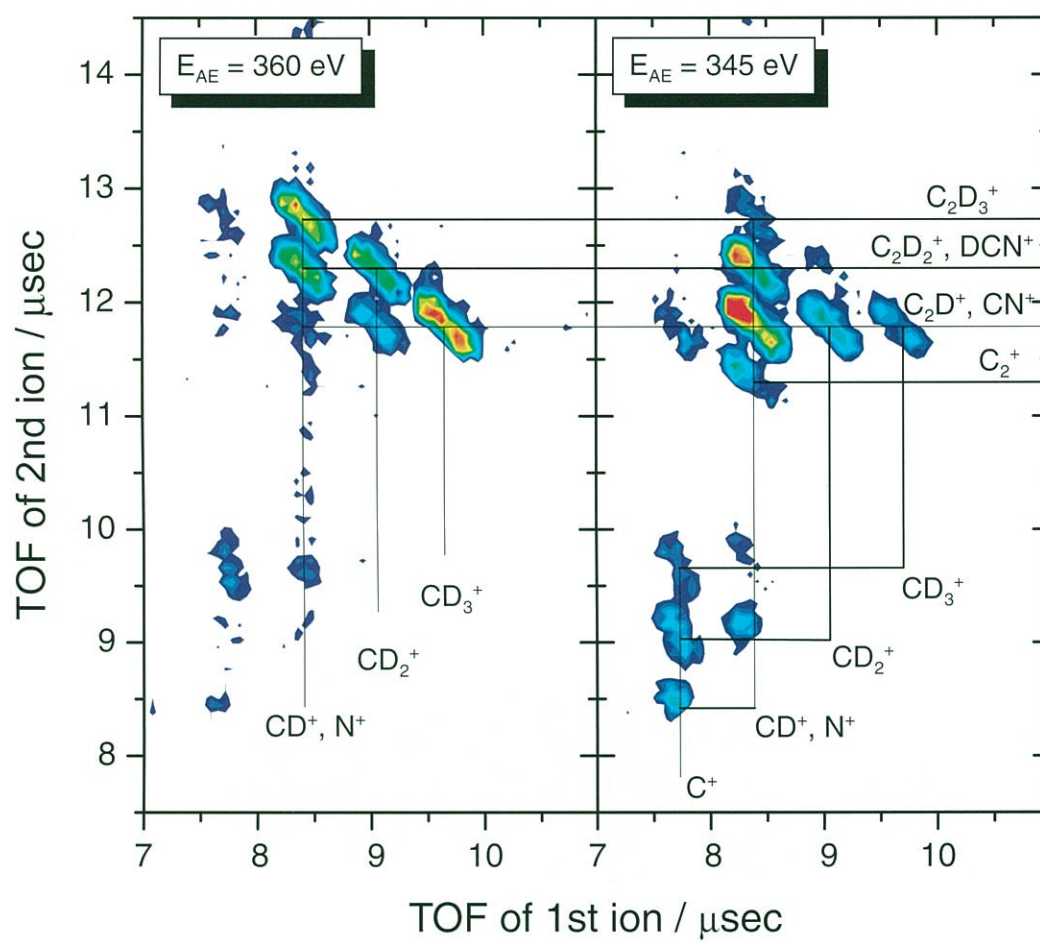


AEPIICO spectra of CD_3CN



Gas-Phase Spectroscopy

BL2B2, 3A2, 3B, 8A1

(BL7B)

Two-dimensional imaging of photoelectron from Xe

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The dynamics of atoms in highly excited states can be investigated by preparing to a given state at a well-defined energy and analyzing energy spectra and anisotropy of photoelectrons emitted. When a count rate is extreme low, two dimensional imaging technique is one of the most powerful tools for obtaining reasonable signals, because it allow us to detect all low energy electrons emitted around. At BL7B we have launched this two-dimensional imaging technique with using a position sensitive detector (PSD). We have successfully measured the image of Xe⁺ signal at the valence region (12.1-14 eV).

Experimental setup is as follows: After the acceleration by ion lens, electrons hit the PSD (Roendek). The determination of position on the detector is based on the time delay between two signals from each end of a wire behind the MCP. The position is obtained by the subtracting of time when each two signals arrive. Since the direction of polarization of SR is parallel to the axis of the tube, and the position of the electrons on the detector provide its velocity and direction. Figure 1 shows the 2D imaging of photoelectrons from Xe excited at 13.5 eV. The inner circle shows the electrons generated via ²P_{3/2} state and the outer one shows via ²P_{1/2} state.

This two-dimensional technique is particularly suitable for pump and probe technique with laser and SR, since its count rate is expected to be less than 10 cps. Although we have tried to measure the ion signal via 5p⁵d state of Xe* combined with the free electron laser (FEL) at UVSOR as the first stage, we have not obtain signals due to low flux photon density of BL7B and relatively high background signals. We are going to apply this technique with the FEL and a undulator in order to investigate of the dynamics of Xe excited state.

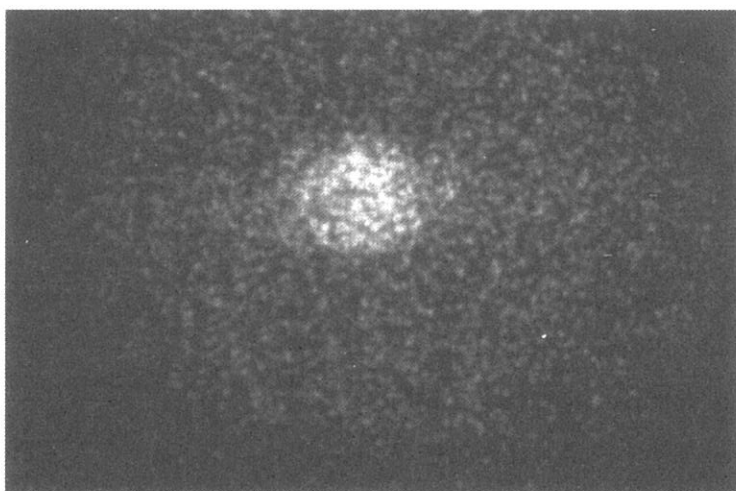


Fig. 1: 2D imaging of photoelectron from Xe excited at 13.5 eV.

