On the ionization energy of CF_3SF_5 in the valence region measured by angle-resolved photoelectron spectroscopy

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Abstract

Ionization energies for valence electrons of CF_3SF_5 were measured in the 12–35 eV region by means of angle-resolved photoelectron spectroscopy. The observed ionization energies were basically consistent with previous ones measured by threshold photoelectron and HeI photoelectron spectroscopy, and the ionization levels at 22.60, 26.92 and 27.86 eV were newly observed. Asymmetry parameter derived at $h\nu = 684.7$ eV was a constant of $\beta = 1.02 \pm 0.04$ in the ionization energy lower than 20 eV, suggesting that lone pair electron of F atom is probably released through $2p \rightarrow \varepsilon d$ like electron emission. Characters of the 22 valence bands were elucidated with the help of ab initio calculations and of the nature of valence orbitals for CF_4 and SF_6.

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Introduction

Trifluoromethyl sulfur pentafluoride, CF_3SF_5, is a polyatomic molecule detected in the terrestrial atmosphere in 1999. The molecule has the highest global warming potential of $\cong 22000$ and is estimated to live in the atmosphere on the order of 1000 years by measuring infrared absorption [1]. Photoabsorption data are the most essential for understanding photochemistry of CF_3SF_5 in the atmosphere. Total photoabsorption cross sections were measured in the $4-26$ eV region by means of photoabsorption [2-6] and electron energy loss spectroscopy [6, 7]. The onset of photoabsorption is around 6 eV and then the cross section increases up to $\cong 120$ Mb at 23 eV with several strong peaks [2, 5-7]. Fragment ion with the lowest appearance energy has been reported to be CF_3^+ at 12.92 ± 0.18 eV [8]. Assignment for the photoabsorption bands still remains open to question since data for ionization energies (IEs) of the valence electrons of CF_3SF_5 are limited. To the best of our knowledge two papers have been published for the valence IEs: Chim et al [8] employed threshold photoelectron spectroscopy (TPES) and reported eight IE levels up to 25 eV. Limão-Vieira et al [6] recorded a HeI (21.22 eV) photoelectron spectrum with ten IE values and then assigned the photoabsorption peaks to Rydberg transitions. The IEs of the two papers are, however, not wholly in agreement. In this paper we present IEs of the valence electrons for CF_3SF_5 measured by angle-resolved photoelectron spectroscopy at photon energy of 684.7 eV, being just before the F K-edge absorption. Details of photoabsorption cross sections and decay pathways for the C, F and S core-excited CF_3SF_5 were already reported in previous publications〔9, 10〕. Photoelectron spectroscopy measured at high photon energy has advantage for characterization of valence molecular orbitals (MOs) though the photoabsorption cross section is small: Kinetic energies of photoelectrons released from valence MOs are high and lie close, and thus detection efficiency of the electrons is hardly affected by the kinetic energies. Photoexcitation by high photon energy is free from resonance excitation of a valence electron to give electron emission. Consequently peak intensity of photoelectron with high kinetic energy is proportional to the number of electrons in a valence MO. We think that the IE values for CF_3SF_5 obtained by the present method different from the previous ones [6, 8] are useful to evaluate them more reliably.

