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Study on the atmospheric photochemical reaction of CF_3 radicals using ultraviolet photoelectron and photoionization mass spectrometer

YAO Li[1,2], DU Lin[1,2], YIN Shi[1,2] & GE MaoFa[1†]

[1] Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory for Structural Chemistry of Unstable and Stable Species, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China;
[2] Graduate University of Chinese Academy of Sciences, Beijing 100080, China

A study of the atmospheric photochemical reaction of CF_3 radical with CO and O_2 was performed by using a homemade ultraviolet photoelectron spectrometer-photoionization mass spectrometer (PES-PIMS). The electronic structures and mechanism of ionization and dissociation of $CF_3OC(O)OOC(O)OCF_3$ were investigated. It was indicated that the two bands on the photoelectron spectrum of $CF_3OC(O)OOC(O)OCF_3$ are the result of ionization of an electron from a lone pair of oxygen and a fluorine lone pair of CF_3 group. The outermost electrons reside in the oxygen lone pair. The experimental and theoretical first vertical ionization energy is 13.21 and 13.178 eV, respectively, with the PES and OVGF method. They are in good agreement. The photo ionization and dissociation processes were discussed with the help of theoretical calculations and PES-PIMS experiment. After ionization, the parent ions prefer the dissociation of the C—O bond and giving the fragments CF_3OCO^+ and CF_3^+. It demonstrated that the ultraviolet photoelectron and photoionization mass spectrometer could be applied widely in the study of atmospheric photochemical reaction.

photochemical reaction, CF_3 radical, ultraviolet photoelectron and photoionization mass spectroscopy, transient species

It is now well established that the chlorofluorocarbons (CFCs) are responsible for the catalytic destruction of the ozone in the atmosphere and global warming[1]. As substitutes for one class of these stable compounds, various hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are presently being considered. Their degradation takes place in the troposphere through a series of photochemical reactions[2]. At present, it is important to study the mechanism, intermediate, and products in the process of the degradation of HCFCs and HFCs[3,4]. Ultraviolet photoelectron spectroscopy (UPS) is an important method to study gaseous transient species[5,6]. To improve our ability on studying transient species, our group has built up a photoelectron spectrometer-photoionization mass spectrometer (PES-PIMS)[7]. The modification of the spectrometer was based on the HeI photoelectron spectrometer. Using this new apparatus, we can not only obtain a direct measure of electronic structure and energy levels of stable and unstable molecules, but also provide the information on the complicated process of reaction, ionization, and dissociation[8,9].

In this work, we combined a newly-made on-line photochemical reactions apparatus to our homemade PES-PIMS, and studied the application of this new apparatus in the study on the photochemical reactions of CF_3 radicals with CO and O_2. With the help of quantum chemical calculation, we investigated the electronic

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†Corresponding author (email: gemaofa@iccas.ac.cn)

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structure and mechanism of ionization and dissociation on the important transient species $CF_3OC(O)OOC(O)OCF_3$. The results indicate the potential applications of the new apparatus and method in the study of atmospheric photochemical reactions.

1 Experimental

1.1 Reagent

$(CF_3CO)_2O$: Aldrich chemical Co. Inc.; CO (>99.99%), O_2 (>99.99%): Beijing AP Beifen Gases Industry Co., Ltd. As CF_3 radical source, perfluoroacetic anhydride was chosen, because its absorption cross section at the emission line of the mercury lamp at 254 nm is quite high[10].

1.2 Experimental apparatus and process

The schematic diagram of the PES-PIMS for the atmospheric photochemical study of transient species is shown in Figure 1. The homemade photochemical reaction apparatus consists of the vacuum system, sample system, and photoreaction system connected to the PES-PIMS through three U-traps. The processes of photoreaction and purification of products follow related references[10,11].

