PHOTOELECTRON SPECTROSCOPY OF TRANSIENT / SHORT LIVED SPECIES

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Introduction:

- **The most striking properties of transient species are short lived, unstable, reactive and even explosive at ambient temperature.**

- **They can be produced by pyrolysis, discharge, or atom – molecule, molecule – molecule, molecule – solid reactions. They play an important role in atmospheric, combustion and biological processes.**

- **Characterization of this type of species is far more difficult than generation. To overcome this we need sophisticated instrumentation .**

- **photoelectron spectroscopy is an excellent technique for the course of the chemical reactions, especially those designed for the generation of transient intermediate.**

Application

In this part we are trying to discuss how photoelectron spectroscopy takes an efficient role to characterize transient species

1> <u>Photoelectron spectroscopy of SF_2 molecule in gas phase</u>

Generation scheme:

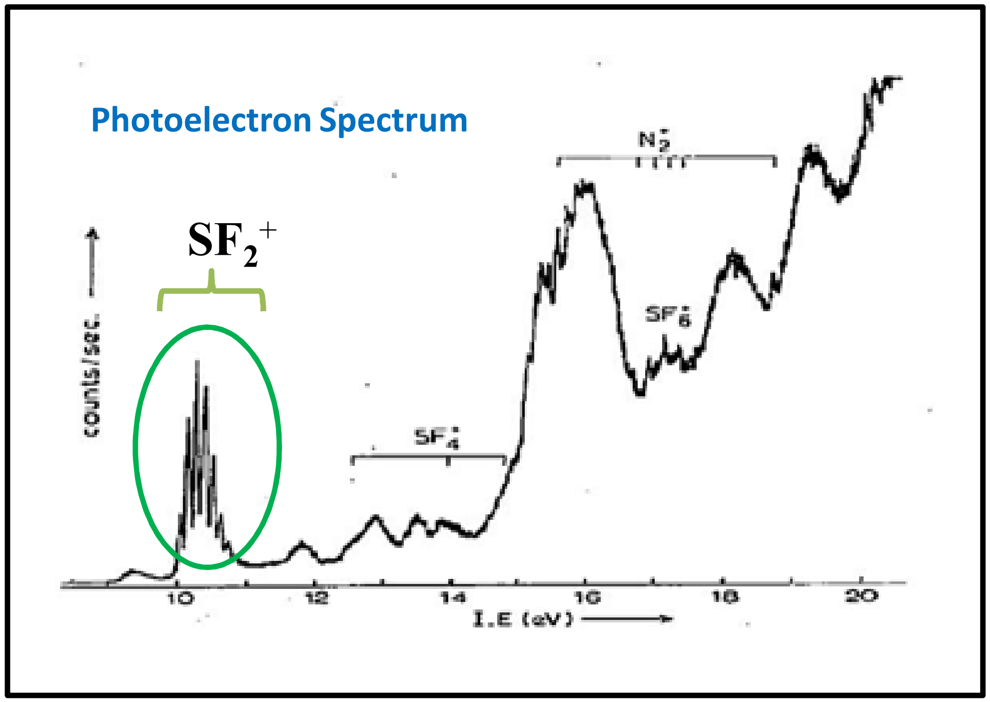
$SF_6/CF_4 \rightarrow F$

$F + OCS \rightarrow SF + CO,$

$SF + SF \rightarrow SF_2 + S,$

$S + SF \rightarrow S_2 + F,$

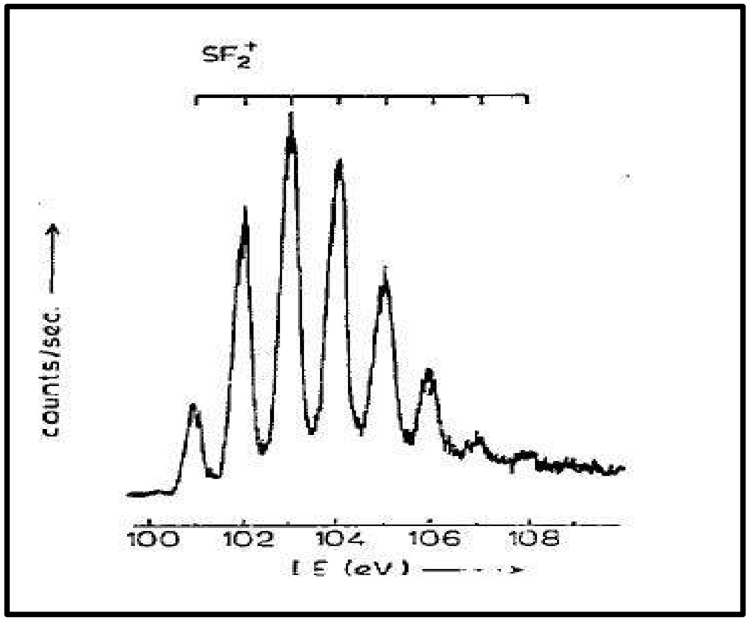
$S + OCS \rightarrow CO + S_2$



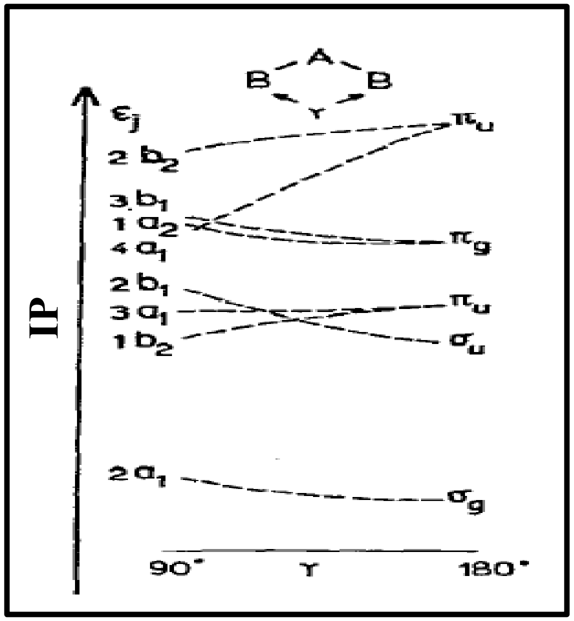
D.M.De Leeuw,R.Mooyman and C.A.De Lange; Chem. Phys. 34(1978)287-294

Photoelectron spectroscopy of SF_2 molecule in gas phase

Regular spacing is of the order of 935 ± 40 cm^{-1}



Expanded band associated with the first ionization energy of SF_2



Walsh diagram for AB_2 molecule with twenty valence electrons

D.M.De Leeuw,R.Mooyman and C.A.De Lange; Chem. Phys. 34(1978)287-294

2> Generation and characterization of nitrosyl thiocyanate

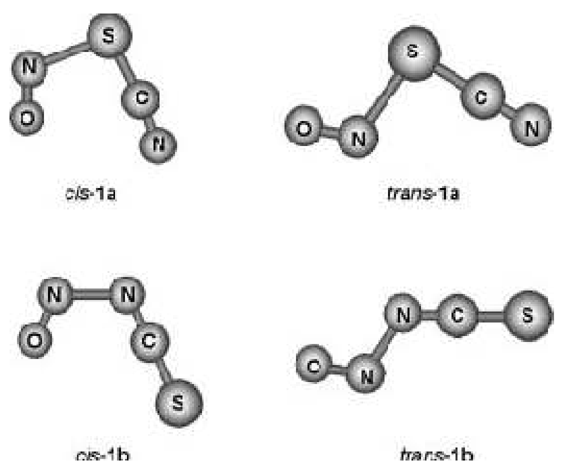
$$ClNO(g) + AgSCN(s) \xrightarrow{-60^0C} ONSCN(g) + AgCl(S)$$