2. Experimental and MO calculations

The light source was synchrotron radiation (SR) from a high resolution monochromator with varied-line-space plane gratings at the c-branch of the soft X-ray photochemistry beamline BL27SU of the SPring-8 facility [11]. Three gratings were installed in the monochromator to cover photon energies of 180–2800 eV. The dispersed photon flux was monitored by measuring the drain current of the post-focusing mirror coated by gold. The radiation from a Figure-8 undulator was linearly polarized either in the plane of the electron storage ring (the 1st order harmonic) or in the plane perpendicular to the ring (the 0.5-th order harmonic) [12]. Experimental setup for measuring photoelectron spectra was described in a previous paper [13]. In brief, an electron energy analyzer of Gammadata Scienta SES-2002 was used for the angle-resolved electron emission measurements by changing the undulator gap from the 1st order to the 0.5-th order harmonic without rotating the electron energy analyzer. Energy scale of the electron spectrometer was calibrated by measuring the $M_4N_{4,5}N_{4,5}$ and $M_5N_{4,5}N_{4,5}$ Auger electron emissions from xenon [14]. The resolution of the energy analyzer was set to 300 meV, and that for the exciting photon was 150 meV. Commercial sample of CF_3SF_5 with a stated purity of >99% (SynQuest Lab.) was used without further purification. The base pressure of the electron energy analyzer was lower than 1×10^{-7} Pa, and the sample pressure was kept at $\cong 7 \times 10^{-4}$ Pa during experiments.

Ab initio self-consistent field calculations were carried out for valence molecular orbitals with the Gaussian 03 program [15]. The basis set used in the present calculation was 6-311G*.

3. Results and discussion

Photoelectron spectrum (PES) at photon energy of 684.7 eV is shown in Fig. 1 where the scales of x-axis are given by kinetic energy at the top and by ionization energy in the bottom. Panel a shows the PES measured by detecting photoelectrons emitted into the direction parallel to the electric vector of SR (the 1st order harmonic and denoted by 0°-spectrum hereafter) and panel b does that at the 0.5-th order harmonic (90°-spectrum). The 0°- and 90°-spectra were normalized by the photon flux monitored. The experimental data are given

by thick dots. Thin solid curves in the 0°-spectrum are the peaks deconvoluted by a least-squares curve fitting with the Voigt functions, and the thick one is the best fitted curve. The peaks with kinetic energies of 657–671 eV shifted in parallel with an increase in the exciting photon energy, and then we assigned them to valence photoelectrons. The baseline given by a dotted line in the panel a originates in molecular Auger electrons with kinetic energies of 650–660 eV. Panel c is the asymmetry parameter (β), being deduced by use of the experimental intensities $I(0)$ and $I(90)$ in the 0°- and 90°-spectra, respectively:

$$\beta = \frac{2[I(0) - I(90)]}{I(0) + 2I(90)} .$$ (1)

When photoelectrons are ejected into isotropic directions or $I(0) = I(90)$ in Eq. 1, we get $\beta = 0$. For a limiting case of $I(0) = 0$, the asymmetry parameter is $\beta = -1$, and for $I(90) = 0$ it is $\beta = 2$. The former case means that electrons are ejected into the direction perpendicular to the linear electronic vector of SR and the latter does that electrons are released into the parallel direction. The panel c giving $0 \leq \beta < 2$ suggests that the photoelectrons from valence MOs are preferentially released into the parallel direction and the molecular Auger electrons are isotropically ejected.

Table 1 gives the peak maxima or IEs in the 0°-spectra, the relative peak intensities, the β value obtained by Eq. 1, and the previously published IE levels [6, 8]. The calculated IEs, the symmetry of MO and the main character given in the sixth to eighth columns were elucidated by means of the ab initio calculations with the Gaussian 03 program [15]. The lowest 14.00 eV is the IE for the HOMO of $32a$', forming a bonding σ_{CS} occupied by two electrons. Uncertainty for the IEs in the present experimental conditions was estimated to be ±0.05 eV. The IE levels measured by three independent experiments are in good agreement up to 20 eV except the IEs of 14.699, 16.147 and 17.199 eV reported in the HeI PES [6]. These peaks are shoulders exposed by a peak fitting with the Gaussian functions [6]. When we tried to deconvolute the 0°-spectrum in Fig. 1 by use of the Gaussian functions, we needed additional peaks at 14.65, 16.34 and 17.05 eV to get a satisfying result (not shown), where the peak intensities at IE = 14.65 and 16.34 eV were 0.5 and 0.3 times that of the first one, respectively. In the HeI PES [6] too, the peak intensities at 14.699 and 16.147 eV are clearly smaller than that of the first band at 13.960 eV. We employ the results obtained by use of the Voigt

functions since we have no reasonable understanding for the small peak intensities (see the following discussion) and the Voigt functions gave better curve fittings than those by the Gaussian ones. In the energy region above 20 eV the IEs measured by TPES [8] agree with the present values. New IEs of 22.60, 26.92 and 27.86 eV were observed in this study.

