

PHOTOELECTRON SPECTROSCOPY OF TRANSIENT / SHORT LIVED SPECIES



Arunava Maity (CY09C003)

Indranath Chakraborty (CY09C016)

Smrajit Pal (CY09C034)

Subrata Mondal (CY09C037)

Tufan Ghosh (CY09C039)

1. Introduction

Ultraviolet photoelectron spectroscopy, since its inception in the early sixties, has demonstrated fully its utility for determination of the electronic structure of a wide range of stable molecules, both inorganic and organic. Detailed analysis of photo electron spectra can provide information on bonding and in combination with quantum mechanical calculation can substantiate the molecular orbital picture of the molecule.

In its maturity, the method has developed into an excellent technique for following the course of the chemical reactions, especially those designed for the generation of transient intermediate. The most striking properties of transient species are short lived, unstable, reactive and even explosive at ambient temperature. The range of transient molecules can extend from very short lifetime (fraction of seconds) radicals, e.g CH₃, HCO through semistable molecules with lifetime of minutes in the gas phase at low pressure, e.g FCP, Cl₂CCO.

These transient species produced by for example , pyrolysis, discharge, atom – molecule, molecule – molecule, molecule – solid reactions are often new and frequently interesting. They play an important role in atmospheric, combustion and biological processes. Studies on these species can provide the impetus for investigating new synthetic procedure, synthesis of new classes of compounds, can provide a rich testing ground for the whole gamut of quantum mechanical methods and can lead to other higher resolution spectroscopic methods.

The knowledge on these transient species are limited and special techniques are needed for their preparation, isolation and subsequent characterization. In order to measure photo electron spectra of transient molecules they must be prepared in sufficient concentration preferably in the absence or low concentration of other compounds to diminish the problem of overlapping bands.

So the characterization of these molecules is difficult enough and require complex and sophisticated instrumentation. The most frequently used technique is low-temperature reaction or pyrolysis combined with cryogenic matrix-spectroscopy (IR, Raman, UV), with which series of important radicals (CF₃OOO, SF₅O_x (x= 0 – 3), phenyl radical C₆H₅, etc.), and metastable compounds (ON-N₃ , OCN-NCO, (CH₃)₂Ge=CH₂ etc.) have been experimentally identified for the first time. Besides, flash laser photolysis (FLP) is also widely used to produce radicals in both ground and excited states.

As already told before, recently great achievements have been made on the generation and characterization of novel transient species based on HeI photo electron spectroscopy. Here we discuss some studies where photo electron spectroscopy have seen to be very powerful technique for the generation and characterization of transient species. Sometime a mass spectrometer is combined with the photo electron spectrometer making the whole instrumentation more efficient to study the transient molecules.

2. Application

In the application part we are try to discuss how photoelectron spectroscopy takes an efficient role to characterized transient species. Here we have taken three examples of which one is older application another two are recent i.e. to compare how recent development has been done on photo electron spectrometer to use it in characterization of transient species

2.1 Photoelectron spectroscopy of SF₂ molecule in gas phase :

SF₂ molecules are generated by reaction between fluorine atoms and flowers of sulphur. The reason for the instability of SF₂ is kinetic rather than electronic. Its instability is caused by the relative stability of SF₄ and the various polymeric forms of sulphur into which SF₂ rapidly disproportionate. In this study the valence ionization energies of SF₂ are determined by He (I) photoelectron (PE) spectroscopy and compared with the PE data of SCl₂, OCl₂, and OF₂.

2.1.1 Experimental section:

He (I) PE spectra of SF₂ were measured on a Vacuum generators Esca 3 spectrometer equipped with a hemispherical electrostatic analyzer, and resolution power of spectrometer was typically 45 meV. The inlet system of the spectrometer was modified to obtain high concentration of fluorine atoms in the ionization chamber [1]. The fluorine atoms can be produced by a microwave discharge in CF₄ or SF₆ in an alumina flow tube, with helium used as diluents. To reduce the wall reactions of fluorine and SF₂ molecules the inlet system of the spectrometer was coated internally with vacuum generators leak sealing compound.

2.1.2 Results and discussion:

Here they give various experimental evidences for the existence of SF₂ transient molecule.

