He^+/He_2^+ + \Delta E$ (-2.78 eV) (17)

Here CH_3HgBr^* is a repulsive state similar to $HgBr_2^*$, $HgBr^*$ = HgBr (B), CH^* = CH(A, B), Hg^* = $Hg(6^3P_{0,1,2})$, Hg^{**} = $Hg(7^3S_1)$ and ΔE is the exothermicity or endothermicity of the reaction.

The exothermicities and endothermicities, ΔE of the collision-induced dissociative charge transfer processes (1) - (9) were calculated by using the ground state ionization potentials[13, 14] of He (24.58 eV), He_2 (22.22 eV), CH_3HgBr

(10.16 eV), HgBr (12.09 eV), Br (11.81 eV), CH (10.64 eV), CH_2 (10.40 eV), CH_3 (9.84 eV), Hg (10.44 eV) and dissociation energies[15-17] of $CH_3HgBr \rightarrow CH_3 + HgBr$ (2.66 eV), $HgBr \rightarrow Hg + Br$ (0.71 eV), CH (3.47 eV), $CH_2 \rightarrow CH + H$ (4.2 eV), $CH_3 \rightarrow CH_2 + H$ (4.9 eV). These values of ΔE indicate that a large number of ionized species such as CH_3HgBr^+, $HgBr^+$, Br^+, CH_3^+, etc. are expected to be produced directly or indirectly during collisions of He^+ and He_2^+ ions with CH_3HgBr molecules. The ΔE values for the collision-induced dissociative excitation processes (10) - (17) indicate that these processes are endothermic. The formation of HgBr (B-state), highly excited states of atomic mercury and CH (A, B) states may be due to the efficient conversion of kinetic energy of the projectile species into the internal energy of the target species through the processes (12), (15), (16), and (17) mainly because of their low endothermicities. Such a conversion of kinetic energy into the internal energy of the product species has been observed in the past[18] in many other ion-molecule reactions. The process (11) may also contribute to the formation of HgBr (B-state), however, observation of the highly excited states of atomic mercury and CH (A, B) cannot be explained by this process.

The emission cross-sections of the strongest band of the (B-X) system of HgBr at 532 nm due to collisions of He^+ and He_2^+ ions with CH_3HgBr at various kinetic energies (lab.) of the projectile ions were calculated (See Table I) by using the expression[19]: $\sigma = I_s/(I_p\ n\ L)$, where I_s is the number of photons emitted per second and corrected for the detection

TABLE 1

Measured cross-sections of HgBr (B) formation due to collisions of He^+ and He_2^+ ions with CH_3HgBr molecules.

Kinetic energy (eV)	Cross-section ($x10^{-20}cm^2$)	
	$He^+ + CH_3HgBr$	$He_2^+ + CH_3HgBr$
1000	0.21	0.38
900	2.31	2.46
700	2.95	3.79
500	1.81	2.10
300	1.00	1.18
100	0.13	0.37

efficiency of the optical system, I_p is the number of ions per second taking part in the reaction at a particular energy of the ion, n is the number density of CH_3HgBr vapor and L is the interaction length (2 cms) of ions with vapor inside the collision cell. There are no experimental or theoretical data available for the vapor density of CH_3HgBr at different temperatures. The vapor density[16] of CH_3HgBr at about 35°C is approximately the same ($\pm$ 30%) as that of $HgBr_2$ at 100°C. The vapor density of $HgBr_2$ was calculated by using the thermochemical data reported by Kubaschewski and Alcock.[20] The accuracy of the measured cross-sections depends upon the accuracy of estimates for the absolute number density of photons emitted and CH_3HgBr molecules taking part in the ion-molecule reactions. The optical system was calibrated by using calibrated lamp traceable to the U.S. National Bureau of Standards in the wavelength range of 300 - 800 nm and rechecked by measuring the emission cross sections of the hydrogen atomic lines observed in charge transfer reactions involving He^+ and H_2 gas at laboratory kinetic energies of 100 and 700 eV. These cross-sections were found to be about 20% higher than those measured by Isler and Nathan.[21]

CONCLUSIONS

Ion-molecule reactions have been studied involving collisions of He^+/He_2^+ ions with CH_3HgBr molecules and emission cross-sections have been measured of the HgBr (B-X) formation corresponding to (0, 22) band at different kinetic energies of the projectile ions in the energy range of 100 - 1000 eV. The efficiency of HgBr (B) formation with He_2^+ ions was observed to be higher than He^+ ions during collisions with CH_3HgBr molecules. Collisions-induced dissociative excitation processes seem to be the dominant mechanism in producing these emissions.

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