Peak intensity in PES is associated with the photoabsorption cross section σ_{ab} and the β parameter [16]:

$$I(\theta) = \frac{\sigma_{ab}}{4\pi}[1 + \beta P_2(\cos\theta)], \qquad (2)$$

where $P_2(\cos\theta) = (1/2)(3\cos^2\theta - 1)$ is the Legendre polynomial of the second order and θ is the angle between the ejected electron and the polarization direction. The σ_{ab} increases with the number of electrons and thus the peak intensities in PES are approximately proportional to the number of electrons in valence MO(s), which are given in the parentheses in the second column of Table 1. Here the relative peak intensities are given after correction for anisotropic ejection since the 0°-spectrum depends upon β, i.e., $I(0) = (\sigma_{ab}/4\pi)(1 + \beta)$ from Eq. 2. The numerical values of β derived by use of Eq. 1 (see the panel c) were employed for the correction. The experimental IEs in the first column thus correspond to those for the 22 valence MOs given in the seventh column.

Full geometry optimization was performed in the MO calculations. The calculated bond lengths, which depend on the position of F atom in the molecule, were 1.295–1.296, 1.875 and 1.553–1.569 Å for the C–F, C–S and S–F bonds, respectively. Bond angles were 109.0–109.6° for the CF$_3$ group and 88.3–93.0° for SF$_5$. These bond lengths and angles are consistent with the reported values [8, 17]. Ionization energies for the optimized geometry based on the Koopmans' theorem are given in the sixth column of Table 1, being a little higher than the experimental ones up to 20 eV and then a little lower. Assignments in the last column are given by a combination of MOs for CF$_4$ and SF$_6$: The electronic configuration of the ground state of CF$_4$ is written as $(3a_1)^2(2t_2)^6$ for the inner valence shells and $(4a_1)^2(3t_2)^6(1e)^4(4t_2)^6(1t_1)^6$ for the outer valence MOs [18], and that for SF$_6$ is $(4a_{1g})^2(3t_{1u})^6(2e_g)^4$ for the inner shells and $(5a_{1g})^2(4t_{1u})^6(1t_{2g})^6(3e_g)^4(1t_{2u})^6(5t_{1u})^6(1t_{1g})^6$ for the outer valence [19]. The notation of $4t_2 + 5t_{1u}$ for the $32a'$, for example, means the MO constructed with the $4t_2$ of CF$_4$ and the $5t_{1u}$ of SF$_6$. The assignments here given are made for

the sake of convenience in understanding of the MO characters.

The asymmetry parameters in the third column of Table 1 are a constant of $\beta = 1.02 \pm 0.04$ in the region of IE ≤ 20 eV. The MOs from $32a'$ to $27a'$ are mainly composed of the two outermost shells of CF_4 and three those of SF_6. These five MOs for CF_4 and SF_6 have the n_F character originating in "near-pure" F$2p$ electrons. The np electron in atomic orbital gives the $\beta = 1$ in an $np \rightarrow \varepsilon d$ ionization and does $\beta = 0$ in $np \rightarrow \varepsilon s$ [16] on the assumption of dipole approximation on a single-electron model. The parameter $\beta = 1.02 \pm 0.04$ observed for CF_3SF_5 suggests thus that the n_F electron with a $2p$ character is probably ionized through a $2p \rightarrow \varepsilon d$ like emission though the electron angular momentum of atom is no longer valid in molecule. In the energy region above 20 eV, the asymmetry parameters lie large at $\beta = 1.42 \pm 0.10$ except the $\beta = 0.85$ at 27.86 eV. The ab initio calculations show that contribution of the C$2s$, S$3p$ and S$3s$ atomic orbitals becomes larger in the MOs at IE >20 eV. Thus electron emission from the MO in IE >20 eV is complex. Ionization through an $ns \rightarrow \varepsilon p$ like electron emission with $\beta = 2$ should be partly responsible for the observed $\beta = 1.42 \pm 0.10$.