Mechanism:

$$H^+ + HNO_2 + SCN^- \leftrightarrow ONSCN + H_2O$$

$$2\ ONSCN \leftrightarrow 2\ NO + (SCN)_2$$

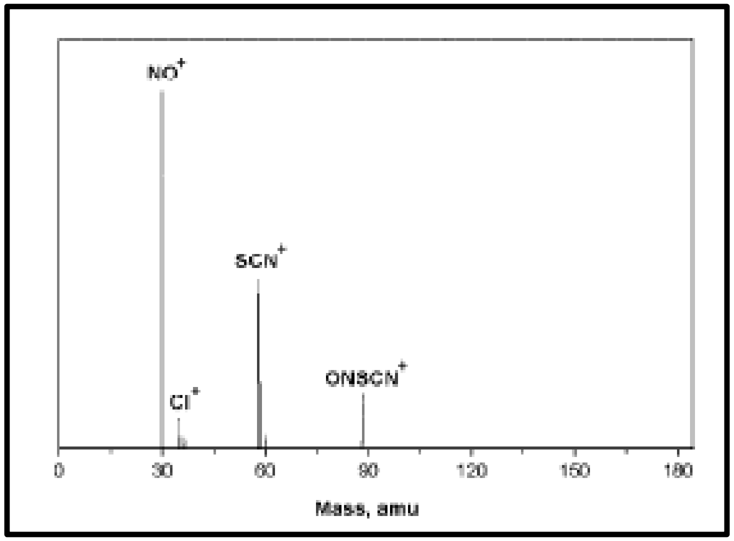
Possible structures of nitrosyl thiocyanate

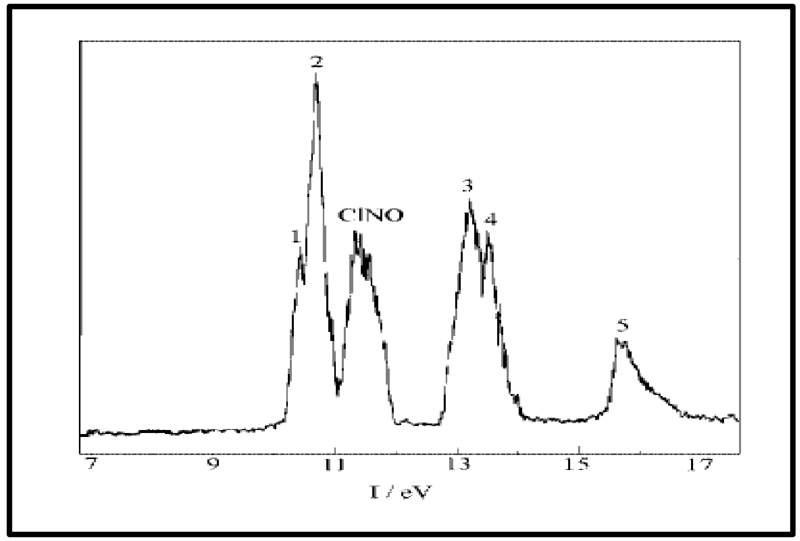


The calculated results predicted that 1(a) is more stable than 1(b) due to soft-soft interaction.