(BL2B2)

Anisotropy of Fragment Ions from SF₆ with Valence- and Sulfur L-Electron Excitation

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Sulfurhexafluoride (SF₆) is one of the most well-known molecules that dissociate to multiple species of fragment ions after photoionization. Therefore, formation of SF_n⁺ (0 ≤ n ≤ 5) has been studied by many authors [e.g. 1,2]. Recently it was reported that the angular distribution of SF₅⁺ is anisotropic with respect to the electric vector of the light in the region of the valence electron excitation (18 – 23 eV) [3]. In the present report the asymmetry parameter β of the fragment ion has been measured in the energy region from the outer-valence to sulfur 2*p* electron excitation (23 – 200 eV).

The apparatus for the measurements of the anisotropy of fragment ions has been constructed at the endstation of BL2B2. At this beam line a Dragon-type monochromator is placed, which provides 23 – 200 eV photons with high-resolution and high-photon flux [4, 5]. The apparatus consists with two sets of an ion detector and three grids, as shown in Fig. 1. The two ion detectors were mounted in the parallel and perpendicular direction against the electric vector of synchrotron radiation. Retarding voltages were applied to the two grids near the detector to reject the parent ion. The last grid nearest the photoionization region was put on the electrical ground level. All fragment ion species have been observed. The base and sample pressure were 5 × 10⁻⁸ and 2 × 10⁻⁵ Torr, respectively. The photon flux was estimated by measuring the photocurrent of the gold mesh at the downstream of the photoionization region.

Figure 2 shows the fragment ion yield from SF₆ and β. The β parameter is calculated by

$$\beta = \frac{2(I_{\parallel} - I_{\perp})}{I_{\parallel} + 2I_{\perp}},$$

where I_{\parallel} and I_{\perp} are the ion yields in the parallel and perpendicular direction against the SR electric vector, respectively. The spectral range includes various regions from the outer-valence electron to sulfur 2*p* electron excitation. The three peaks at > 170 eV are assigned to the resonance excitations from 2*t*_{1u} (sulfur 2*p*) to unoccupied valence orbitals (6*a*_{1g}, 2*t*_{2g} and 4*e*_g).

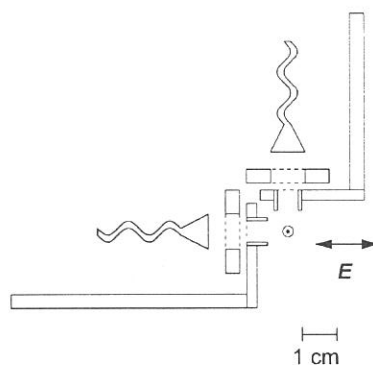


Fig. 1. The schematical layout of the apparatus for measurement of the anisotropy of fragment ions.

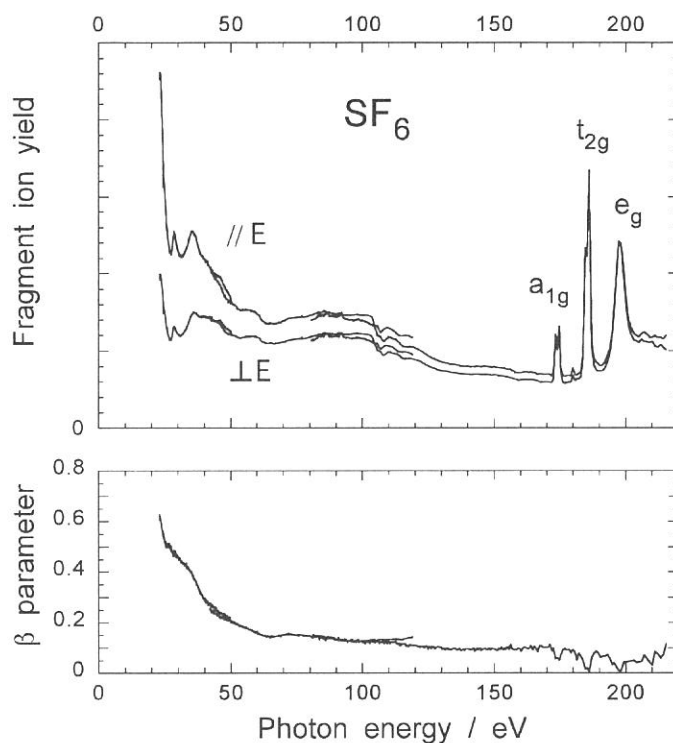


Fig. 2. Ion yield spectra and asymmetry parameter of the fragment ions from SF_6 . A retarding voltage is set to 0.4 V.

The β value involving the contribution only of the $2p$ electron excitation is constant at these resonance positions. Then the β parameter has been set deliberately to 0, because it is likely that the fragmentation occurs isotropically, and because no correction has been made on the difference in the detection efficiency between the two detectors.

Several features around 20 – 60 eV are found to resemble those in the absorption spectrum. The structures around 110 eV are artifact and arise from an imperfect photon flux normalization process. The β parameter increases with decreasing photon energy. This trend can be explained qualitatively by the assumption that SF_5^+ ions has much more anisotropic distribution than other fragments from SF_6 .

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(BL3A2)

Dissociative single and double photoionization of CF_4 and ionic fragmentation of CF_4^+ and CF_4^{2+} in the range from 23 to 120 eV

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Single and particularly double photoionization and subsequent dissociation processes of CF_4 have not quite been examined so far. Therefore, we have studied these processes with time-of-flight mass spectrometry and the photoion-photoion-coincidence (PIPICO) method by use of synchrotron radiation in the photon energy range of 23-120 eV. The TOF mass spectra and the PIPICO spectra were measured at an angle of $\sim 55^\circ$ with respect to the polarization vector where the second-order Legendre polynomial is close to zero. Under these conditions, the effects of anisotropic angular distributions of fragment ions are minimized [1]. Appropriate optical filters (Sn and Al) were used to eliminate higher order radiation. To obtain accurate ion branching ratios, the radio frequency (rf) signal of the storage ring was used as the start signal of a time-to-amplitude converter (TAC) under the single bunch mode operation of the storage ring [2].

The present study focuses on the determination of the ratio of double to single photoionization (σ^{2+}/σ^+) and the partial cross sections for single (σ^+) and double (σ^{2+}) photoionization as a function of photon energy. Second, the ion branching ratios and the partial cross sections for the individual ions produced from the parent CF_4^+ and CF_4^{2+} ions are separately determined. Third, the dissociation ratio of the parent CF_4^{2+} ions into two ionic fragments is determined. Some of the results are presented in this report.