The photoreactor consisted of a 15 W low-pressure mercury lamp surrounded by quartz tubes, which were placed in the middle of a 5 L glass round-bottom flask. The outside of the flask was cooled to about 0℃ and connected to the vacuum line equipped with capacitance pressure gauges. After evacuation of the photoreactor, the inner surface was conditioned with $(CF_3CO)_2O$ vapor for 2 h to remove residual water from the surface. In a typical experiment, the bulb was charged with partial pressures of 3 mbar $(CF_3CO)_2O$ (0.6 mmol), 10 mbar CO (2 mmol), and 20 mbar O_2 (4 mmol). The photolysis was performed at 0℃ for 6 h, and every hour about 2 mmol of additional CO was introduced into the photoreactor. After finishing the photolysis, the product was studied by the PES-PIMS through trap-to-trap condensation.

The PES-PIMS consists of two parts: one part is the double-chamber UPS-II machine, and the other is a time-of-flight mass spectrometer. The photoelectron spectrum was recorded on the double-chamber UPS-II machine which was built specifically to detect transient species at a resolution of about 30 meV as indicated by the $Ar^+(^2P_{2/3})$ photoelectron band[12]. Experimental vertical ionization energies were calibrated by the simultaneous addition of a small amount of argon and methyl iodide to the sample. Mass analysis of ions was achieved

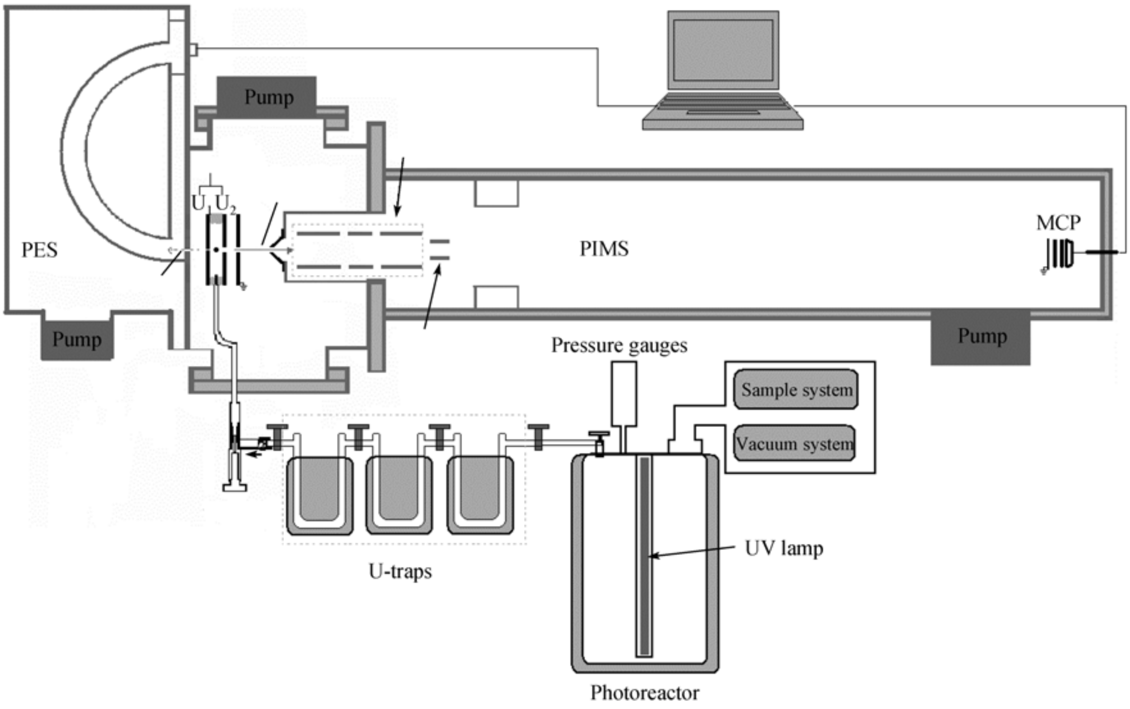

Figure 1 Schematic diagram of the PES-PIMS apparatus designed for the atmospheric photochemical study of transient species.

with the time-of-flight mass analyzer mounted directly to the photoionization point. Due to the relatively soft ionization provided by single-wavelength HeI radiation, the PIMS could provide strong parent ions. The fragments could provide the information on the molecular structure and dissociation.

