

$\text{HBr}^+(\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi_i)$ Fluorescence Produced by Ne I Photoionization

Toshio IBUKI and Nobuyuki SUGITA

Received July 9, 1983

The emission spectra of HBr^+ ions in the electronically excited $\text{A}^2\Sigma^+$ state were found in the photoionization of HBr by the neon resonance lines (16.85 and 16.67 eV). Only the emission from the $\text{HBr}^+(\text{A}^2\Sigma^+, v'=0,1) \rightarrow \text{HBr}^+(\text{X}^2\Pi_i, v'')$ 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 $\text{He}(^3\text{S})\cdot\text{HBr}$ and $\text{He}^+\cdot\text{HBr}$ collisions.

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

Fluorescence spectra of HBr^+ molecular ion were first analyzed by Norling¹⁾ in 1935 by using a hollow-cathode discharge of HBr gas. The assignments of the $\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi_i$ electronic transition have been confirmed by several different experiments 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 $\text{HBr}^+(\text{A}^2\Sigma^+)$ 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 $\text{A}^2\Sigma^+$ state is produced: in the electron beam excitation¹⁰⁾ 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 $\text{HBr}^+(\text{A}^2\Sigma^+)$ 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).

* 伊吹紀男, 杉田信之: Laboratory of High Pressure Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

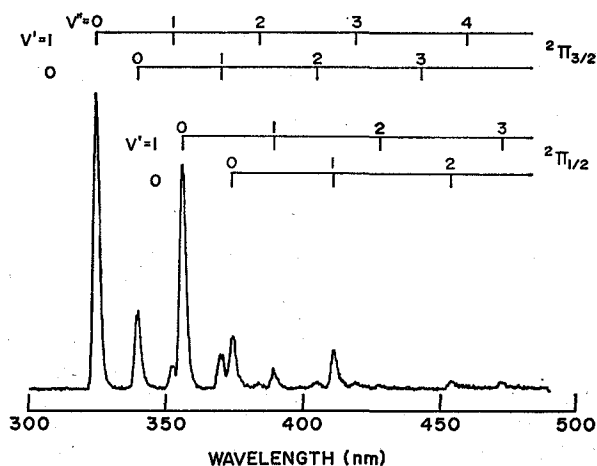


Fig. 1. Fluorescence spectra of $\text{HBr}^+(\text{A}^2\Sigma^+ \rightarrow \text{X}^2\Pi_i)$ produced by the direct photoionization with neon resonance lines.

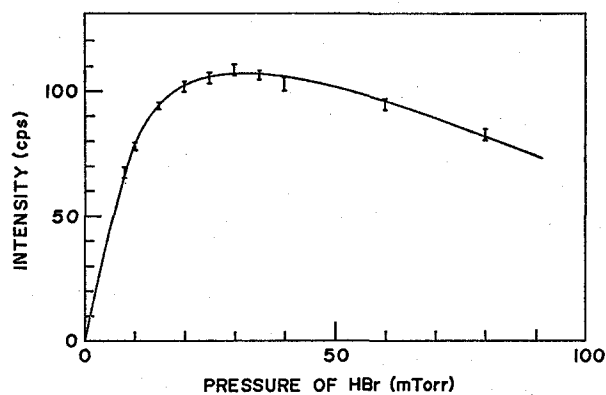


Fig. 2. Pressure dependence of the emission intensity.

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

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 %.

HBr⁺($A^2\Sigma^+ \rightarrow X^2\Pi_i$) fluorescence produced by Ne I photoionization

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 eV¹⁴⁾ 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 bombardment¹⁰⁾ 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 exist 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.

ACKNOWLEDGMENT

The authors acknowledge Y. Ichikawa and M. Yasumoto for their assistance of the construction of the experimental apparatus made of stainless steel.

REFERENCES

- (1) F. Norling, *Z. Phys.*, **95**, 179 (1935).
- (2) R. F. Barrow and A. D. Caunt, *Proc. Roy. Soc.*, **A66**, 617 (1953).
- (3) L. Marsigny, J. Lebreton, J. Ferran, and R. Lagrange, *C. R. Acad. Sci. Paris*, **C266**, 176, 1731 (1968).

- (4) L. Marsigny, J. Lebreton, and Y. Petit, *C. R. Acad. Sci. Paris*, **C270**, 1632 (1970).
- (5) J. Lebreton, *J. Chim. Phys.*, **70**, 1188 (1973).
- (6) M. J. Haugh, B. S. Schneider, and A. L. Smith, *J. Molec. Spectrosc.*, **51**, 123 (1974).
- (7) M. J. Haugh and K. D. Bayes, *J. Phys. Chem.*, **75**, 1472 (1971).
- (8) M. J. Haugh, *J. Chem. Phys.*, **56**, 4001 (1972).
- (9) W. C. Richardson and D. W. Setser, *J. Chem. Phys.*, **58**, 1809 (1973).
- (10) G. R. Möhlmann and F. J. de Heer, *Chem. Phys.*, **17**, 147 (1976).
- (11) C. E. Brion and P. Crowley, *J. Electron Spectrosc. Relat. Phenom.*, **11**, 399 (1977).
- (12) W. C. Richardson and D. W. Setser, *Chem. Phys. Lett.*, **12**, 349 (1971).
- (13) (a) T. Ibuki, *Bull. Inst. Chem. Res. Kyoto Univ.*, **59**, 142 (1981). (b) T. Ibuki, N. Sato, and S. Iwata, *J. Chem. Phys.*, **79**, 4805 (1983).
- (14) K. P. Huber and G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. 4, Van Nostrand Reinhold, New York, N. Y., 1979.