Shown in Fig. 1 is a typical time-of-flight mass spectrum measured at a photon energy of 100 eV. The spectrum is complicated because two or three bunches pass the front end of the beam line in the time range of the mass spectrum. Metastable CF_4^{2+} ions are not observed. The ion branching ratios and the absolute partial cross sections for the production of singly charged CF_3^+ , CF_2^+ , CF^+ , F^+ , and C^+ ions, as well as doubly charged CF_3^{2+} and CF_2^{2+} ions have previously reported [3]. The ratio of double to single photoionization is shown in Fig. 2, increasing monotonically with photon energy. The threshold of double ionization 37.5 ± 0.5 eV is in good agreement with the value 37.6 ± 0.6 eV reported by Codling et al. [4]. Above 100 eV, the ratio exceeds 0.3. Since the total photoabsorption cross section of CF_4 in this photon energy range has been reported by Au, Burton, and Brion [5], the σ^{2+}/σ^+ ratio can be converted to the absolute cross sections for single and double photoionization.

Ion branching ratios for the individual ions respectively produced from the parent CF_4^+ and CF_4^{2+} ions are determined separately, thus enabling more detailed study of the dissociation processes of the CF_4^+ and CF_4^{2+} ions. These results are shown in Figs. 3 and 4. Looking at the ion branching ratios of CF_4^+ (Fig. 3), we notice that the major ions produced are CF_3^+ and their ratio still increases at higher photon energies. The ratio for C^+ also increases with photon energy up to about 85 eV. In Fig. 4, we see interesting behavior of the fragmentation of CF_4^{2+} as a function of photon energy. Two body dissociation $\text{F}^+ + \text{CF}_3^+$ takes place first. Depending on the number of neutral fluorine atoms in the dissociation, the different channels ($\text{F}^+ + \text{CF}_2^+ + \text{F}$, $\text{F}^+ + \text{CF}^+ + 2\text{F}$, and $\text{F}^+ + \text{C}^+ + 3\text{F}$) appear one after another. This matter will be discussed in a separate report.

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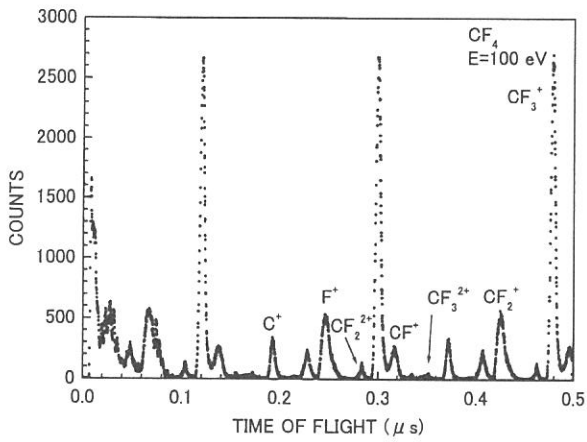


FIG. 1. A typical time-of-flight mass spectrum measured at a photon energy of 100 eV.

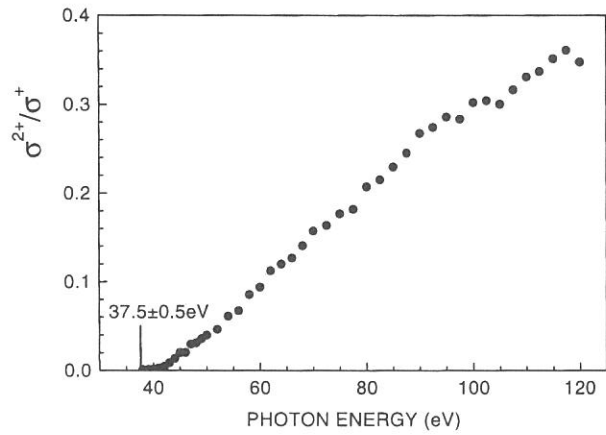


FIG. 2. Ratios of double to single photoionization cross section of CF_4 .

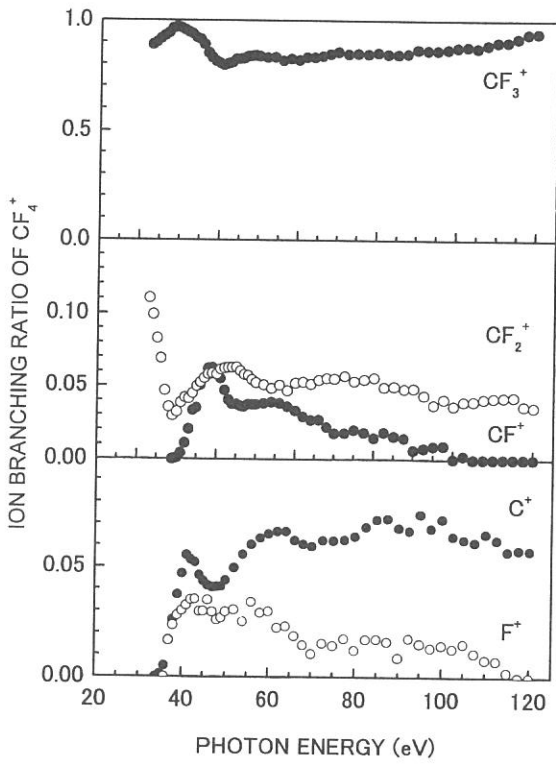


FIG. 3. Ion branching ratios of single photoionization of CF_4 .

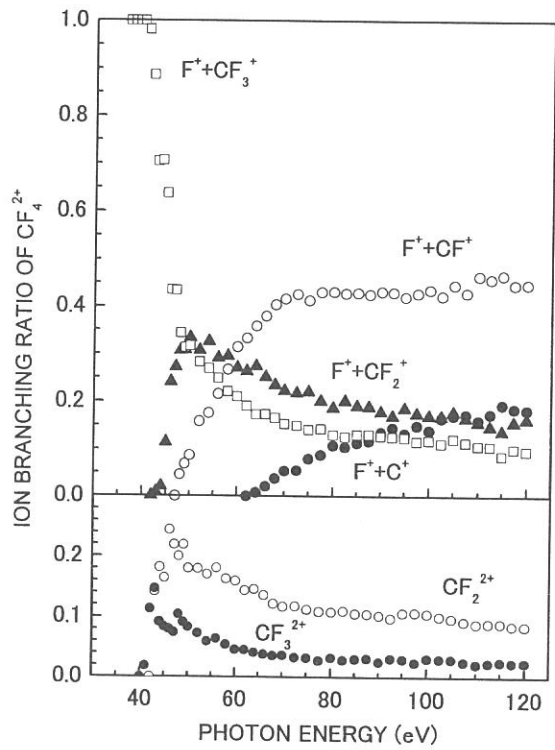


FIG. 4. Ion branching ratios of double photoionization of CF_4 .

