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HeI photoelectron spectroscopy (UPS) of iodine atoms

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Abstract

High concentrations of iodine atoms are directly obtained from methyl iodide on a Double-Chambers UPS Machine II, which was built specifically to detect transient species. A complete and well-resolved HeI photoelectron spectrum of iodine atom is recorded for the first time using a modified sample inlet system. Five peaks which come from the transition from ground state $^2P_{3/2}$ iodine atom to $^3P_{2,1,0}$, $^1D_2$ and $^1S_0$ ionic states have clearly been observed. The relative photoelectron intensities of ionic states are fairly close to their statistical ratios.

1. Introduction

In the HeI photoelectron spectroscopic studies of atomic species in the gaseous phase Jonathan et al. [1] first reported the HeI photoelectron spectra of some atomic halogens. De Leeuw et al. [2] obtained high concentrations of fluorine, chlorine and bromine, and provided the HeI photoelectron spectrum of ionic states partly for iodine atoms and then pointed out that attempts to measure the HeI photoelectron spectrum of iodine atoms directly from discharges in molecular iodine and methyl iodide were unsuccessful. Afterwards Kimura et al. [3] observed well-resolved HeI photoelectron spectra of atomic chlorine and bromine with essentially no background electrons and provided the first experimental data for relative photoionization cross sections for atomic chlorine and bromine.

It was well known that methyl iodide is of particular interest, in part because it was used as a generally acknowledged standard for the calibration of a HeI photoelectron spectrum, and plays a well-known, important role in ozone depletion in the stratosphere [4,5]. In the course of HeI photoelectron spectroscopic studies of microwave-discharged species in this State Key Laboratory, the present authors have directly observed well-resolved HeI photoelectron spectra of iodine atom from a methyl iodide discharge. Five peaks which come from the transition from ground state $^2P_{3/2}$ iodine atom to $^3P_{2,1,0}$, $^1D_2$ and $^1S_0$ ionic states have clearly been observed using a modified sample inlet system, and we wish to report this spectrum in the present Letter.

2. Experimental

Iodine atoms are generated by means of a microwave discharge (using a MR-301 microwave power generator) of a mixture of methyl iodide in argon and then introduced into the ionization chamber of a Double-Chambers UPS II, which was built specifically to detect transient species [6] through a flow quartz tube. Argon is added as required to this mix-

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ture for further dilution. Discharge powers up to 100 W were applied. In order to minimize surface catalyzed atom recombination reactions the inside of the discharge tube was carefully pre-treated with phosphoric acid. As a modified sample inlet system, the internal diameter of the flow quartz tube was expanded to 8.5 mm from the usual 4.2 mm and the exit hole of the tube was also expanded to 5.0 mm from the usual 0.2–0.5 mm to improve the flow speed of the discharged species, and then was connected to the spectrometer using Viton O-rings as vacuum seals. The distance between microwave discharge and ionization chamber is approximately 16 cm, as schematically shown in Fig. 1. The resolution is typically 25 meV as measured from Argon (fwhm) using HeI radiation. According to our experience, higher sensitivity of the spectrometer is important in order to obtain the HeI photoelectron spectrum of iodine atom from methyl iodide. When the pressure of the sample chamber was maintained at 1×10^{-4} Torr, a good HeI photoelectron spectrum is usually obtained. In the above-mentioned condition only HeI photoelectron spectrum of chlorine atoms produced by the microwave discharge of the freon has been recorded, with essentially no spectra of recombination products [7].

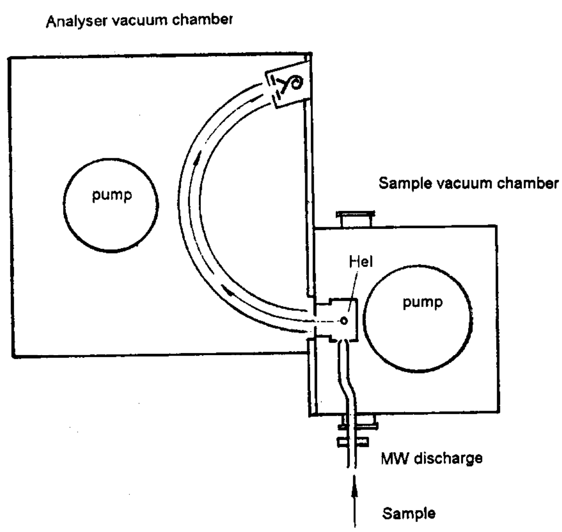

Fig. 1. Schematic diagram of the arrangement of the microwave discharge tube on the Double-Chambers UPS machine II.