Yao Li et al, Eur. J. Inorg. Chem. 2006, 2469-2475

Generation and characterization of nitrosyl thiocyanate



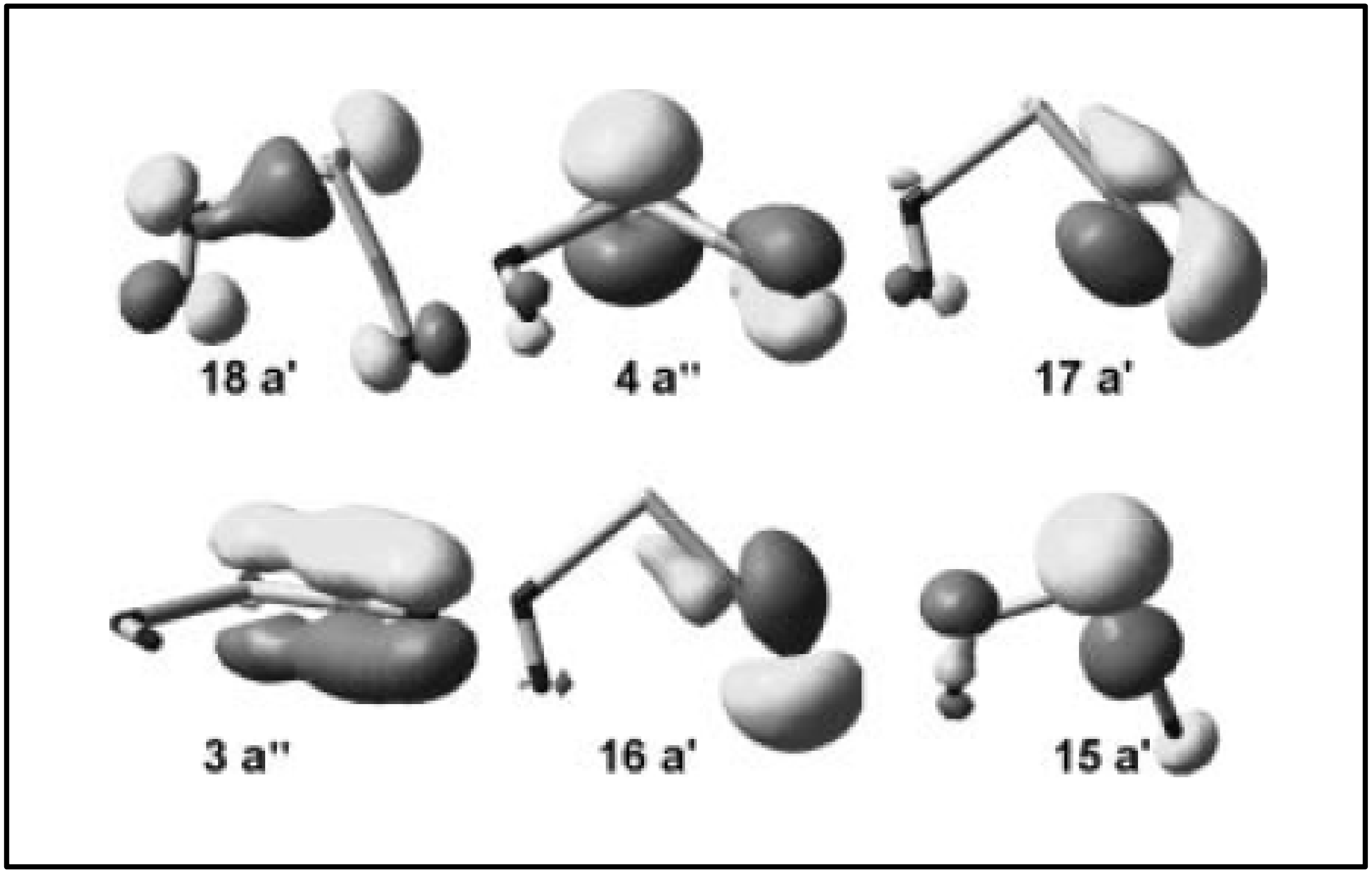


The HeI photoionisation mass spectrum and Photoelecrton spectrum observed at -60^{0}C

Band 1 is due to vertical ionization of the lone pair of electron of sulphur
Band 2 derives from ionization of 4a'' orbital
Bands 3 & 4 are due to ionization of two π oritals and terminal SCN pσ orbital
Band 5 is corresponding to ionization of 15a' orbital