(BL3A2)

Fragmentation of doubly charged CF_4^{2+} ion

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The doubly charged CF_4^{2+} ion has received much attention recently by the advent of synchrotron radiation. Recently Hall et al. [1] reported the threshold for double ionization to be 37.5 ± 0.5 eV using threshold photoelectron(s) coincidence (TPEsCO) spectroscopy and presented direct information on the two-hole states of CF_4 . Experimental information on the CF_4^{2+} dication has also been obtained via Auger spectroscopy, double-charge-transfer (DCT) spectroscopy, PIPICO, and PEPIPICO experiments. Among these experiments, Codling et al. [2] determined the thresholds for the ion-pair formation of CF_4^{2+} into $\text{F}^+ + \text{CF}_3^+$ (37.6 eV), $\text{F}^+ + \text{CF}_2^+$ (42.4 eV), $\text{F}^+ + \text{CF}^+$ (47.5 eV), and $\text{C}^+ + \text{F}^+$ (62.0 eV) and tentatively correlated these thresholds with specific two-hole states of CF_4 calculated by Larkins and Tulea [3].

In the present study, we have studied dissociative double photoionization processes with the photoion-photoion-coincidence (PIPICO) method by use of synchrotron radiation. The PIPICO spectra were measured at an angle of $\sim 55^\circ$ with respect to the polarization vector to minimize any effects of anisotropic angular distributions of fragment ions [4]. Al optical filter was used to eliminate higher order radiation.

Shown in Fig. 1 are the PIPICO branching ratios of CF_4^{2+} . The thresholds for the respective fragmentation channels reported by Codling et al. are indicated with vertical lines. The two-body fragmentation $\text{F}^+ + \text{CF}_3^+$ may occur in the narrow energy range of 37.6-42.4 eV. The three-body fragmentation $\text{F}^+ + \text{CF}_2^+ + \text{F}$ starts at 42.4 eV. The four-body ($\text{F}^+ + \text{CF}^+ + 2\text{F}$) and the five-body ($\text{F}^+ + \text{C}^+ + 3\text{F}$) fragmentation channels appear according to priority with increasing photon energy. The PIPICO branching ratios for these many-body fragmentation channels increase at different photon energies, indicating the existence of fragmentation pathways at these different photon energies. In order to correlate these fragmentation pathways more clearly to the electronic states of CF_4^{2+} , the PIPICO branching ratios for these fragmentation channels were differentiated with respect to the photon energy.

The results are shown in Fig. 2 with electronic states of the dication calculated by Larkins and Tulea [3] by vertical lines. They have calculated the energy of the 107 two-hole states associated the seven outermost orbitals. The electron configuration of the ground electronic state of CF_4 is $(1a_1^2 1t_2^2)(2a_1^2)(3a_1^2 2t_2^6)(4a_1^2 3t_2^6 1e^4 4t_2^6 1t_1^6): ^1A_1$. The important bonding orbitals are $4t_2$, $4a_1$, $2t_2$, and $3a_1$ [2]. In the attempt to correlate initial states of the CF_4^{2+} ion with the above thresholds for fragmentation, Codling et al. [2] used various simplifying assumptions: the first one is that no fragmentation occurs where both orbitals are non-bonding or antibonding ($1t_1$, $1e$, $3t_2$), and they shifted the calculation of Larkins and Tulea by 4.8 eV. The 80 electronic states shown in Fig. 2 are those concerned with fragmentation following the above description with the shift by 4.8 eV. First, we notice that the three-body fragmentation occurs in a relatively narrow energy range from the threshold to about 49 eV, where 14 two-hole states, $1t_1$, $4t_2(2)$, $3t_2$, $4t_2(7)$, $1e$, $4t_2(2)$, $4a_1$, $1t_1(2)$, and $4a_1$, $4t_2(1)$ lies. The value in the parentheses represents the number of the states in this range. That is, only the outer-valence electrons are involved. The four-body fragmentation takes place in a rather wide energy range from the threshold to about 80 eV, where both inner-valence and outer-valence electrons are involved.

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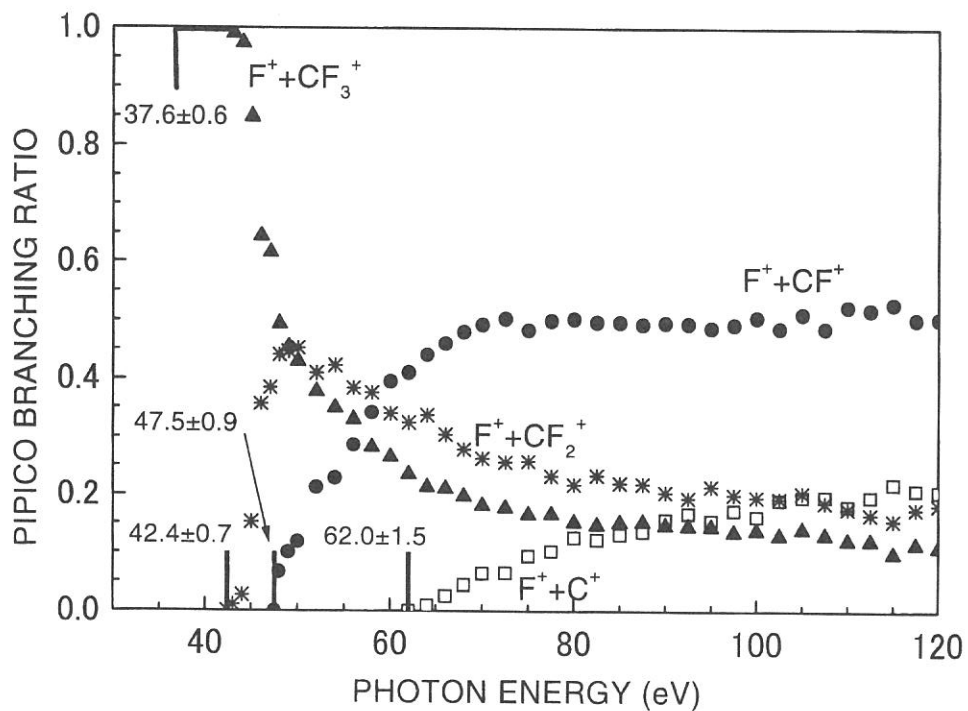


FIG. 1. PIPICO branching ratio of CF_4^{2+} .

