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$HBr^+(A^2\Sigma^+ \rightarrow X^2\Pi i)$ Fluorescence Produced by Ne I Photoionization

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The emission spectra of HBr^+ ions in the electronically excited $A^2\Sigma^+$ state were found in the photoionization of HBr by the neon resonance lines (16.85 and 16.67 eV). Only the emission from the $HBr^+(A^2\Sigma^+, v'=0,1) \rightarrow HBr^+(X^2\Pi_i, v'')$ was observed because of the predissociation at $v' \geq 2$ levels. The vibrational distribution of the $v'=0$ and 1 levels in the Ne I photoionization agrees well with the data of the photoelectron spectroscopy and the electron impact on HBr, but not with those of the He(^{3}S)-HBr and He^+-HBr collisions.

KEY WORDS: XUV photolysis/ Emission/ Excited state/ Vibrational population/

Fluorescence spectra of HBr^+ molecular ion were first analyzed by Norling[1] in 1935 by using a hollow-cathode discharge of HBr gas. The assignments of the $A^2\Sigma^+ \rightarrow X^2\Pi_i$ electronic transition have been confirmed by several different expreriments including discharges,[2-5] the ion-HBr collisions,[7-8] the Penning ionization optical spectroscopy (PIOS),[9] and the energy controlled electron impact on HBr.[10] The photoelectron (PES) and the Penning ionization electron spectroscopy (PIES) have shown that the vibrational levels up to $v'=4$ of $HBr^+(A^2\Sigma^+)$ state are excited,[11] whereas in the emission analysis only the $v'=0$ and 1 levels have been detected.[9] Moreover the relative vibrational population of the $v'=0$ to the $v'=1$ level depends on how the $A^2\Sigma^+$ state is produced: in the electron beam excitation[10] the relative vibrational population, $N_{v'=0}/N_{v'=1}$, has been found to be 0.55 but in the collisions with noble gas atoms[8,9,12] the reverse populations have been obtained.

In the present work we used the Ne I photon (73.6 nm) to produce the vibrationally excited $HBr^+(A^2\Sigma^+)$ ions. This investigation is the first report of the emission spectrum of photoionized HBr^+.

The experimental setup is basically the same as that described previously.[13] Hydrogen bromide (99.8% purity) was supplied by Matheson Co. and used without further purification. The gas pressure was monitored by a MKS capacitance manometer and was kept constant by using a MKS 244/245-pressure controller. The fluorescence was dispersed at a right angles to the primary exciting beam by Jobin-Yvon H20UV monochromator with a resolution of 1.5 nm. The detecting system response was corrected by a standard bromine lamp with a known spectral irradiance (Usio Electronic Co. type JPD-100-500CS).

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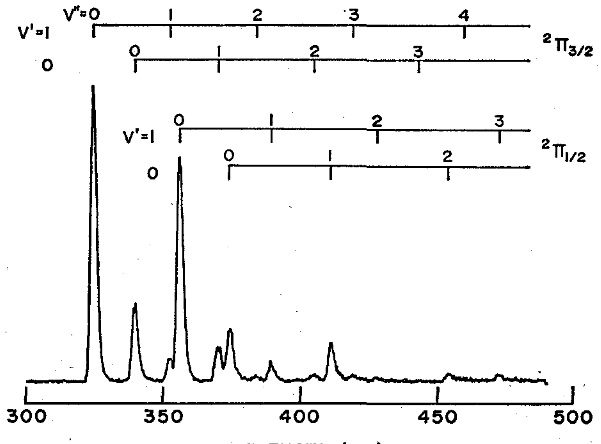

Fig. 1. Fluorescence spectra of $HBr^+(A^2\Sigma^+ \rightarrow X^2\Pi_i)$ produced by the direct photoionization with neon resonance lines.

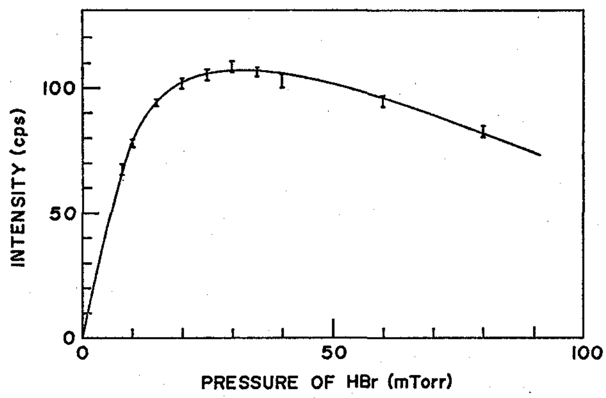

Fig. 2. Pressure dependence of the emission intensity.

Table I. Relative fluorescence cross sections for the observed $HBr^+(A^2\Sigma^+ \rightarrow X^2\Pi_i)$

Bandhead	Incident light Ne I (73.6 nm)[a]
0–0	16.8
0–1	12.0
0–2	4.5
0–3	1.2
0–4	0.7
1–0	52.7
1–1	6.1
1–2	1.9
1–3	3.9
1–4	0.2

a) Expressed in %.

Table II. Relative vibrational population of $HBr^+(A^2\Sigma^+, v'=0,1)$

$N_{v'=0}/N_{v'=1}$	Experimental method	Ref.
0.54	Photoionization	Present work
0.55	Electron beam	10
0.53	PES	11
1.3	PIES	11
~9	He^+ collision	8
~100	PIOS	9

The typical fluorescence spectrum of HBr^+ is presented in Fig. 1. The ionization potential of the $v'=2$ level of $HBr^+(A^2\Sigma^+)$ is 15.62 eV[14] and the photon energy of Ne I is 16.85 eV. Thus no emission from the $v'\geq 2$ levels in Fig. 1 is consistent with the previous observation that $HBr^+(A^2\Sigma^+)$ ion predissociates at the $N'=12$ in the $A^2\Sigma^+$ $v'=1$ level.[7] The fluorescence intensity depends strongly on the HBr pressure as shown in Fig. 2. The nonlinearity is mainly explained by a collisional quenching of the excited ion.

Table I gives the distribution of the relative emission intensities obtained under the HBr pressure less than 10 mTorr. The error was estimated within $\pm 10\%$ for each bandhead. The relative intensities of two series of progressions, $(A^2\Sigma^+ \rightarrow X^2\Pi_{3/2})/(A^2\Sigma^+ \rightarrow X^2\Pi_{1/2})$, were found to be almost equal for every v'–v'' transition. The averaged value was 0.98 ± 0.03 which is close to the expected statistical value of unity, although in the PIES measurement a little larger value of 1.16 ± 0.05 has been reported.[11]

The ratio of the vibrational population, $N_{v'=0}/N_{v'=1}$, is shown in Table II with the values previously obtained by using different techniques. The present value agrees well with those obtained by an electron bombardment[10] and the He I PES.[11] This agreement implies that the HBr^+ $A^2\Sigma^+$ state is produced directly by photoabsorption and the collisional quenching of the excited HBr^+ ion is very small under the condition of the HBr pressure less than 10 mTorr. The similar tendency has been also observed in the case of the photoionization of HCl.[13] The large inverse populations in the PIOS or the He^+-HBr collision suggest that there would exsist a strong interaction during the action of the ionization between HBr and $He(^3S)$ atom or He^+ ion, which may form a collision complex having a long enough lifetime to redistribute the excess energy.

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