Yao Li et al, Eur. J. Inorg. Chem. 2006, 2469-2475

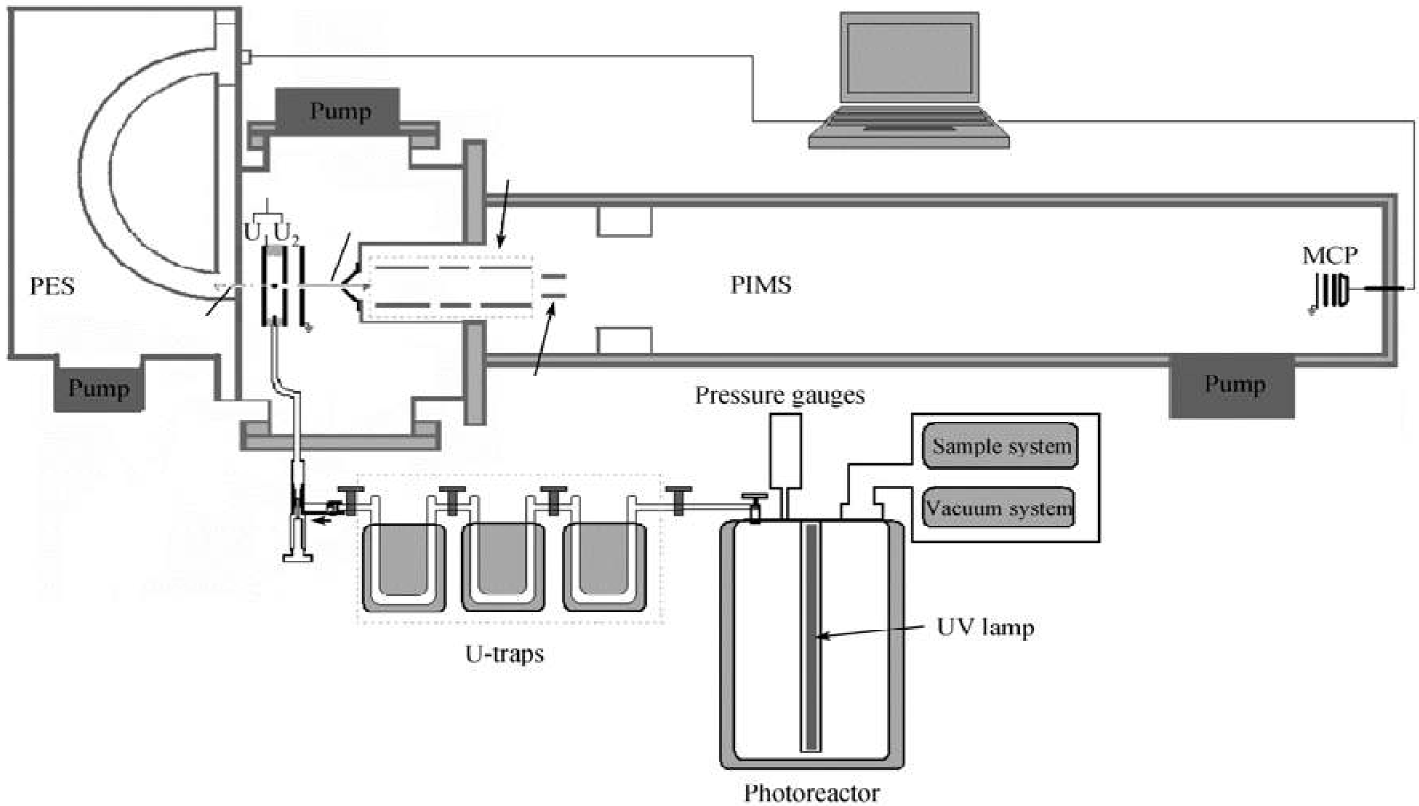
Generation and characterization of nitrosyl thiocyanate



Characters of the first six highest occupied molecular orbital for cis-1a

Yao Li et al, Eur. J. Inorg. Chem. 2006, 2469-2475

Recent instrumental development:



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

Y.Li,D.Lin,Y.Shi & G.Maofa. Sci China Ser B-Chem. Apr2008.51(4)316-321

3> Study on the atmospheric photochemical reaction of CF_3 radicals

For this study they have selected $(CF_3CO)_2O$ as a reactant and getting $CF_3OC(O)OOC(O)OCF_3$ as a transient product .Aim is to know the electronic structures and mechanism of ionization and dissociation of transient product.

In the atmosphere:

$$CF_3 + CO + O2 \longrightarrow CF_3OC(O)OOC(O)OCF_3$$

In the reaction chamber:

$$(CF_3CO)_2O + CO + O2 \longrightarrow CF_3OC(O)OOC(O)OCF_3$$

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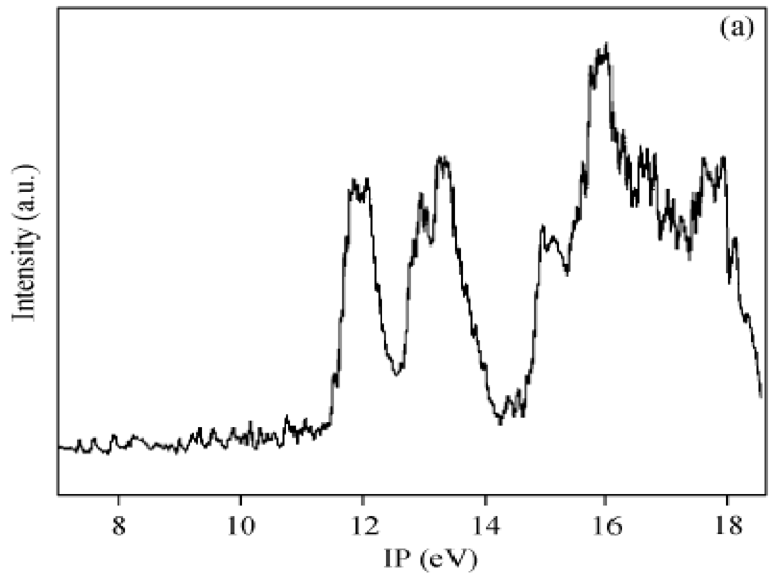
Study on the atmospheric photochemical reaction of CF_3 radicals



He (I) photoelectron spectra of (a) the reactant $(CF_3CO)_2O$

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}

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

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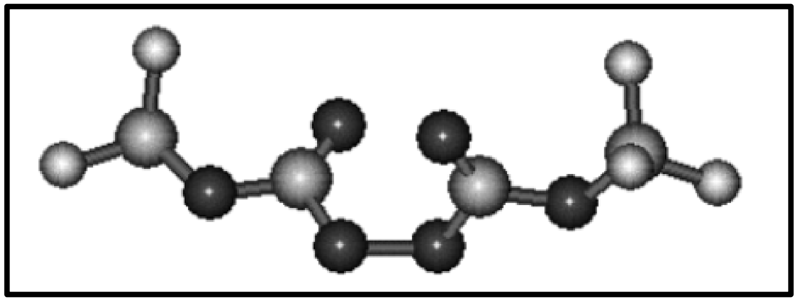
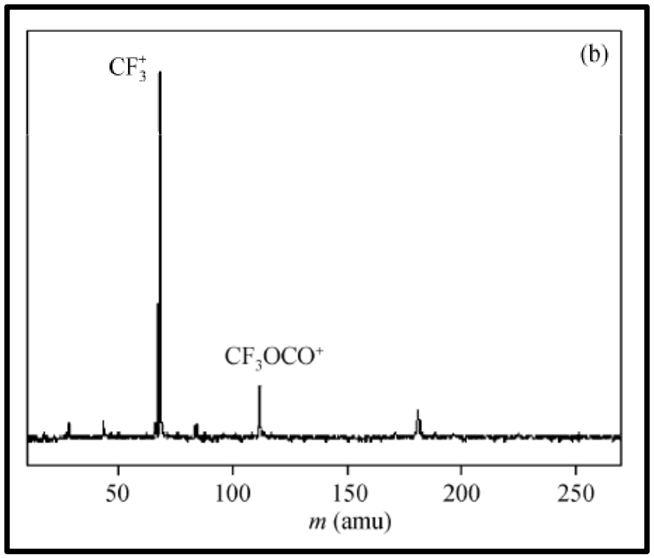
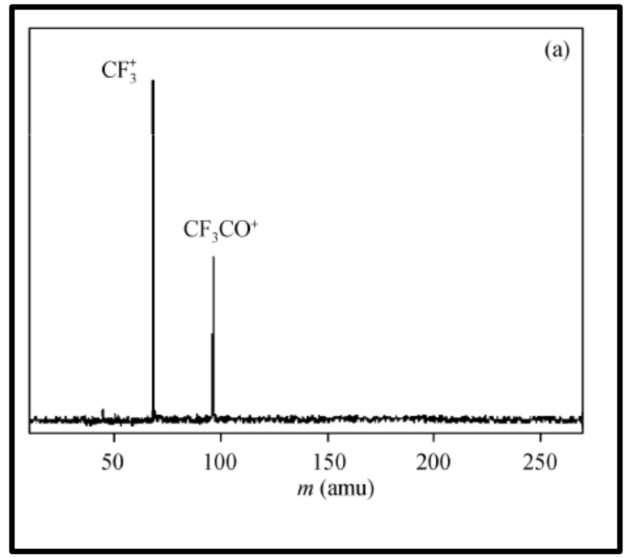
Study on the atmospheric photochemical reaction of CF_3 radicals