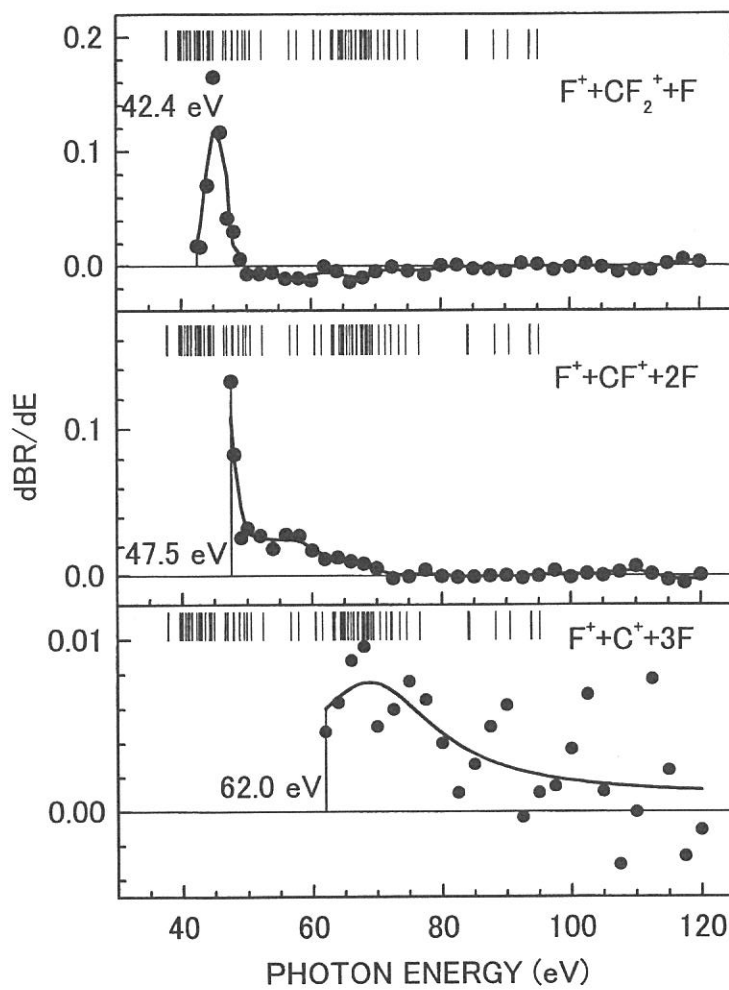


FIG. 2. Differential spectrum of PIPICO branching ratios for the three fragmentation channels.

(BL3A2)

Molecular and dissociative single and double photoionization of CS₂

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Molecular and dissociative single and double photoionization processes of carbon disulfide have been studied with time-of-flight (TOF) mass spectrometry in the 20-120 eV range by the use of synchrotron radiation. Sn and Al optical filters were used to eliminate higher order radiation. The TOF mass spectra were measured at an angle of about 55° with respect to the polarization vector of synchrotron radiation to minimize any effects of anisotropic angular distributions of fragment ions. To obtain accurate ion branching ratios, the radio frequency (rf) signal (90.115 MHz) of the storage ring was used as the start input of a time-to-amplitude converter (TAC) under the single bunch mode operation of the storage ring.

The observed ions are CS₂⁺, S₂⁺, CS⁺, S⁺, C⁺, and CS₂²⁺. The ion branching ratios for these fragment ions increase at various photon energies, indicating the presence of dissociation pathways at these photon energies. In order to correlate these dissociation pathways more clearly to the electronic states of CS₂⁺ and CS₂²⁺, the ion branching ratios for these ions were differentiated with respect to the photon energy. These differential spectra are similar by nature to those measured by threshold photoelectron-photoion coincidence spectroscopy (TPEPICO) except for a low spectral resolution of the present spectra.

Typical examples of the resultant photoion spectra (dBR/dE) are shown in Figs. 1 and 2 for CS⁺ and CS₂²⁺, respectively. The first peak in the photoion spectrum for CS⁺ (Fig. 1) indicates that the C state of CS₂⁺ dissociates into CS⁺ (and also into S⁺) in agreement with the observation of Brehm et al. [1] and dipole breakdown scheme of Carnovale et al. [2]. The satellite bands due to configuration interaction have been observed in the 19.1-35 eV range by Carnovale et al. [3]. The first peak in Fig. 1 covers the lower part of the satellite bands, meaning that the lower part of the satellite bands dissociates into CS⁺. The threshold for formation of the metastable CS₂²⁺ ions lies at 27.05±0.02 eV (the best previously reported value) measured by TPEsCO spectroscopy [4]. Roy et al. suggested that the bands with binding energies above 27 or 28 eV originate from direct double ionization continua [5]. Theoretical calculation of the energies of the low-lying electronic states of the dication is available [6]. These states are shown in the figure by vertical lines. The second peak in Fig. 1 locates in the double ionization region, probably indicating that the CS⁺ ions are formed by the charge separation CS⁺+S⁺ of the dication. It is interesting to note that the CS⁺ ions are formed only in a restricted energy range from about 31 to about 42 eV.

Fig. 2 shows an interesting behavior for the formation of the CS₂²⁺ ions, i.e., the dication is formed only in a narrow energy range from 27.05 to about 35 eV with a peak at about 29 eV. Hochlaf et al. have reported the potential energy curves along the SC-S coordinate for 14 electronic states of CS₂²⁺ using complete active space self-consistent field (CASSCF) approach and have shown that all low-lying electronic states of CS₂²⁺ are separated by large barriers from their dissociation asymptotes [6]. They have further mentioned that all electronic states up to about 32-33 eV have bound parts on their potential curves and are stable with respect to the dissociation. The present observation is essentially in agreement with their calculation.