1.3 Calculation

Because the values and the order of the molecular orbital (MO) energies depend on the molecular geometry, the geometries of the neutral ground state and lowest-lying cationic state of parent molecule and fragments were optimized using density functional theory (B3LYP) at the 6-31G basis sets level. To assign the PE spectrum, the outer-valence Green's function (OVGF) calculations[13], which include sophisticated correlation effects of the self-energy, were applied to the molecules to give accurate results of the vertical ionization energies. All calculations were carried out using the Gaussian series of programs[14].

2 Results and discussion

The atmospheric degradation of HFCs leads in the first instance mainly to $FC(O)O_x$ and CF_3O_x ($x = 1,2$) radicals, which may interact with atmospheric trace gases in different ways. The reaction with NO_2 in which peroxynitrates are formed is important in this regard. The peroxynitrates $FC(O)OONO_2$[15], CF_3OONO_2[16], and $CF_3C(O)OONO_2$[17], which are all fully characterized, may serve as reservoir molecules for either peroxy or NO_2 radicals. Peroxy radicals are also effective catalysts for the CO oxidation. In particular the catalytic cycle of CO oxidation by CF_3O_x ($x = 1,2$) radicals has been investigated in several laboratories[18－20]. The reactive intermediates bis(trifluoromethyl)peroxy dicarbonate, $CF_3OC(O)OOC(O)OCF_3$ have been studied by NMR, vibration, and UV spectroscopy[10]. Recently, the geometry structure[11] (Figure 2) and pyrolysis[21] have also been reported. By using a homemade ultraviolet photoelectron spectrometer-photoionization mass spectrometer (PES-PIMS), we investigated the photochemical reaction of CF_3 radicals with CO and O_2. The electronic structures and mechanism of ionization and dissociation for the product collected at −60℃, $CF_3OC(O)OOC(O)OCF_3$, were studied.

2.1 Photoionization mass spectrum

The PIMS results of the reactant $(CF_3CO)_2O$ and the product $CF_3OC(O)OOC(O)OCF_3$ collected at −60℃ by the traps are shown in Figure 3.

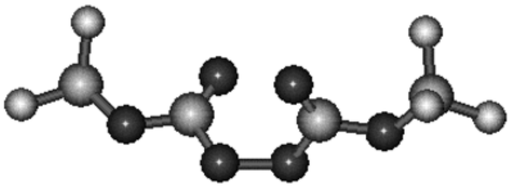

Figure 2 Structure of $CF_3OC(O)OOC(O)OCF_3$.

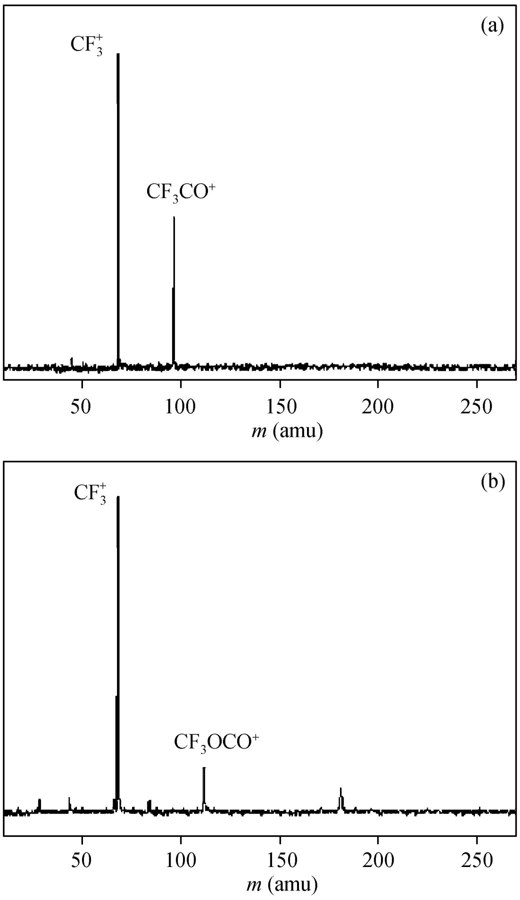

Figure 3 HeI photoionization mass spectra of the reactant $(CF_3CO)_2O$ (a) and the product $CF_3OC(O)OOC(O)OCF_3$ (b).