- (1) If the products of a discharge in SF₆ are directly fed into the ionization chamber, only signals due to fluorine atoms, SF₆, and SF₄ [2] are detected.
- (2) If the mixtures of CF₄ or SF₆ with sulphur containing compounds like CS₂, OCS, or SO₂ are passed through microwave discharge again bands for SF₂ are detected.
- (3) Reaction between fluorine atoms and OCS generate SF₂. This reaction has been used to study the very short lived SF radical with mass spectroscopy [3]. The decrease in SF concentration indicates the formation of SF₂.

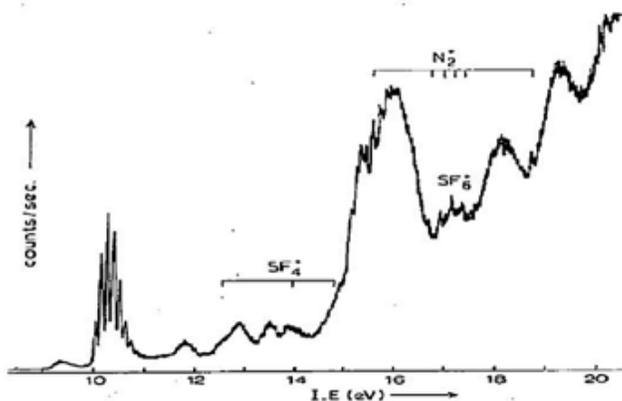


- (4) In this experiment the bond found clearly do not belong to the S₂F₂ isomers, the PE spectra of which are well documented [4].

So, this cumulative experimental evidence strongly supports the existence of the unknown spectrum to the transient species SF₂.

2.1.3 Photoelectron spectrum of SF₂:

The PE spectrum of SF₂, shown in fig. 1, and it is calibrated against the known ionization energies of molecular nitrogen.



2.1.4 Conclusion

The corresponding photoelectron spectral data shows a direct agreement with quantum mechanical calculation by HFS method. Although these calculations indicating the d-orbital participation in the MO's of SF₂ is only about 1 percent. Except the first one, all other valence ionization energies are shifted to higher energies by about 0.5 eV, which improving the agreement with experimental spectrum. From which we can conclude that PES is an useful tool for short lived species like SF₂.

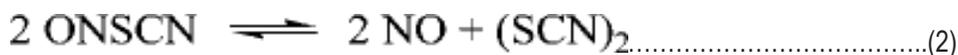
2.2 Experimental observation of gas-phase nitrosyl thiocyanate :

The unstable nitrosyl thiocyanate molecule has been generated in the gas phase for the first time from an in situ heterogeneous reaction at low temperature. The product was detected and characterized by a photoelectron spectrometer photo ionization mass-spectrometer (PES-PIMS). The electronic and geometric structures of the molecule were investigated with the help of quantum chemical calculations. The joint spectroscopic and theoretical studies provided evidence for the formation of nitrosyl thiocyanate, and indicated that the molecule adopts an open-chain, bent structure with the NO and SCN groups bonding by a relatively strong interaction.

2.2.1 Basic characteristics of reactant:

The thiocyanate group, SCN, is ambidentate and has the potential to bond through sulfur or nitrogen forming RSCN or RNCS type molecules. It forms during detoxification of cyanide and normally occurs in blood at a concentration less than 2 mg per 100 mL.[5] Given the biochemical significance of NO/NO⁺, nitrosyl thiocyanate, ONSCN, is a species of potential biochemical interest. The highly unstable ONSCN is blood-red compound, which is formed by mixing a very acidic solution of sodium nitrite with a solution of potassium thiocyanate. At room temperature ONSCN decomposes into NO and (SCN)₂ which is shown by the following reactions.





The structure of ONSCN is unknown since it is very unstable at high concentration and room temperature. Westwood et al. pointed out that potential media for generating and investigating the dilute gas-phase or an inert low-temperature matrix, which would provide important information on its full electronic and geometric characterization. The calculated results predicted that has planar, bent structures and that isomer ON–SCN (**1a**) is more stable than ON–NCS (**1b**),[6–8] in agreement with the notion that S–nitrosation is more favorable through a soft-soft interaction, characterized by a large charge transfer from the nucleophile to the electrophile.

