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HeI photoelectron spectroscopic of microwave-discharged species on CF_2Cl_2 systems[1]

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Abstract— HeI (21.22 eV) photoelectron spectrum of microwave-discharged (MD) species of CF_2Cl_2 is reported in this paper. And HeI photoelectron spectra of reaction products between O_2 and the species generated by MD of CF_2Cl_2, between CF_2Cl_2 and the species generated by MD of O_2, and between the products generated by MD of CF_2Cl_2 and O_2 mixed gases are also given. The chlorine atomic species is obtained by the MD method. So the mechanism of ozone depletion in the stratosphere by the freon is conceived.

Keywords: HeI (21.22 eV) photoelectron spectroscopy (UPS); microwave discharge; freon.

1 Introduction

The appearance of "the ozone hole" in the stratosphere leads to a shock not only among scientists, but also among politicans of the world. To protect living-environment of mankind, prevent enlargement of the hole and renovate the depleted hole are some of the most crucial tasks of the entire human race. Among numerous materials which can deplete the ozone layer in the stratosphere and which are excreted by mankind, it is known, freon series compounds are some of the most important ones. Under atmospheric conditions, in chemical and photolysis reactions, production species from freon can result directly in the destruction of the ozone layer. But the reaction channel and mechanism between ozone and freon is not clear (Green, 1976; Chang, 1987; U. S. EPA, RIA, 1987).

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It is well known that HeI (21.22 eV) photoelectron spectroscopy (UPS) not only provides a great deal of information concerning orbital energies, electronic states and bonding characters of the studied molecules, but was also successfully used for the studies of chemical reaction processes. And the microwave discharge (MD) is a good method to generate the transient species which is studied by HeI photoelectron spectroscopy. In order to probe into the destruction of the ozone shell in the atmosphere from the freon series compounds, the HeI P. E. studies of microwave-discharged (MD) species of CF_2Cl_2 is reported in this paper. And the HeI P. E. results of reaction products between O_2 and the species generated by the MD of CF_2Cl_2, between CF_2Cl_2 and the species generated by the MD of O_2 are also given to attempt understanding the nature of ozone shell depletion by the freon.

2 Experimental

CF_2Cl_2 (CFC-12) is obtained from Koyama Aerosol Industry Co. Ltd, Japan, and the purity is 99.95%. O_2 gas is bought from Analytical Instrument Factory in Beijing and the purity is 99.999%.

The HeI photoelectron spectra of the systems under the study are measured on the UPS machine-II which is built specifically to detect transient species as described elsewhere (Wang, 1991; Wang 1992c). The operational resolution for $^2P_{3/2}$ peak of Argon is 20−25 meV. The calibrations of the spectra are performed with the Argon ^2P and methyl iodide ^2E double lines. The 1024 point digitized spectra, time-average for periods of around 40 min are obtained. A single-scan spectrum may also be recorded on the X-Y recorder (Wang, 1992a; Wang, 1992b).

Atom productions are obtained using a 2450 MHz MD-301 microwave generator which is made in Japan.

3 Results and discussion

3.1 HeI photoelectron spectra of microwave discharged species of CF_2Cl_2

HeI photoelectron spectra of CF_2Cl_2 and its microwave discharge, species are given in Fig. 1.

It is known that the chlorine lone-pair electrons of CF_2Cl_2 molecule have $a_1+a_2+b_1+b_2$ symmetries in the C_{2v} point group. According to the ionization potentials, these symmetries correspond with $^2B_2$, $^2B_1$, $^2A_2$, and $^2A_1$ electronic states which appear four narrow bands in low ionization potential region, as shown in Fig. 1, and corresponding ionization potentials are 12.25, 12.59, 13.17 and 13.45 eV,