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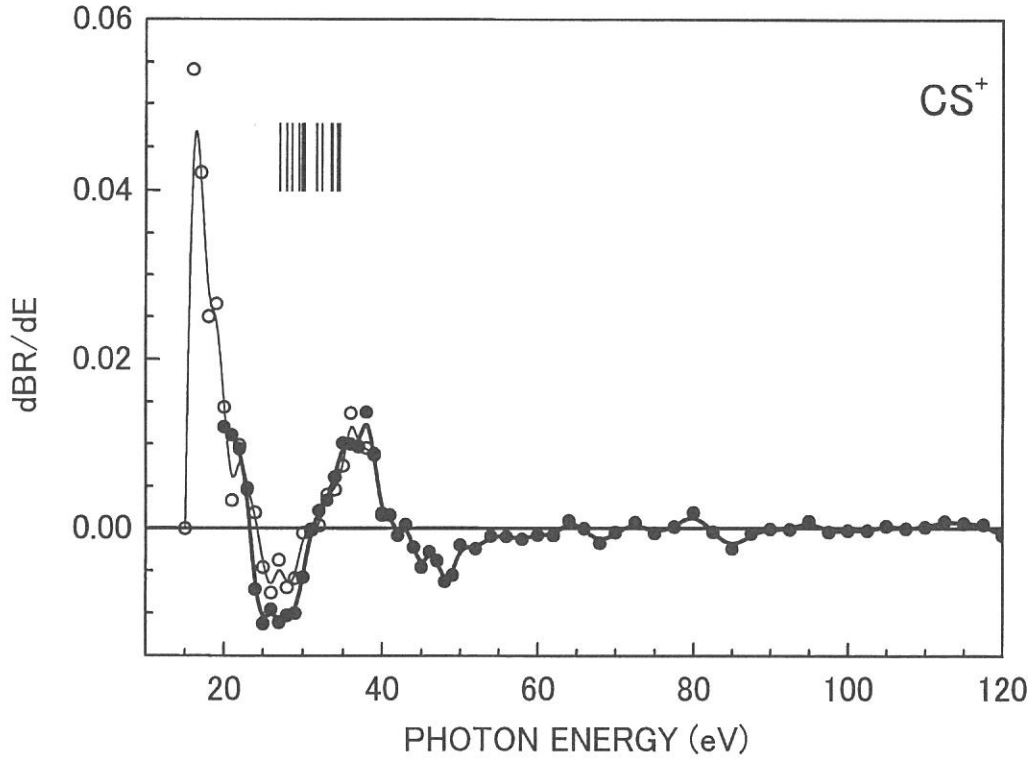


FIG. 1. Differential spectrum of ion branching ratios for CS^+ . ● and fat solid line, present result; ○ from ref. 3, thin solid curve is a fitting result to their data. Vertical lines indicate the electronic states of CS_2^{2+} from ref. 6.

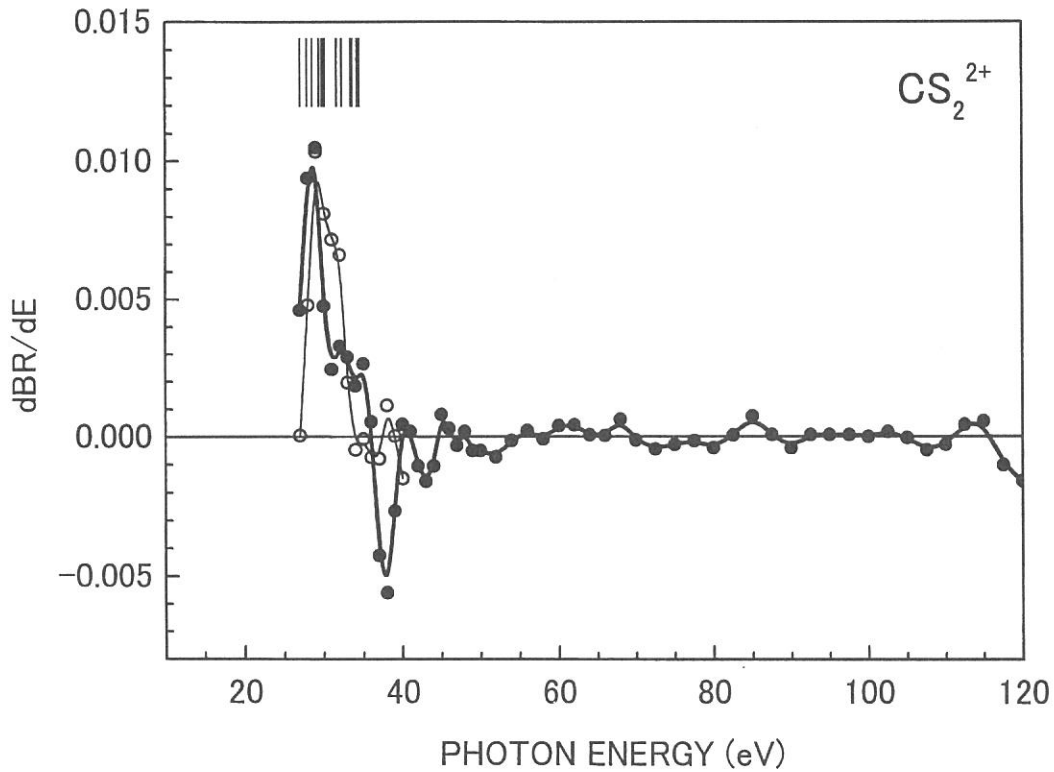


FIG. 2. Differential spectrum of ion branching ratios for CS_2^{2+} . ● and fat solid line, present result; ○ from ref. 3, thin solid curve is a fitting result to their data. Vertical lines indicate the electronic states of CS_2^{2+} from ref. 6.

(BL3A2)

Laser Induced Fluorescence Spectroscopy of $\text{CN}(X^2\Sigma^+)$ Radicals Produced by Vacuum UV Photoexcitation of CH_3CN with Synchrotron Radiation

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Synchrotron radiation-pump and laser-probe spectroscopy is employed to observe CN radicals in the vibronically ground state produced from CH_3CN . The photon energy of synchrotron radiation is changed from 13.6 to 18.6 eV. The laser induced fluorescence signal is measured as a function of the photon energy with the laser wavelength fixed at the $\text{CN}(B^2\Sigma^+, v_B = 0 \leftarrow X^2\Sigma^+, v_X = 0)$ transition. The onset of 15.4 eV of the fluorescence signal indicates that the detected $\text{CN}(X^2\Sigma^+)$ radicals result from dissociative ionization of CH_3CN . The partial cross section for the formation of $\text{CN}(X^2\Sigma^+)$ is estimated to be 0.1 – 0.5 Mb and is compared with that for the CH_3^+ formation.