In this work they report the first gas phase generation and characterization of the unstable molecule **1** and its investigation by HeI photoelectron spectroscopy–photo ionization mass spectroscopy and quantum chemical calculation.

2.2.2 Results and discussion:

The thiocyanate and isothiocyanate exist for the CH₃ derivatives, they have performed an identical calculation for the molecules **1a** and **1b**. By a *ab initio* calculations [6–8], it shown that both **1a** and **1b** both have planar, bent structure. Each molecule has, in principle, two rotational isomers, the *cis* and *trans* isomers.

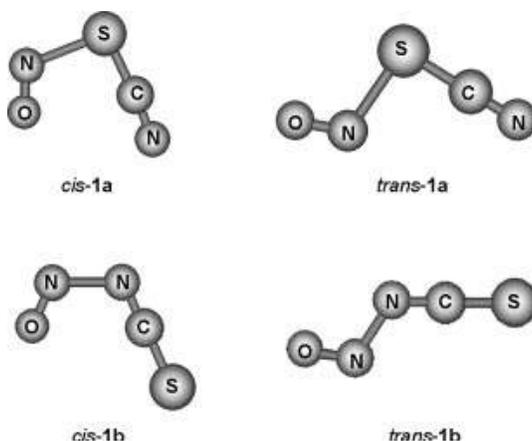


Figure 4. Stable conformers of nitrosyl thiocyanate.

By doing different calculations they predicted that **1a** to be the more stable in the gas phase. the more stable *cis-1a* isomer gives a total energy less than that of *cis-1b* by 11.2 kcalmol⁻¹.

In several molecules containing triatomic pseudohalide groups e.g. -SCN, -NCO, -NNN, etc., it has been established that the atoms are not colinear. When combining the SCN ligand with NO, the SCN angle shows a deviation of about 5° from linearity, which is similar to those of XSCN (X = CN[9], SCN[10], Cl[11], Br[8]). Comparing the predicted NO bond with experimentally determined bond lengths of similar molecules, we find that the predicted O–N bond of **1** (1.136–1.154 Å) lies between the diatomic NO (1.151 Å)[13] and CINO (1.139 Å), favoring CINO slightly.

2.2.3 Photo ionization mass spectroscopy:

He I photo ionization mass spectrum (Figure 5) observed at –60 °C is relatively simple. The main peaks in the spectrum are NO⁺, SCN⁺, ON–SCN⁺, and Cl⁺, respectively, with the dominant feature being the NO⁺ peak. Since there are no NO, SCN, and Cl photoelectron peaks in the PE spectrum (Figure 5), it is suggested that the signals of NO⁺, SCN⁺, and Cl⁺ come from the dissociation of parent ions. For some molecules, He I photo ionization produces a fragmentation ion distribution similar to that of electron impact ionization. This may be rationalized by a similar energy deposition mechanism for the two methods, as the interaction energies (some tens of eV) are comparable. The dominant fragment ions NO⁺ and X⁺ (X = SCN) in the He I photo ionization mass spectra are analogous to those of other ONX molecules (X = Cl, CH₃) in

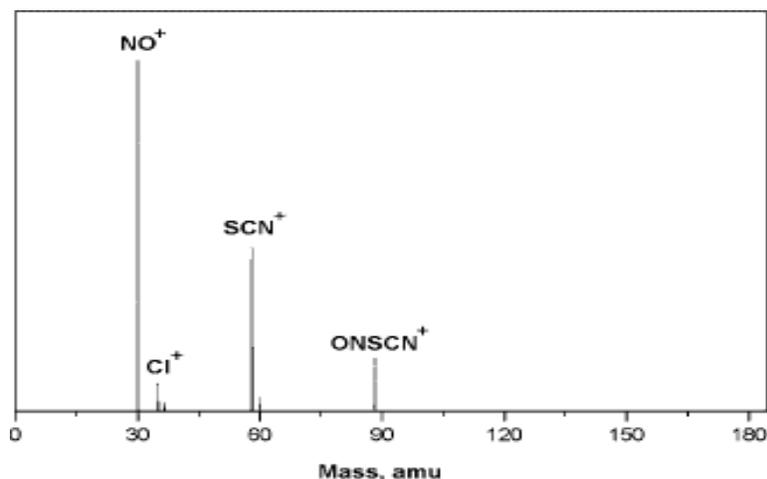


Figure 5. The HeI photoionization mass spectrum of nitrosyl thiocyanate

the electron impact spectra. They mostly result from the direct dissociation of the parent ions ONX+. Although there is no parent ion peak for CINO in the photo ionization mass spectra of the products, the PE bands of the CINO molecule appear in the photoelectron spectrum (Figure 6).