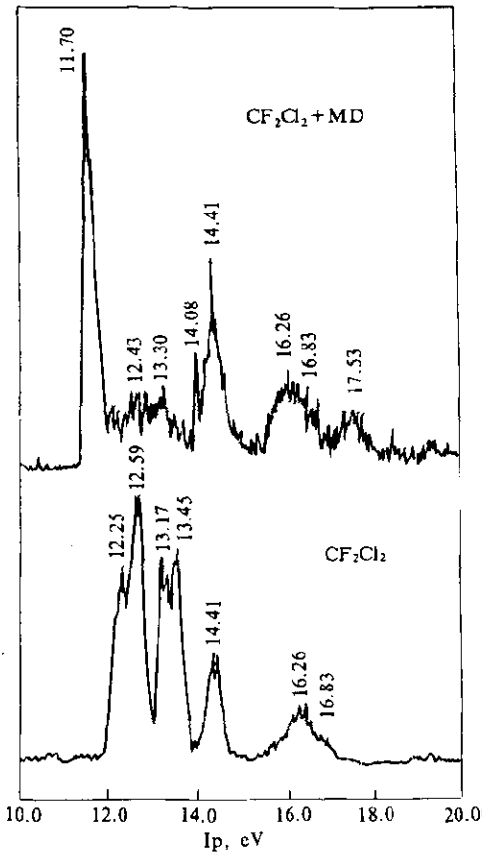

Fig. 1 HeI photoelectron spectra of CF_2Cl_2 and its MD species

respectively. The ionization bands in deeper energy levels locate at 14.38, 16.22 and 16.83 eV, respectively. These results are consistent with the reported results (Cvitas, 1977) for the HeI photoelectron spectrum of CF_2Cl_2.

It is seen clearly from Fig. 1 that after the MD of CF_2Cl_2, the bands which indicate the characters of chlorine lone-pairs electron ionizations in the CF_2Cl_2 molecule are reduced. New and stronger bands appear at 11.70, 14.41 and 16.26 eV, respectively. The HeI photoelectron spectrum of the MD species of CF_2Cl_2 is consistent not only with the HeI spectrum of Cl_2 molecule in the values of ionization potentials, but with the forms of the bands and in the relative intensity also (Potts, 1971). The HeI photoelectron spectrum of the MD species of CF_2Cl appears basically the spectrum of Cl_2 molecule. And the HeI photoelectron spectrum of the remained CF_2Cl_2 also appears in the spectrum of the MD species of CF_2Cl_2, but has lower intensity. So the result which comes from the MD species of CF_2Cl_2 shows that chlorine atom is firstly generated in the MD of CF_2Cl_2, and then the recombination of chlorine atoms forms the Cl_2 molecule. So the HeI P. E. spectrum of Cl_2 molecule appears in the HeI P. E. spectrum of the MD species of CF_2Cl_2. This process is suggested as follows:

(1) $$CF_2Cl_2 \xrightarrow{MD} Cl + CF_2Cl,$$

(2) $$CF_2Cl_2 \xrightarrow{MD} 2Cl + CF_2,$$

(3) $$2\,Cl \longrightarrow Cl_2.$$

3.2 HeI photoelectron spectra of the MD species between CF_2Cl_2 and O_2

HeI P. E. spectra of reaction productions between the MD species of O_2 and CF_2Cl_2, and between the MD species of CF_2Cl_2 and O_2 are given in Fig. 2. From Fig. 2, it is seen that the HeI P. E. spectrum of reaction productions between the MD species of CF_2Cl_2 and O_2 is the same as that of the MD species of CF_2Cl_2 and O_2 equivalent pressure mixed-gases. In fact, high intensive HeI P. E. spectrum of Cl_2 molecule appears in this spectrum. Three bands of Cl_2 molecule locate at 11.70, 14.41 and 16.26 eV of the spectrum, respectively. And the bands which indicate the vibration structures and locate at 12.30 and 18.15 eV appear also in the spectrum. Those are the bands of O_2 molecule. The third and fourth bands for HeI P.E. spectrum of O_2 molecule overlap on the band of Cl_2 molecule which locates at 16.26 eV. So the band displays the vibration fine structure. These results show that the spectrum after the MD of O_2 and CF_2Cl_2 mixed-gases mainly displays the character of the MD species of CF_2Cl_2. So, chlorine atom is mainly the species of the MD. As the above-mentioned, the recombination of chlorine atoms forms the Cl_2 molecule. So the spectrum of Cl_2 molecule emerges also on the spectrum of the MD species of O_2 and CF_2Cl_2 mixed-gases.

