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High Resolution Photoionization Spectrum of HBr measured with Frequency Tripled Laser Radiation

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The photoionization spectrum of HBr around the first ionization limit was measured at resolution of up to 5×10^{-4} nm. The ionizing vacuum ultraviolet radiation was generated by frequency tripling of the second harmonic output of a dye laser. Three sets of Rydberg series, each converging to the ground state ($^2\Pi_{3/2}$) of HBr^+, were observed on the longer wavelength side of the ionization limit. By extrapolation of the Rydberg series, the ionization potential of HBr was determined to be 11.666 ± 0.001 eV.

KEY WORDS: Photoionization; Rydberg state; HBr; VUV laser; ionization potential; frequency tripling.

INTRODUCTION

Recent availability of high-power narrow-band dye lasers has made it a practical technique to generate coherent vacuum ultraviolet (VUV) radiation by means of the third-order non-linear optical effect in an isotopic medium[1]. In addition to the wavelength tunability, the laser-based VUV light has a marked advantage over the conventional continuum lamp source or the synchrotron radiation in its resolution

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and brightness. Of additional importance in application to molecular spectroscopy is its relative convenience with high accuracy of wavelength calibration: the harmonic wavelength in the VUV should be determined with reference to the wavelength of fundamental visible dye laser light that is readily calibrated against the iodine spectrum[2,3].

The present paper reports a preliminary study of one photon ionization efficiency curve of an HBr beam measured at around 106 nm. The tunable VUV light was generated by tripling the second harmonic output of a dye laser. The VUV absorption of HBr at a wavelength longer than 119.2 nm has been extensively studied in many electronic states[4–8]. The autoionizing Rydberg states observed in absorption of the 80–100 nm region were also analyzed[9]. However, no high resolution photoionization spectrum around the first ionization limit (106 nm) has ever been reported. Since dissociation of HBr is known to compete with ionization[10], the photoionization spectrum may involve features differing somewhat from the absorption spectrum.

EXPERIMENTAL

The second harmonic output of a YAG laser-pumped dye laser (Quanta-Ray, DCR-1A and PDL) is focused by a lens of 50-mm focal length into a gas cell containing xenon to produce the third harmonics in the VUV. The dye laser with DCM dye (Exciton) in methanol is scanned from 640 to 637 nm, corresponding to the VUV range of 106.7–106.2 nm. The frequency tripling in xenon is efficient in the wavelength region shorter than the $5d'[3/2]_1$ resonance line at 106.8 nm[11,12]. The dye laser is normally of 0.3 cm^{-1} resolution and is capable of up to 0.07 cm^{-1} resolution by employing an intracavity etalon.

A schematic diagram of the apparatus is shown in Figure 1. The xenon gas cell consists of a stainless steel tube, 150 mm in length and 20 mm in diameter, with quartz and lithium fluoride windows on the input and output port, respectively. The uncollimated VUV light irradiates a molecular beam at about 15 cm distant from the LiF window. The generated VUV light is monitored by the detection of the scattered VUV light with a photomultiplier (Hamamatsu, R331), the photocathode of which is replaced by a LiF window. Then the signal