As shown in Figure 3(a), the reactant $(CF_3CO)_2O$ dissociates directly into fragments CF_3^+ and CF_3CO^+ after one-electron ionization by the radiation of ultraviolet. It is in agreement with the result of EI source[22]. However, the fragment CF_3CO^+ disappears in the PIMS of the product. This indicates that the photolysis of the reactant $(CF_3CO)_2O$ takes place completely in the condition of our experiment. The spectrum of $CF_3OC(O)OOC(O)OCF_3$ shows two peaks: CF_3^+ and CF_3OCO^+, with the dominant features being the CF_3^+ peaks.

In order to understand the mechanism of ionization and dissociation of $CF_3OC(O)OOC(O)OCF_3$, the geometries of parent molecule and fragments were optimized using density functional theory. The energetics of the dissociation of the parent ion into possible fragments was calculated. From Figure 4, we can see that the energy for the dissociation of parent molecule into the radical $CF_3OC(O)O$ (0.87 eV) is much lower than that of heterolysis to form the radical $CF_3OC(O)$ (3.07 eV). However, under the radiation of HeI light, the parent ion generated by the one-electron ionization prefers the heterolysis (0.43 eV) and dissociation of the C—O bond to form $CF_3OC(O)^+$. Therefore, there are no signals of the parent ion and $CF_3OC(O)O^+$. Furthermore, the weak CF_3^+ signal can be formed by the subsequent dissociation of $CF_3OC(O)^+$, as well as by direct dissociation of the parent ion.

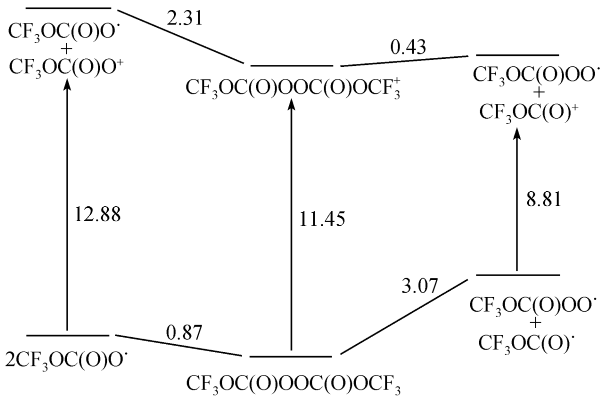

Figure 4 Schematic energy profile showing ionization and dissociation pathways of $CF_3OC(O)OOC(O)OCF_3$ (in eV).

2.2 Photoelectron spectrum

The HeI photoelectron spectra of the reactant $(CF_3CO)_2O$ and the product $CF_3OC(O)OOC(O)OCF_3$ are presented in Figure 5.

From Figure 5(a), we can see that there are three bands in the low ionization region below 14.0 eV, and a broad band in the high ionization region. The first vertical ionization is 12.21 eV. Table 1 lists the PES experimental vertical ionization energies, the theoretical vertical ionization energies, the molecular orbital (MO) symmetries, and the characteristics of the outer valence shells for $(CF_3CO)_2O$ from the OVGF calculations. The analysis of orbital characteristics shows that the three highest molecular orbitals are characterized by the oxygen lone pair.