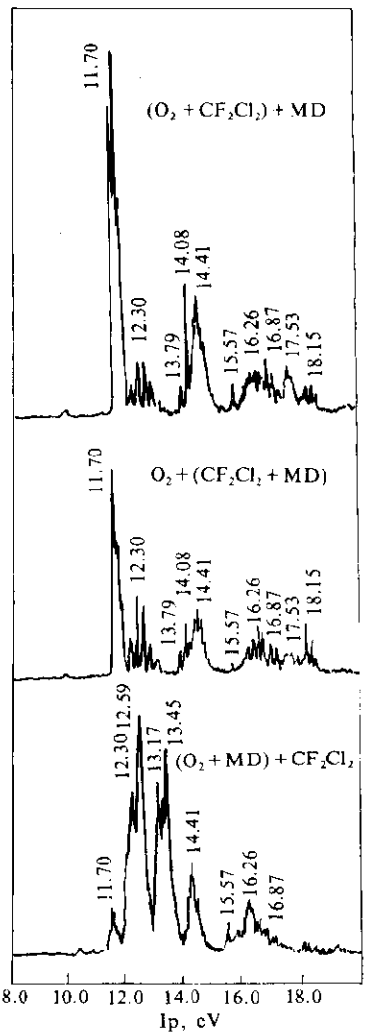

Fig. 2 HeI photoelectron spectra of the MD species on the CF_2Cl_2 and O_2 systems

It is very interesting from both spectra of reaction productions between the MD species of CF_2Cl_2 and O_2, and the MD species of O_2 and CF_2Cl_2 mixed-gases that there are three sharp bands which locate at 13.79, 14.08 and 15.57 eV, respectively. Their assignments will be further inquired.

HeI P. E. spectrum of reaction productions between the MD species of O_2 and CF_2Cl_2 is also shown in Fig. 2. This spectrum displays clearly as the HeI P. E. spectrum of CF_2Cl_2. The low intensive band

which locates at 11.70 eV can be assigned as the spectrum of Cl_2 molecule. This is the result of the MD of small amount CF_2Cl_2 in the inlet system. Here, there is no spectrum of oxygen atom which is generated by the MD of O_2 and the spectrum of O_3 molecule which is formed by the recombination of oxygen atoms.

The very similar UPS experiments are performed on the CF_2Cl_3 (CFC-11) and $CHFCl_2$ gases. HeI P. E. spectrum of Cl_2 molecule is obviously displayed on the spectrum of their MD species. These results not only show that the MD is an efficient method to generate atomic species, but also that the split of chlorine atom from the freon series compounds is easy by using the MD method.

It is clearly seen that these studied results provide a basis for inquiring the mechanism of ozone layer depletion in the atmosphere by freon series compounds.

References

Chang JS, Kautman P. J Chem Phys, 1977; 66:4980
Cvitas T, Gusten H, Klasinc L. J Chem Phys, 1977; 67:2687
Green RE, Wayen RP. Journal of Photochemistry, 1976; 6:375
Potts AW, Price WxC. Trans Faraday Soc, 1971; 67:1242
U. S. EPA. R1A. 1987
Wang Dianxun, Wang Tong, Zhao Hengqi. J of Chemical Physics (China), 1992a; 8:809
Wang Dianxun, Wang Tong, Zhao Hengqi. J Phys Chem (China), 1992b; 5:467
Wang Dianxun, Xu Guangzhi. Huaxue Tongbao, 1992c; 10:11
Wang Dianxun, Zhao Hengqi, Xu Guangzhi. J Analytical Instru (China), 1991; 4:23

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