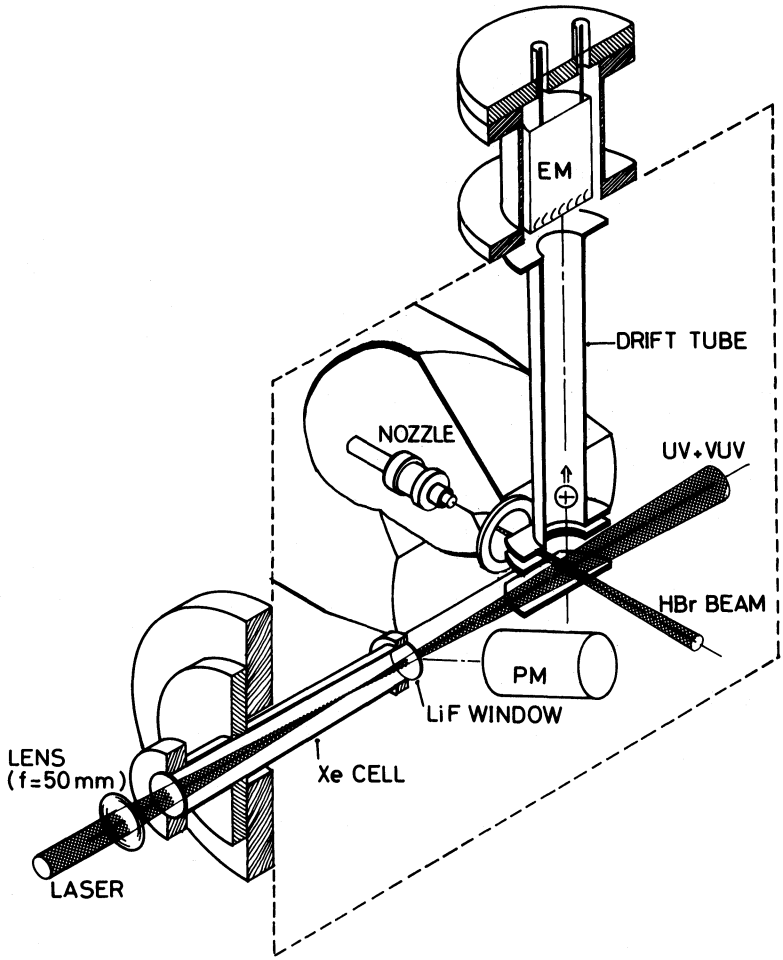

Figure 1 Schematic drawing of the cross-sectional view of the apparatus. Supersonic beam of HBr is expanded through a pulsed nozzle, and intersects the laser beam at right angles. Generated ions are extracted from the intersectional zone to a drift tube. EM: solar blind electron multiplier; PM: photomultiplier with LiF window.

intensity of the photomultiplier was found to be linear in the photoion current.

The molecular beam apparatus employed in this experiment was described in our previous papers on the crossed beam chemical reactions[13–15]. The supersonic HBr beam is generated in a 10-Hz

repetitive pulse of 0.5-ms duration through an automobile fuel injector of 0.2-mm nozzle diameter. The beam is collimated by a skimmer and enters into an ionization chamber. The translational temperature of the beam was found to be below 20 K from a time-of-flight spectrum of the beam.

The photoionization takes place at the intersectional zone of the laser with the HBr beam. The generated ions are accelerated by weak electric field of less than 50 V/cm into a field-free drift tube of 20-cm length, and are detected by a solar blind electron multiplier (Hamamatsu, R499). The signal from the electron multiplier is amplified, fed to a digital memory of 10-ns time resolution (Iwatsu, DM901), and is accumulated in a microcomputer (NEC, PC9801). From the time-of-flight mass spectrum, influence of scattered or fluorescent VUV light[10] was found to be negligible for the ion detection. The photoionization spectrum is recorded by a three-channel gated integrator followed by the A/D conversion and signal storage in the microcomputer. In a high resolution experiment, a small portion of the visible laser beam is admitted to an iodine cell. The laser-induced fluorescence spectrum of I_2 is recorded simultaneously with photoionization spectrum for the wavelength calibration.

RESULTS AND DISCUSSION

The tuning curve for the third harmonic generation in xenon of pressure 15 Torr is shown in the top of Figure 2. Many unidentified dips, wider than the laser bandwidth, are involved therein as indicated by open triangles in the figure. The absorption by impurity gas or xenon gas is presumably responsible for these dips. The bottom trace in Figure 2 shows the photoionization spectrum of HBr observed at a resolution of 0.002 nm ($1.8\,cm^{-1}$). Among many peaks in the spectrum, no distinct stepwise feature at the first ionization limit is visible. The spectrum is reminiscent of the photoionization spectrum of HI[16].

A part of the photoionization spectrum of HBr recorded at a higher resolution is shown in Figure 3 together with the I_2 reference spectrum. According to spectroscopic constants of HBr(X) and $HBr^+(X)$[17], even rotational lines of the Q-branch transition would have been resolved with this improved resolution. As a result, no additional finer structure is visible in Figure 3.