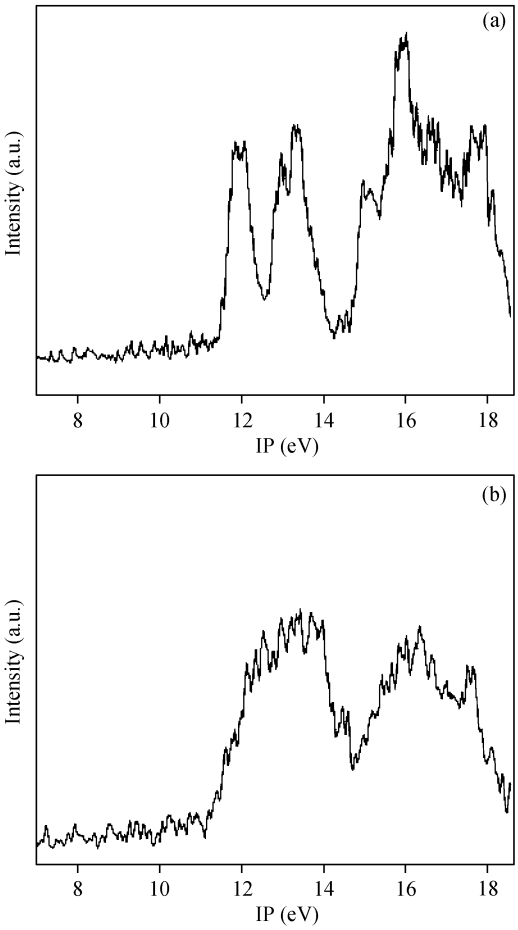

Figure 5 HeI photoelectron spectra of the reactant $(CF_3CO)_2O$ (a) and the product $CF_3OC(O)OOC(O)OCF_3$ (b).

Table 1 Experimental and calculated vertical ionization potentials and molecular characteristics for $(CF_3CO)_2O$

Exptl. I_V (eV)	Calcd. $-\varepsilon$ (eV)	MO	Character
12.21	12.596	25*b* (51)	n_O
13.02	13.450	26*a* (50)	n_O
13.41	14.011	24*b* (49)	n_O
15.05	15.908	25*a* (48)	π_{CO}
15.79	16.034	23*b* (47)	σ_{CC}
	16.101	24*a* (46)	π_{CO}

Compared with the spectrum of the reactant, the spectrum of the product shows remarkable change with two broad bands (Figure 5(b)): one is centered at 13.21 eV with an ionization onset of 11.23 eV; the other is located at 16.35 eV with an ionization onset of 14.73 eV. Table 2 lists the experimental and theoretical vertical ionization energies. Some theoretical vertical ionization energies from different orbitals are very close, which could cause the overlapping of bands corresponding to different orbitals. The first calculated adiabatic ionization energy, by taking the difference between the energy of the neutral and the ion, is 11.45 eV, in agreement with the experimental result. According to C_2 symmetry, the molecular orbital of the valence shell would be in the following order of increasing energy: $\sim 27b^2 28a^2 29a^2 28b^2 30a^2 29b^2 31a^2 30b^2 32a^2 31b^2$. Combined with DFT theoretical analysis, we designate that the first band of $CF_3OC(O)OOC(O)OCF_3$ is the overlapped results of removal of the electron from the 30*a*, 29*b*, 31*a*, 30*b*, 32*a*, and 31*b* orbitals. All the six highest molecular orbitals are characterized by the oxygen lone pair (see Table 2). The second band with an ionization onset of 14.73 eV and the weak band at 17.61 eV correspond to the ionization of electron of the fluorine lone pair. The character of molecular orbitals of valence shell is shown in Figure 6.

Table 2 Experimental and calculated vertical ionization potentials and molecular characteristics for $CF_3OC(O)OOC(O)OCF_3$

Exptl. I_V (eV)	Calcd.		
	$-\varepsilon$ (eV)	MO	character
13.21	13.178	31*b* (63)	$n_{O\,(C=O)}$
	13.323	32*a* (62)	$n_{O\,(C=O)}$
	13.800	30*b* (61)	$n_{O\,(C=O,O-O)}$
	14.038	31*a* (60)	$n_{O\,(C=O,O-O)}$
	14.311	29*b* (59)	$n_{O\,(C-O,O-O)}$
	14.354	30*a* (58)	$n_{O\,(C-O)}$
16.35	15.831	28*b* (57)	n_F
	16.123	29*a* (56)	n_F
	16.147	28*a* (55)	n_F
	16.301	27*b* (54)	n_F
	16.302	27*a* (53)	n_F
	16.691	26*b* (52)	n_F
	16.713	26*a* (51)	n_F
	16.775	25*b* (50)	n_F
	16.797	25*a* (49)	n_F, σ_{O-O}
17.61	17.351	24*b* (48)	n_F
	17.516	24*a* (47)	n_F
	17.586	23*b* (46)	n_F
	17.634	23*a* (45)	n_F
	17.721	22*b* (44)	n_F