This indicates that the signals of Cl+ and a part of NO+ originate from the dissociation of CINO+, which is very unstable and dissociates to Cl+/NO or NO+/Cl once it is formed. This also agrees with the electron impact mass spectrum of CINO, which also shows no CINO+ peak. In a word, we demonstrated that we generated **1** under our experimental conditions though we could not distinguish.

2.2.4 Photoelectron Spectrum:

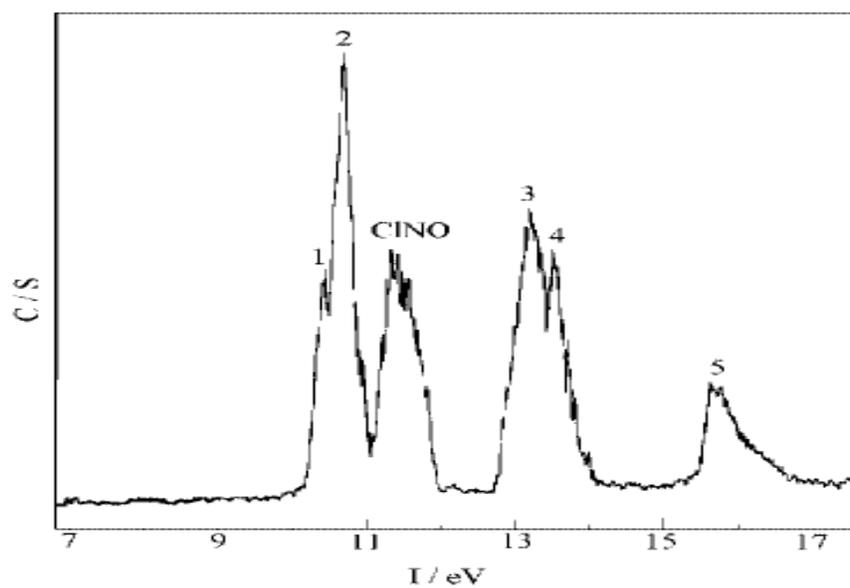


Figure 6. The He I photoelectron spectrum of nitrosyl thiocyanate

This is a He I photoelectron spectrum of compound (**1**) which was taken at -60 °C shown in figure 6. This is not showing any decomposition but only the reactant CINO with an unnumbered band between 11.0 and 12.0 eV. This PE spectrum a group of distinct bands below 11 eV, another group in the 12.5–14 eV range, and one additional band above 15 eV. In previous photoelectron spectroscopy experiments, XSCN (X = Cl, Br), instead of XNCS, was produced by passing gaseous halogen over solid AgSCN. This PES also agree with the ROVGF and CBS-QB3 calculations on **1a** than those on **1b**. There is no noticeable difference between the orbital energies of the two most stable conformers of two most stable conformers of cis- and trans-**1a**. So this discussion is reduced to the analysis of the slightly more stable conformer *cis*-**1a** only. The unstable nitrosyl thiocyanate (**1**) can be characterized by its three

groups of bands, which can be attributed to the lone electron pair of sulfur, the π system, and the S–C bond. The electronic structure of the SCN group can be explained in two ways. One can assume a single S–C bond and a triple C–N bond. In this case the appearance of two new bands resulting from the C–N π bonds is expected in the low energy region of the spectrum. Another interpretation is that the SCN unit is considered as a two perpendicular four-electron three-centre π system, which suggests four new band in the spectrum. The shape and intensity of the first group of bands suggest that it should be attributed to two ionization processes. The vertical ionization potential of the first band (10.45 eV) is in good agreement with the calculated ionization energy of cis-1a. The second band at 10.65 eV is sharp and characteristic of a nonbonding orbital with considerable lone-pair characteristic. The two bands between 12.5–14.0 eV come from the ionization of the two bonding π orbital's.