A wide wavelength range of synchrotron radiation was searched for the LIF signal of $\text{CN}(X^2\Sigma^+)$ with the laser and monitored wavelength fixed at 388 and 420.8 nm, respectively. Fig. 1 shows a plot of the LIF intensity, the difference between the fluorescence signal counts with and without the laser, as a function of the photon energy E_{SR} of synchrotron radiation in the range of 13.6 – 18.6 eV. This plot represents the yield curve for the formation of $\text{CN}(X^2\Sigma^+, v_X = 0)$. Though the data points show some scatter around the background level, the LIF intensity has an onset at $E_{\text{SR}} = 15.4$ eV and makes a peak around 15.6 eV. Similar E_{SR} dependences of the LIF intensity have been obtained at other laser wavelengths between 387 and 388.5 nm. The onset energy of 15.4 eV is in a reasonable agreement with the appearance potential of the CH_3^+ ion reported in the photoionization mass spectrometric study of CH_3CN [2]. This indicates that the CN radical detected by LIF spectroscopy originates from CH_3CN^+ which subsequently dissociates:



The photoionization efficiency of CH_3^+ has an onset of 15.34 eV, increases gradually with the photon energy up to 17.5 eV and almost levels off thereafter [2]. On the contrary, the LIF signal intensity in Fig. 1 rapidly decreases beyond the peak at 15.6 eV and settle down to the background level at > 16 eV. The absence of the LIF signal above 16 eV is ascribed to a large kinetic energy release on the way of the

dissociation of CH_3CN^+ . The quicker the $\text{CN}(X^2\Sigma^+)$ fragment escapes from the probe region, the lower its time-averaged number density becomes.

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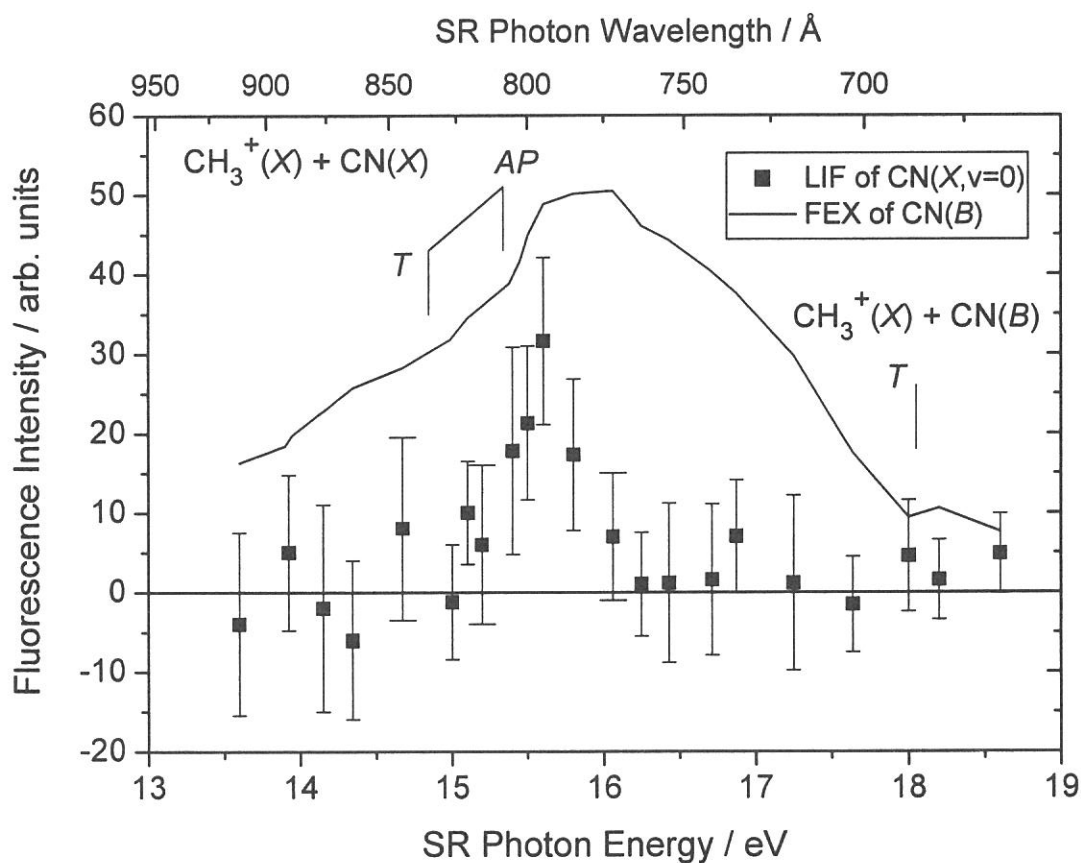


Fig. 1. LIF signal intensity (\blacksquare) of the $\text{CN}(X^2\Sigma^+, v_X = 0)$ fragment produced from CH_3CN plotted against the photon energy of synchrotron radiation. The solid curve represents the fluorescence excitation spectrum of CH_3CN for the $\text{CN}(B-X)$ emission. In both cases, the $(X^2\Sigma^+, v_X = 1) \leftarrow (B^2\Sigma^+, v_B = 0)$ transition was monitored. The thermochemical thresholds (T) for the dissociative ionization of CH_3CN and the appearance potential (AP) of CH_3^+ are indicated.

(BL3A2)

UV and Visible Emission Spectra from Photodissociation of Carbonyl Sulfide Using Synchrotron Radiation at 15 – 30 eV