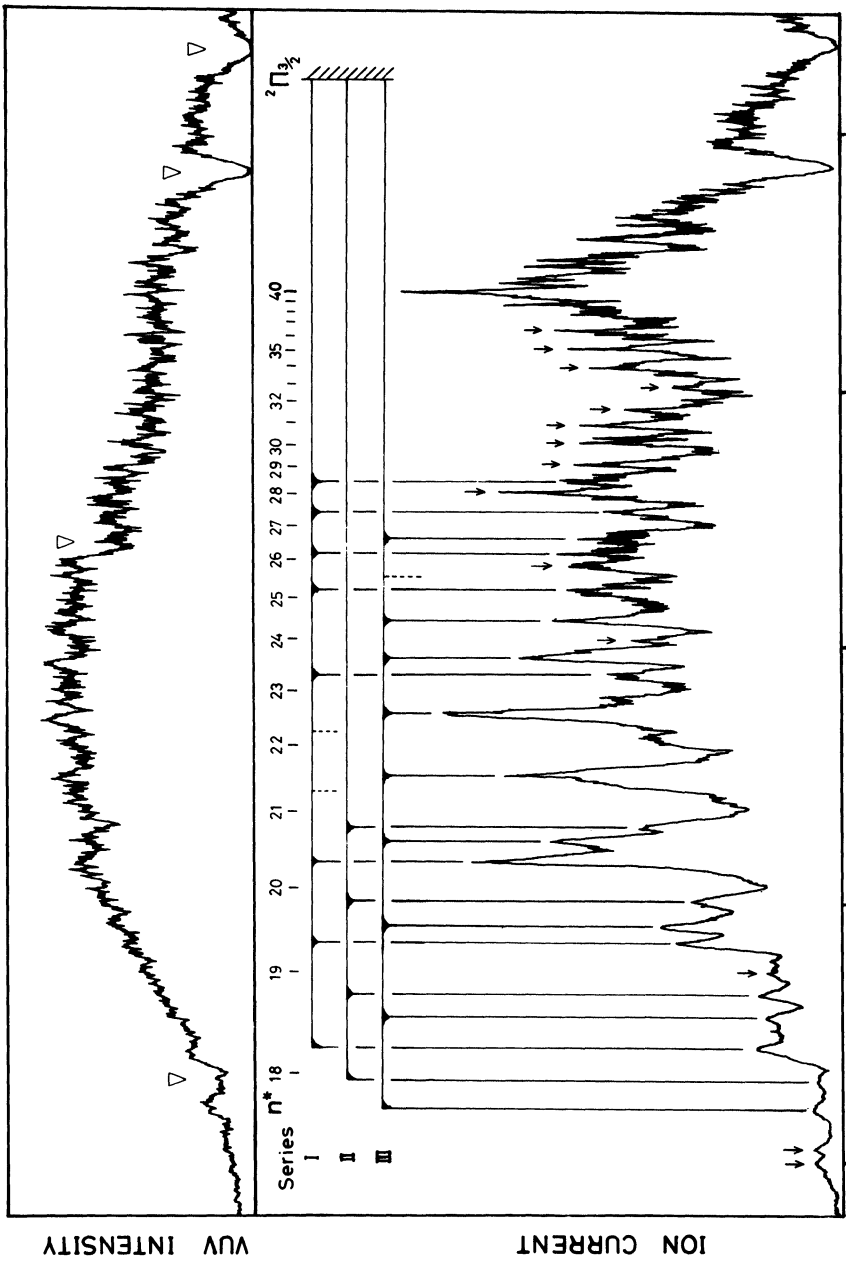

Figure 2 Tuning curve for the third harmonic generation in xenon of pressure 15 Torr (top) and photoionization spectrum of HBr beam (bottom). Assignment to Rydberg series I, II and III is shown by vertical lines. Unidentified peaks are indicated by arrows.