2.2.5 Experimental Section:

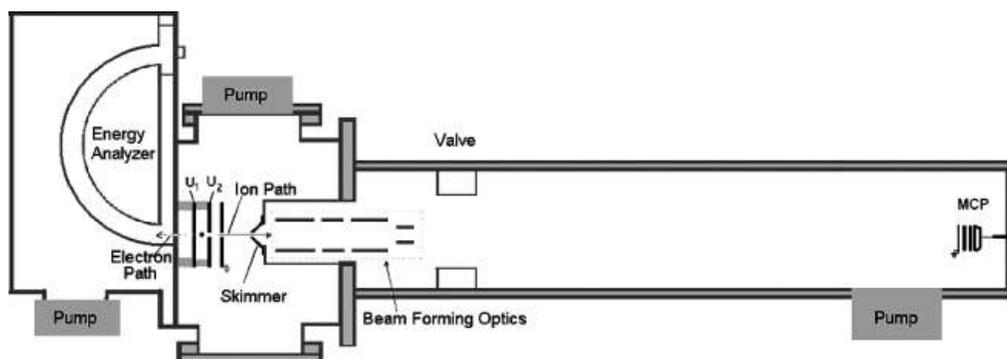


Figure 7. Schematic diagram of the experimental apparatus PES-PIMS. It mainly consists of an ultraviolet photoelectron spectrometer and a home-made time-of-flight mass spectrometer (TOFMS). The photo source (HeI) in the ionization region is marked with a dot.

Using photoelectron spectroscopy and infrared matrix isolation spectroscopy, Dyke et al. studied the thermal decomposition of organic azides[13]. By combining HeI photoelectron spectroscopy with mid-infrared absorption and mass spectroscopy Westwood and colleagues investigated ground, excited and ionic states of various small unstable molecules. The intermediate was generated at $-60\text{ }^{\circ}\text{C}$ by passing gaseous ClNO over finely powdered AgSCN, similarly for producing other unstable species like ONNCO and NSSCN. The reaction was monitored simultaneously in situ by photoelectron and photo ionization mass spectra. The reaction is be represented by Equation (3).



AgSCN (ACROS) was dried in vacuo (10–4Torr) for 2 h at 60 °C before the experiment was performed. ClNO was prepared as reported [8] and identified by photoelectron[10] and photo ionization mass spectroscopy.

2.2.6 Conclusion

From the above result it can be concluded that nitrosyl thiocyanate can be generated in situ by reacting gaseous nitrosyl chloride with silver thiocyanate at low temperature. By using PES-PIMS they are able to determine electronic and geometric structure of above transient molecule which is consistent with the ROVGF and CBS-QB3 calculation. Which suggest that molecule adopts an open chain, bent structure. It is indicated that NO and SCN moieties bond by means of a relatively strong interaction and that is related to the inversion of the first two pi orbitals. The whole statement proves that PES-PIMS can be used as a powerful tool for the investigation of transient species in gas phase.

2.3 Study on the atmospheric photochemical reaction of CF₃ radicals using ultraviolet photoelectron and photoionization mass spectrometer^[14]

This an example where they studied atmospheric photochemical reaction of CF₃ radical with CO and O₂ using a homemade ultraviolet photoelectron spectrometer-photo ionization mass spectrometer (PES-PIMS). They investigated the electronic structure as well as the mechanism of ionization and dissociation of CF₃OC(O)OOC(O)OCF₃. They indicated in the photoelectron spectrum of CF₃OC(O)OOC(O)OCF₃ is having two bands which are result of ionization of an electron from a lone pair of oxygen and a fluorine lone pair of CF₃ group. The experimental and theoretical first vertical ionization energy is 13.21 and 13.178 eV, respectively with PES and OVGf method, so they are in good agreement. Here we will discuss only photoelectron spectroscopy as far as we are considering our topic.

Now, before going to discussion about the above topic we need to know why the photochemical reaction of CF₃ radical is important? As we all know that the chlorofluorocarbons (CFCs) are responsible for the catalytic destruction of the ozone in the atmosphere and global warming^[15]. 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^[16]. So it is very important to study the mechanism, intermediate, and products in the process of the degradation of HCFCs and HFCs^[17,18]. Ultraviolet photoelectron spectroscopy (UPS) is an important method to study gaseous transient species^[19,20].