3. Results and discussion

Using a modified sample inlet system the HeI spectrum of iodine atoms obtained by the microwave discharge of methyl iodide is shown in Fig. 2A, consisting of photoelectron peaks attributed to atomic iodine (I), molecular iodine (I_2) and hydrogen iodide (HI),

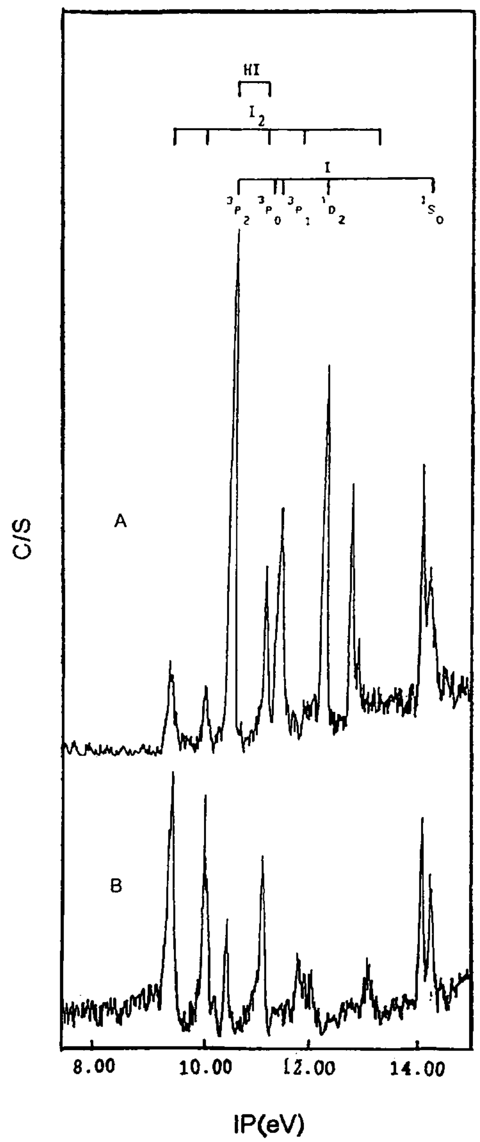

Fig. 2. HeI photoelectron spectra of discharged methyl iodide. (A) HeI spectrum of iodine atom obtained using a modified sample inlet system. (B) HeI spectrum of discharged methyl iodide using an original sample inlet system.

Table 1
Ionization energies and relative intensities observed in HeI photoelectron spectrum of iodine atoms

Atom	Ionic state	Ionization energy			Relative intensity	
		this work	ref. [2]	ref. [7] [a]	this work [b]	statistical ratio
I	$^3P_2$	10.44	10.43	10.451	1.00	1.0
	$^3P_1$	11.33	11.30	11.330	0.59	0.6
	$^3P_0$	11.24	11.23	11.250	0.19	0.2
	$^1D_2$	12.16	12.13	12.153	0.89	1.0
	$^1S_0$	14.11		14.108	0.17	0.2

[a] Used 1 eV = 8065.5 cm^{-1}.
[b] Corrected for analyzer electron energy sensitivity. Relative values were determined with experimental errors of ±0.02.

which was produced by reaction of atomic iodine with the surface of the discharge tube. Five peaks which come from the transition from ground state $^2P_{3/2}$ iodine atom to $^3P_{2,1,0}$, $^1D_2$ and $^1S_0$ ionic states are clearly observed. The HeI spectrum of microwave-discharged species obtained by a usual sample inlet system is shown in Fig. 2B, consisting of photoelectron peaks attributed to molecular iodine (I_2) and hydrogen iodide (HI). There is no signal of iodine atoms in this HeI spectrum. The background electrons are almost removed from both HeI spectra. Double peaks at 13.889 and 14.067 eV which come from the spin–orbit splitting of the argon ^2P electronic state through the HeI_β radiation also appear in both HeI spectra.

In Fig. 2A a sharp peak corresponding to $^3P_2$ ionic state at 10.44 eV is overlapped with a peak of HI at 10.42 eV. So its fwhm is wider than that of the peak of $^1D_2$ ionic state at 12.16 eV. Of particular interest is the band centered near 11.31 eV with an obvious shoulder (11.24 eV) on the side of low ionization potential (IP in eV). The intensity of the shoulder is about one third of the main peak at 11.33 eV (see Table 1). It is well-known that the degeneracies of the ionized states may be given by $2J+1$ (where $J=2$, 1, 0), so that the statistical ratios are simply the relative values of $2J+1$ with respect to the $^3P_{2,1,0}$ ionic states. The shoulder at 11.24 eV in the band centered near 11.31 eV should be designated as the $^3P_0$ ionic state. The main peak at 11.33 eV is the result of the transition from the $^3P_{3/2}$ ground state to the $^3P_1$ ionic state. This reversal in the order of ionization potentials between $^3P_0$ and $^3P_1$ ionic states is consistent with corresponding spectroscopic data earlier reported by Huffman et al. [8]. As can be seen from comparison of both spectra, on the side of high ionization potential of the spin–orbit splitting peaks for the argon ^2P electronic state caused by the HeI_β radiation, there is a shoulder at 14.11 eV in Fig. 2A. This can be designated as the result of the transition of $^2P_{3/2}$ ground state to the $^1S_0$ ionic state.

Another interesting feature is the peak at 12.63 eV which is always accompanied by appearance of the peaks of iodine atom in the HeI spectrum of the species discharged in methyl iodide. The origin of this peak is not clear at the present time. However we would like to guess it is the result of the transition from the $^2P_{1/2}$ excited state of iodine atoms to an ionic state. This study is now in progress.

Ionization potentials obtained here for atomic iodine from the HeI spectrum are summarized in Table 1, and are essentially the same as those earlier determined spectroscopically by Huffman et al. [8]. According to the method proposed by Kimura et al. [3], the relative values of HeI photoelectron intensities for iodine atom are also summarized in Table 1, indicating relative values of differential photoionization cross sections at an angle of 90° with respect to the incident 584 Å radiation. It is clearly seen that the relative photoelectron intensities for iodine atom are fairly close to their statistical values.

Acknowledgement

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