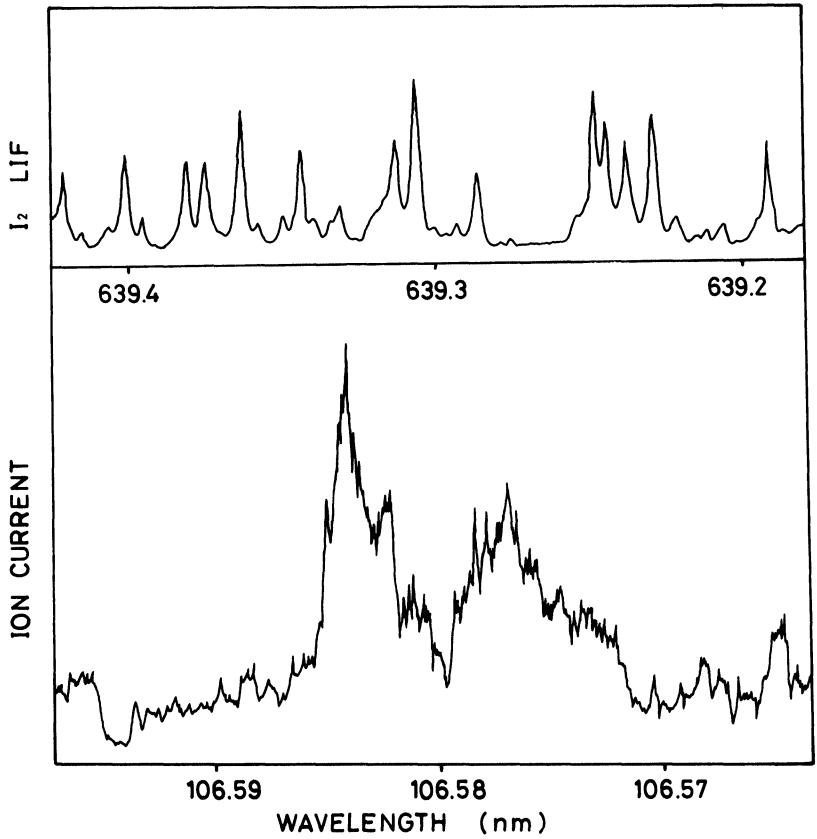

Figure 3 Expanded representation of a portion of the photoionization spectrum of HBr in four times higher resolution than that of Figure 2. The wavelength is calibrated against the iodine spectrum (top).

At an early stage of the present study, the observed peaks were thought to represent rotational structures since the spacing between some of the adjacent peaks are comparable to twice the rotational constant B of HBr. But the interpretation was ruled out on the basis of the later finding. The photoionization spectrum was also recorded for thermal HBr gas of pressure 5×10^{-5} Torr. The resultant spectrum showed no distinct difference from that of the supersonic beam. If the peaks described above were related to rotational structures, their

intensities should be strongly dependent on the internal temperature of HBr.

The spectral similarity of the supersonic beam to thermal gas also suggests that the observed structures are not due to dimer nor to any other van der Waals complexes. Besides, influences of collisional ionization are safely ignored in both conditions. Therefore, the observed structures are most probably due to congested autoionization states similar to those observed for HI[16]. As for HI, weak and complicated structures observed below the first ionization limit were assigned to the states of two sets of the Rydberg series both attributable to the *nd* states.

As shown in Figure 2, almost all peaks are assigned to components of three sets of the Rydberg series (I, II and III), each converging to the ground state of HBr^+ ($^2\Pi_{3/2}$). The observed wavelength of each peak position and effective principal quantum number n^* are collected in Table I. Those peaks which are not attributable to the above series are indicated by arrows in Figure 2 and are summarized in Table II together with the n^* with reference to the same ionization limit. The ionization limit was determined to be 11.666 ± 0.001 eV by extrapolation of the series. The error limit is three times the standard deviation. The accuracy is restricted mainly by the irregularity of the

Table I Wavelength and effective principal quantum numbers, n^*, of Rydberg states converging to the $^2\Pi_{3/2}$ ($v = 0$).

Series I wavelength (nm)	n^*	Series II wavelength (nm)	n^*	Series III wavelength (nm)	n^*
		106.669	17.96	106.682	17.64
106.657	18.24	106.635	18.78	106.645	18.54
106.617	19.30	106.599	19.81	106.609	19.52
106.584	20.31	106.571	20.77	106.577	20.56
				106.551	21.52
				106.528	22.52
106.512	23.26			106.506	23.61
				106.491	24.40
106.480	25.11				
106.465	26.11			106.460	26.47
106.450	27.26				
106.438	28.30				

Ionization limit 11.666 ± 0.001 eV.

Table II Wavelength and effective principal quantum numbers of unidentified peaks.

Wavelength (nm)	n^*
106.700	17.27
106.695	17.37
106.626	19.02
106.498	24.03
106.470	25.73
106.442	27.95
106.430	29.00
106.423	29.71
106.416	30.56
106.411	31.12
106.401	32.40
106.394	33.34
106.387	34.53
106.381	35.47
106.363	39.21

observed peak positions. The present determination of ionization limit to $^2\Pi_{3/2}$ is an order of magnitude more precise than the previous photoionization result of 11.66 ± 0.02 eV[18]. The present value is higher than the value determined by photoelectron spectroscopy, 11.645 ± 0.005 eV[19], and is lower than that derived from several references, 11.677 ± 0.004 eV[20].

Among the Rydberg series converging to the $^2\Pi_{3/2}$ state, $ns\sigma$, $nd\sigma$, $nd\pi$ and $nd\delta$ are expected to have relatively large transition probabilities from the ground state. Transition to the np series may be of weak intensity because the highest occupied lone pair orbital from which an electron is removed is almost of pure p character. None of the observed peaks may be attributable to the $ns\sigma$ series, since n^* of the series is known to be close to an integer[21]. Therefore, the observed series is more preferably assigned to the nd series. Further electronic character of these Rydberg states has yet to be studied. Rydberg states are to be characterized on the basis of the spectroscopic correspondence to low-lying electronic states. Such an analysis is difficult at the present stage because the excited states of HBr observed so far have not been interpreted in terms of a one-electron Rydberg model[7].