In concluding we measured the ionization energies for valence electrons of CF_3SF_5 in the 12–35 eV region by means of angle-resolved photoelectron spectroscopy. The ionization energies obtained in the present work were able to be reliably evaluated by use of ab initio MO calculations and of the nature of valence bonds for CF_4 and SF_6.

Acknowledgments

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Table 1. Ionization energies, relative peak intensities, the asymmetry parameter β and assignments for the valence orbitals of CF_3SF_5.

PES[a] 684.7 eV	Relative Intensity[b]	β value	PES[c] HeI 21.22 eV	TPES[d]	IE calcd	MO[e]	Character[f]	Assignment[g]
14.00	1.0 (2)	1.02	13.960 (14.699)	14.13	15.90	$32a'$	σ_{CS}	$4t_2 + 5t_{1u}$
15.61	1.8 (4)	1.05	15.632 (16.147)	15.68	18.57	$15a''$	n_F	$1t_{1g}$
					18.68	$14a''$	n_F	$1t_1 + 1t_{1g}$
16.55	1.9 (4)	1.00	16.461		18.72	$31a'$	n_F	$1t_1 + 1t_{1g}$
					19.04	$13a''$	n_F	$1t_1$
17.01	1.8 (4)	1.02	16.845 (17.199)	16.94	19.48	$30a'$	n_F	$4t_2 + 5t_{1u}$
					19.59	$29a'$	n_F	$1t_1 + 5t_{1u}$
17.93	1.8 (4)	1.05	17.894	17.86	19.63 (2)	$28a'/12a''$	n_F	$5t_{1u}/1e - 1t_{2u}$ or $4t_2 + 1t_{2u}$
18.88	1.1 (2)	0.94	18.721		19.68	$11a''$	n_F	$4t_2 + 5t_{1u}$
19.54	1.0 (2)	1.03	19.365	19.44	19.75	$27a'$	n_F	$4t_2 + 1t_{2u}$
21.23	1.2 (2)	1.40		21.34	20.08	$26a'$	n_F	$3e_g$
22.04	3.6 (8)	1.43		22.01	20.71	$10a''$	n_F	$1e$
					20.96	$25a'$	n_F	$1e + 1t_{2u}$
					22.06 (2)	$24a'/9a''$	n_F	$1e + 1t_{2g}/ 3t_2 - 1t_{2g}$
22.60	0.9 (2)	1.26			22.23	$23a'$	n_F	$3t_2 - 4t_{1u}$ or $3t_2 + 5t_{1u}$
24.64	2.0 (4)	1.53		24.67	22.74	$8a''$	n_F	$1t_{2g}$
					24.39	$7a''$	n_F	$3t_2 + 1t_{2g}$
26.92	2.2 (4)	1.48			24.42	$22a'$	n_F	$3t_2 + 1t_{2g}$
					25.11	$21a'$	n_F	$3t_2 + 4t_{1u}$
27.86	1.1 (2)	0.85			25.12	$6a''$	n_F	$3t_2 + 4t_{1u}$

[a] Estimated uncertainty is ±0.05 eV.

[b] Relative peak area corrected for the β value. Number of electrons is given in the parentheses.

[c] Values in the parentheses are the IEs for shoulder peaks exposed by a curve fitting with the Gaussian functions [6].

^d Threshold photoelectron spectrum from Ref. [8].

^e Molecular orbitals from ab initio calculations. The HOMO is $32a'$, meaning that it is the 32th MO belonging to the symmetry a'.

^f Main character of MO is expressed with conventional symbol of σ_{CS} for the sigma C–S bond or n_F for nonbonding electrons on F atom.