Structure of $CF_3OC(O)OOC(O)OCF_3$





The HeI photoionization mass spectrum of the reactant $CF_3(CO)_2O$ (a) and the product $CF_3OC(O)OOC(O)OCF_3$

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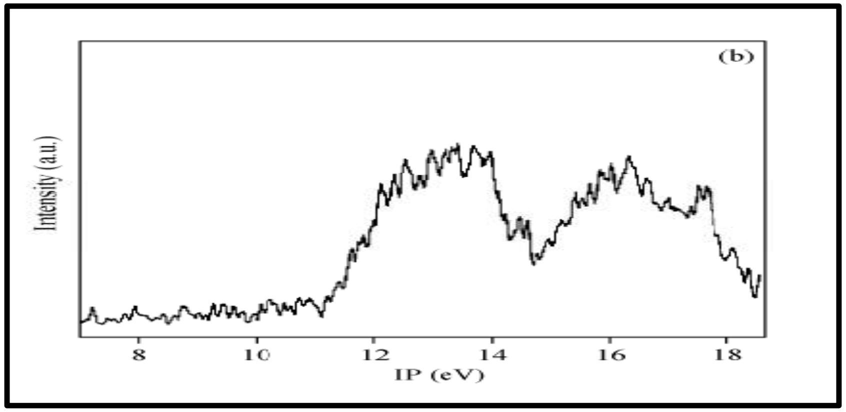
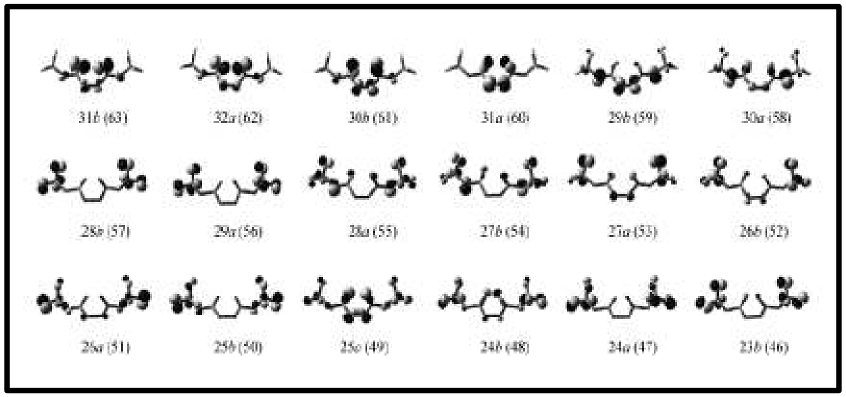
Study on the atmospheric photochemical reaction of CF_3 radicals



He(I) photoelectron spectrum of (b) product $CF_3OC(O)OOC(O)OCF_3$



Characteristics of first eighteen highest occupied molecular orbitals 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)	π_F
	16.713	26*a* (51)	π_F
	16.775	25*b* (50)	π_F
	16.797	25*a* (49)	π_F, σ_{O-O}
17.61	17.351	24*b* (48)	π_F
	17.516	24*a* (47)	π_F
	17.586	23*b* (46)	π_F
	17.634	23*a* (45)	π_F
	17.721	22*b* (44)	π_F

Experimental and calculated vertical ionization energies and characteristics for $CF_3OC(O)OOC(O)OCF_3$

Y.Li,D.Lin,Y.Shi & G.Maofa. Sci China Ser B-Chem. Apr2008.51(4)316-321

Conclusion

★ Photoelectron spectroscopy is an excellent tool for characterization of electronic structure of transient species.

★ It also can predict the geometrical structure of transient molecule which are consistent with the theoretical prediction (ROVGF calculation).

★ It can also predict the dissociation and ionization mechanism of atmospheric transient molecule .

★ Finally PES-PIMS can be used as a powerful tool for the investigation of transient species in gas phase

THANK YOU