2.3.1 Experimental apparatus and process:

For the study of these kind of transient species they has built a special instrument by combining a newly-made on-line photochemical reactions apparatus to their homemade PES-PIMS. The schematic diagram of the PES-PIMS for the atmospheric photochemical study of transient species is shown in Figure 7. 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 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°C 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°C 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.

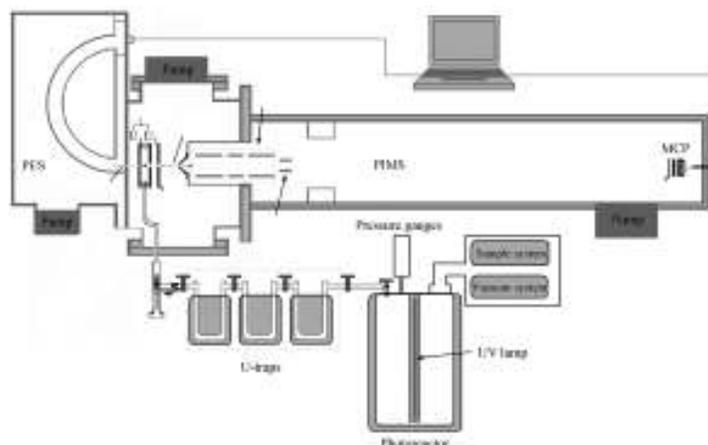


Figure 8. Schematic diagram of the PES-PIMS apparatus designed for the atmospheric photochemical study of transient species

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 $\text{Ar}+(2\text{P}2/3)$ photoelectron band^[21]. 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 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.

2.3.2 Photoelectron spectrum:

The HeI photoelectron spectra of the reactant $(\text{CF}_3\text{CO})_2\text{O}$ and the product $\text{CF}_3\text{OC}(\text{O})\text{OOC}(\text{O})\text{OCF}_3$ are shown in the Figure 7.

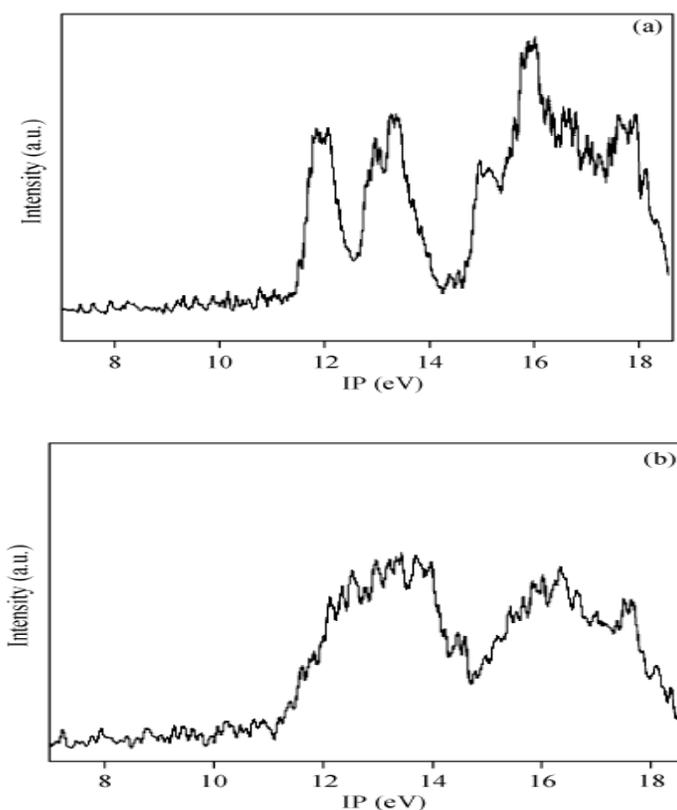


Figure 9: Hel photoelectron spectra of (a) the reactant $(\text{CF}_3\text{CO})_2\text{O}$ and (b) product $\text{CF}_3\text{OC}(\text{O})\text{OOC}(\text{O})\text{OCF}_3$.

