HeI photoelectron spectroscopic of microwavedischarged species of methyl iodide*

Wang Guohong, Yang Wenxiang

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Wang Dianxun, Xu Guangzhi

Institute of Chemistry, Chinese Acedemy of Sciences, Beijing 100080, China

Abstract—The detection of the microwave-discharged species of methyl iodide by HeI photoelectron spectroscopy (UPS) is reported for the first time. The UPS spectra of I₂ and HI molecules clearly indicate in the spectrum of microwave discharged species of methyl iodide. So the mechanism of the change of methyl iodide under microwave discharge proposed. The result provides the basis for understanding depletion of the ozone shell of the atmosphere by halogenated methane.

Keywords: Hel photoelectron spectroscopy (UPS); microwave discharge; methyl iodide.

1 Introduction

The appearance of "The Ozone Hole" in the stratosphere causes the shock of the scientific and political circles in the world. The pursuit in the cause of forming this hole is also the task of scientists. Considering to the photochemical reactions of halogenated methane, there are a lot of the facts which proved the relations of the ozone depletion with halogenated methane. But the reaction channel and mechanism between the ozone and halogenated methane is not clear. It was well known that HeI (21.22 eV) photoelectron spectroscopy (UPS) has provided a great deal of information concerning orbital energies, bonding characters and electronic states of the studied molecules (Wang, 1981; 1992), there has so far no report in the literature of the successful detection of producing species of methyl iodide under microwave discharge. To understand the action of these species to depletion of the ozone, the UPS studies in the microwave discharged species of CH,I has been carried out in

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this paper. Using a photoelectron spectrometer built specifically to detect transient species and reaction species we have obtained the first spectra for these producing species, and wish to report these spectra in this paper.

2 Experimental

The UPS spectrum of microwave discharged species of methyl iodide is recorded in the UPS machine II which was built specifically to detect transient species (Zhao, 1991). The calibrations of the spectra are performed with the argon ²P and methyl iodide ²E double lines. And the spectral resolution under this condition is about 25 meV for the Argon Ar⁺ ²P_{3/2} line.

The microwave discharge employs MR-301 microwave power generator which was made by Japan. The adjustable scope of the power is 0-200W. The UPS results of microwave discharge in the 100 W power condition are given in this paper.

3 Results and discussion

The spectrum of methyl iodide (CH,I) had been well measured and usually used a calibration of UPS spectra for other studied compounds. After the treatment of 100 W power microwave discharged which is 17 cm far from the ionization point, the spectrum obtained for microwave discharged species of CH₃I is shown in Fig. 1. From the comparison the UPS of microwave discharged species with the UPS spectrum of CH₃I, it is well seen that both spectra are very different. The ionization potentials (Ip eV) of different bands in the UPS spectrum of obtained microwave discharged species are 9.326, 9.993, 10.398, 11.031, 11.838 and 12.944 eV, respectively. The peaks which possess respectively 9.326, 9.993, 11.031, 11.838 and 12.994 eV ionization potentials (Ip) are consistent with the UPS spectrum of I, molecule (Kimura, 1982), and also in the shape and relative intensities of the spectrum. The peak which possess 10.398 and 11.031 eV IP are the same with the spectrum of HI molecule (Kimura, 1982) and also in the shape and the relative intensities of the spectrum. The peak which has 11.031 eV Ip should be wider and lower intensity in the spectrum of I, molecule. But this peak in the spectrum obtained by microwave discharge of CH₁I is sharp and high intensity. This is considered as the result of the overlapped peaks of I₂ and HI molecules in 11.01 eV ionization potential. So the obtained spectrum for this peak under the microwave discharge of CH₂I (Fig. 1) should be the complexes spectra of methyl iodide may be deduced as follows:

(1)
$$CH_3I \xrightarrow{MD} CH_3+I$$
, $2I \xrightarrow{} I_2$

(2)
$$CH_3 \xrightarrow{MD} CH_2 + H$$
, $I'+H' \longrightarrow HI$ and $2CH_3 \longrightarrow CH_2CH_3$, $2CH_2 \longrightarrow CH_2 = CH_2$

And the (1) is the principal reaction.

Due to the photoionization cross section of the orbital which reflect the weight of the lone-pair character of iodide atom is large in the lower ionization potentials, the bands which come from the band of 11.99 eV ethane and the bands of 10.51 and 12.85 eV ethylene are not displayed in the spectrum of microwave discharged species of CH₃I. From UPS results of microwave discharged species of CH₃I, it may be imagined that the depletion of ozone in the stratosphere by halogenated methane series compounds is results of atom-molecule reaction between halogen atom and ozone.

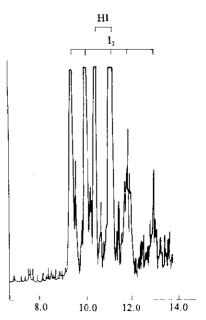


Fig. 1 The UPS of spectrum of microwave discharged species of CH₃I

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