The observed series include complicated features both in peak positions and in intensities. The complexity may be brought out more clearly in Figure 4, where the photoionization spectrum shown in

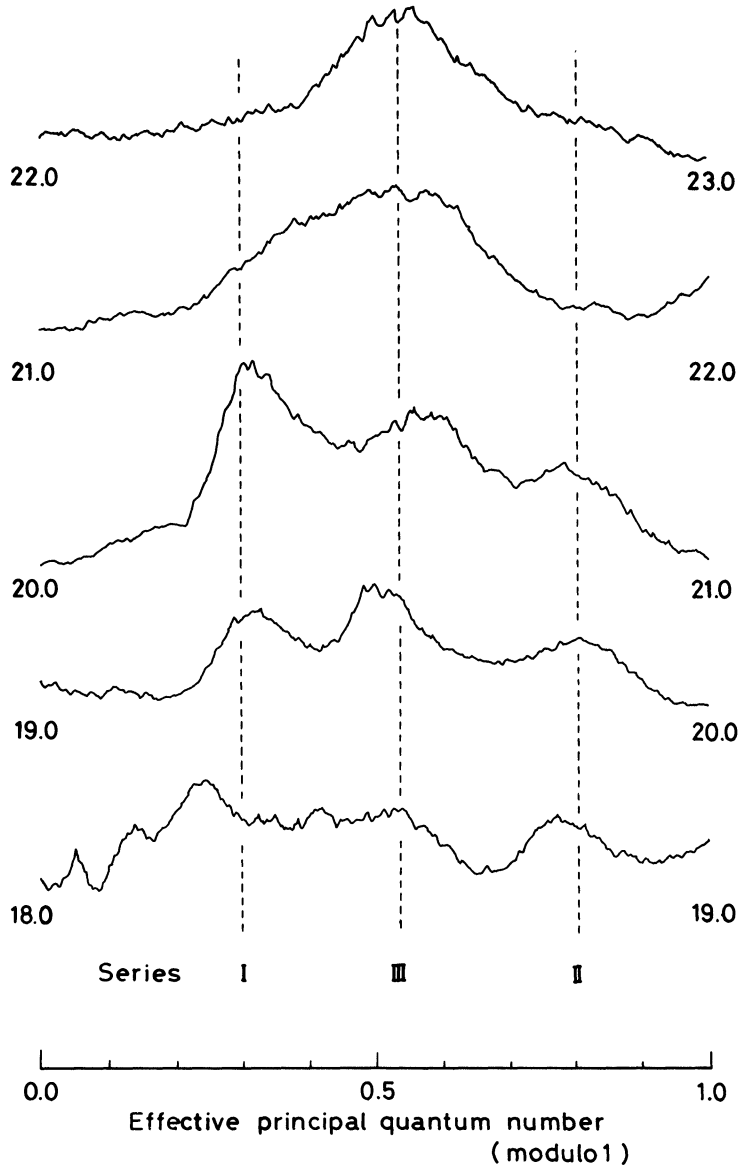

Figure 4 Photoionization curves of HBr redrawn on the scale of n^* for each range indicated in the figure. The vertical broken lines are the average of n^* for the series I, II and III.

Figure 2 is normalized to the VUV intensity and is represented on the scale of n^* (modulo 1) instead of the wavelength. In the case of krypton or xenon, the photoionization spectrum of autoionizing Rydberg series is known to be periodic in n^*, and such a representation of different n^* is superimposable on each other[16,22]. In contrast to the case of the atomic Rydberg series, none of the curves in Figure 4 is superimposable. The vertical broken lines are the average of the n^* (modulo 1) for the series I, II and III. The peaks of series III are intense over a relatively wide range of n^*, while those for series I and II abruptly fall off at $n^* > 21$. Such changes in shapes and intensities of Rydberg peaks may provide information on electronic interaction of states and/or changes in angular momentum coupling schemes. More comprehensive analysis of the Rydberg states awaits further high resolution spectroscopic work.

HBr is ionized either through the one-photon process followed by autoionization or through the two-step process in which the Rydberg state molecule excited by VUV light is ionized by the fundamental ultraviolet light. The former process seems more realistic in the present experimental situation where the laser beam is not focused onto the ionization zone. Although the present analysis is not influenced by what the actual ionization process is, the measurement of photoelectron energy distribution is very desirous in order to ascertain the above respect.

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