3 Conclusion

The atmospheric photochemical reaction of CF_3 radical with CO and O_2 was investigated by the homemade PES-PIMS with the new on-line photochemical apparatus. The electronic structure and mechanism of ionization and dissociation of the product $CF_3OC(O)OOC(O)OCF_3$ were studied. With the help of theoretical calculation, the two bands on the PES of $CF_3OC(O)OOC(O)OCF_3$ were assigned to be the ionization of an electron from a lone pair of oxygen and a fluorine lone pair of CF_3 group, respectively. The experimental and theoretical first vertical ionization energies are in good agreement. With the spectroscopic and theoretical investigations, it is indicated that $CF_3OC(O)OOC(O)OCF_3$ prefers dissociation of C—O bond after one-electron ionization by the HeI radiation to form the fragment CF_3^+ and CF_3OCO^+. This fact proves that our homemade PES- PIMS can be used as a powerful tool for the investigation of transient species in the atmospheric photochemical reaction.

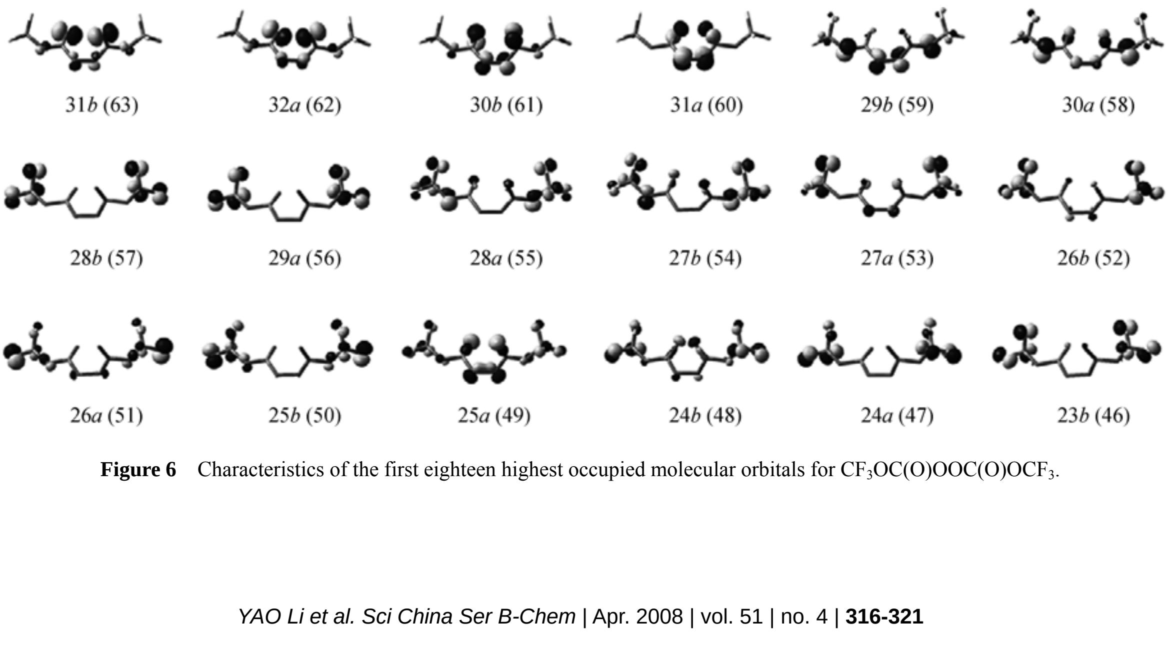

Figure 6 Characteristics of the first eighteen highest occupied molecular orbitals for $CF_3OC(O)OOC(O)OCF_3$.

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