2.3.3 Result and discussion

From the Figure 8(a), we can see there are two bands in the lower ionization region below 14.0 eV and a broad band in the higher ionization region. The first vertical ionization energy is 12.21 eV. Table 1 lists the PES experimental vertical ionization energies, the theoretical vertical ionization energies, the molecular orbital symmetries, and the characteristics of the outer valence for $(CF_3CO)_2O$ from the OVGf calculations.

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

Table1. Experimental and calculated vertical ionization energies and characteristics for $(CF_3CO)_2O$

From the analysis of the orbital characteristics we can say that the three highest molecular orbitals can be characterized by the oxygen lone pair (n_O).

On the other hand we can see remarkable changes in the photoelectron spectra of the product while compared to the reactant. From the Figure 8(b) we can see that there are two broad bands: one is centered at 13.21 eV with an ionization onset of 11.23 eV; the other one is centered at 16.35 eV with an ionization onset of 14.73 eV. Table 2 lists the values of the experimental and the theoretical calculated ionization energies. From the Table 2 we can see that some of the theoretical vertical ionization energies from different orbitals are very close, which results the overlapping of bands corresponding to different orbitals. The calculated first ionization energy is 11.45 eV, which has a good agreement with experimental value. They combined the DFT calculation with the MO calculation and then came to conclude that the all the six highest molecular orbitals are characterized by the oxygen lone pair (n_O). The second band with an ionization onset of 14.73 eV and the weak band at 17.61 eV corresponds to the ionization of electron of the fluorine lone pair. The following Figure 9 shows the character of molecular orbitals of valence shell.

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

Table 2: Experimental and calculated vertical ionization energies and characteristics for $\text{CF}_3\text{OC}(\text{O})\text{OOC}(\text{O})\text{OCF}_3$

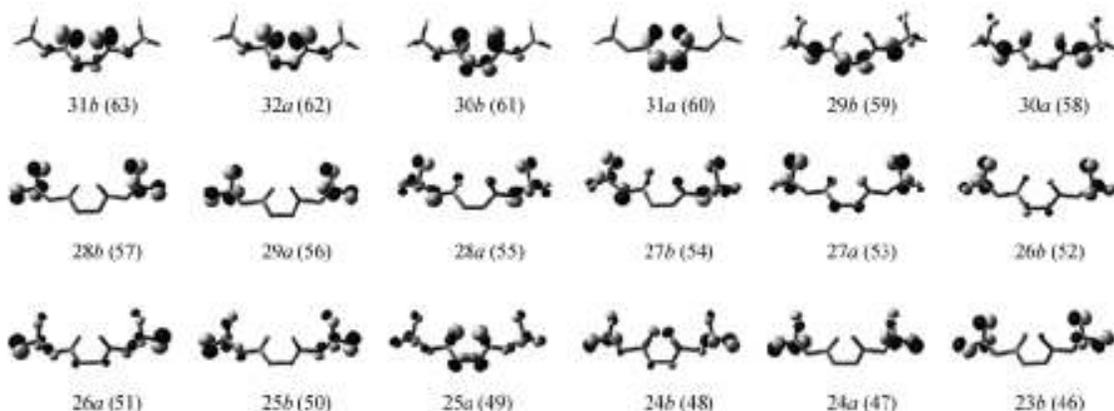


Figure 10: Characteristics of first eighteen highest occupied molecular orbitals for $\text{CF}_3\text{OC}(\text{O})\text{OOC}(\text{O})\text{OCF}_3$

2.3.4 Conclusion

The PES-PIMS with an on-line photochemical apparatus can also be a useful tool for the atmospheric photochemical reaction. They have studied the electronic structure and mechanism of ionization and dissociation of the product $\text{CF}_3\text{OC}(\text{O})\text{OOC}(\text{O})\text{OCF}_3$. Based on theoretical calculation, the two bands on the PES of above molecule were assigned. One of them is the ionization of an electron from a lone pair of oxygen and other one is from fluorine lone pair of CF_3 group. The spectroscopic and theoretical investigation gives an important feature which tells us that the above molecule prefers dissociation of C-O bond after one-electron ionization by the HeI radiation to form the fragment CF_3^+ and CF_3OCO^+ . Which

concludes that PES-PIMS can also be a powerful tool for investigation of transient species in the atmospheric photochemical reaction.

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