^g Assignments based on the MOs of CF_4 and SF_6. See the text for details.

Figure caption

Fig. 1. Photoelectron spectra and the asymmetry parameter β. Panel a was measured by detecting photoelectrons in the direction parallel (0°) to the electric vector of synchrotron radiation. Thick dots are the experimental data, thin solid curves are the peaks deconvoluted by the Voigt functions and the thick curve is the sum of the thin ones. Panel b was measured at the perpendicular direction (90°).

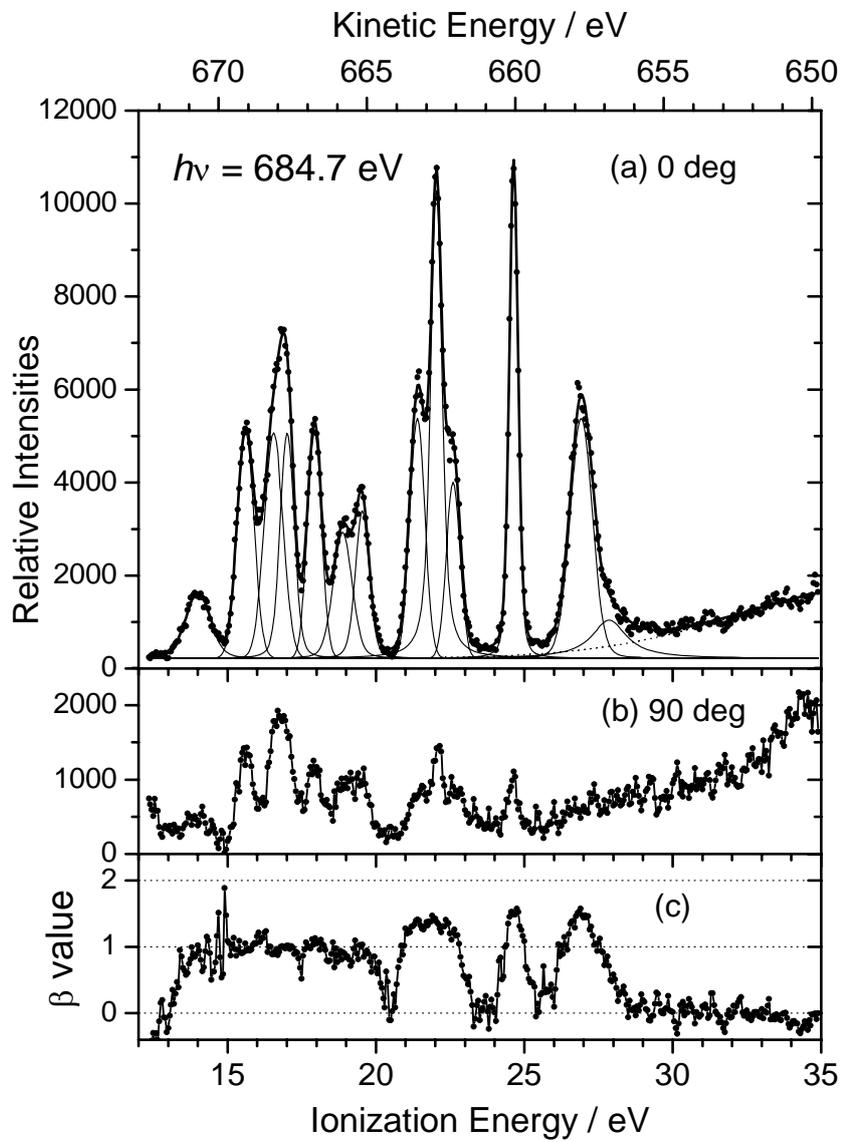Kinetic Energy / eV

$h\nu$ = 684.7 eV

(a) 0 deg

(b) 90 deg

(c)

Relative Intensities

β value

Ionization Energy / eV

Fig. 1. Ibuki et al