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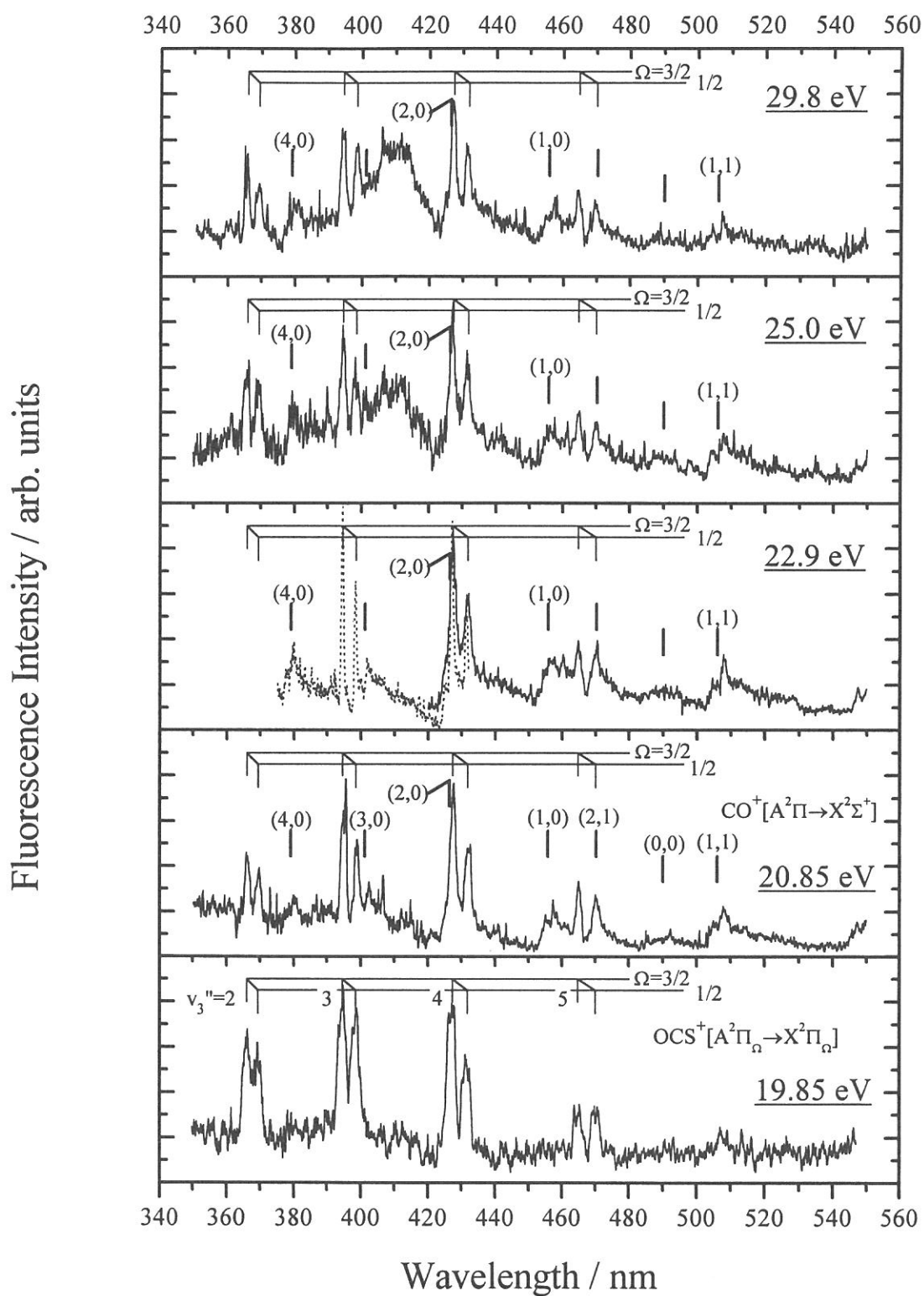
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Photofragmentation of OCS in the excitation photon energy range of 15 – 30 eV has been studied by dispersed fluorescence spectroscopy using monochromatized undulator radiation supplied from the UVSOR facility. The following emission band systems have been identified: $\text{OCS}^+[A^2\Pi_{\Omega}(0,0,0) \rightarrow X^2\Pi_{\Omega}(0,0,v_3'')]$, $\text{CO}^+(A^2\Pi_{\Omega} \rightarrow X^2\Sigma^+)$, $\text{CS}^+(B^2\Sigma^+ \rightarrow A^2\Pi_{\Omega})$, and $\text{CO}(a^3\Delta \rightarrow a^3\Pi)$. All the transitions except $\text{OCS}^+[A^2\Pi_{\Omega} \rightarrow X^2\Pi_{\Omega}]$ are newly obtained from photodissociation of OCS in the vacuum UV region. The fluorescence excitation spectra for the $\text{OCS}^+[A^2\Pi_{\Omega}(0,0,0) \rightarrow X^2\Pi_{\Omega}(0,0,v_3'')]$ and $\text{CS}^+(B^2\Sigma^+ \rightarrow A^2\Pi_{\Omega})$ transitions were measured in the photon energy range of 15.1 – 15.75 and 21.8 – 26 eV, respectively. The emission spectra obtained at 20.85 and 22.9 eV exhibit atomic transitions of $\text{S}[nd^3D^{\circ} \rightarrow 4p^3P^{\circ} (n=6-9)]$ which result from neutral dissociation of superexcited Rydberg states of OCS into $\text{S}(nd^3D^{\circ}) + \text{CO}$. Possible excited states of the counterpart CO were discussed on the basis of the difference in the n distribution between the two spectra.

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Fig. 1. Dispersed fluorescence spectra of OCS encompassing the wavelength region of 360 – 530 nm at five photon energies between 19.85 and 29.8 eV. All spectra were measured by using the imaging spectrograph equipped with a 600 grooves/mm grating which has a nominal blaze wavelength of 500 nm. A 1200 grooves/mm grating with a nominal blaze wavelength of 300 nm was employed to obtain the dashed curve in the panel of $E_{\text{hv}} = 22.9$ eV. The entrance slit width of the imaging spectrograph was set to 500 μm at $E_{\text{hv}} = 19.85$ eV and 250 μm at the other four photon energies. The thin vertical lines indicate a vibrational progression in the antisymmetric stretch v_3 mode of the $\text{OCS}^+[A^2\Pi_{\Omega}(0,0,0) \rightarrow X^2\Pi_{\Omega}(0,0,v_3'')]$ transition with $v_3'' = 2 - 5$. The number of the excited quanta are given in the panel of $E_{\text{hv}} = 19.85$ eV. Each vibrational band is split into two spin-orbit components specified with $\Omega = 3/2$ and $1/2$. The thick vertical lines indicate the band origins of the $\text{CO}^+(A^2\Pi_{\Omega}, v' \rightarrow X^2\Sigma^+, v'')$ emission band system. The (v', v'') mark denotes the vibrational band due to the upper vibrational state v' and the lower state v'' .



(BL3B)

Superexcitation and Subsequent Decay of Triatomic Molecules Studied by Two-Dimensional Photoelectron Spectroscopy

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Photoionization and photodissociation processes of SO₂ and CS₂ in the vacuum UV are studied by using two-dimensional photoelectron spectroscopy with a monochromatized synchrotron radiation source. The principal focus is on the mechanisms of autoionization and neutral dissociation of superexcited states. Photoelectron spectra of SO₂ exhibit characteristic peaks at the electron kinetic energy below 1.8 eV which are assigned as resulting from autoionizing transitions of excited atomic sulfur, S*, into the ground S⁺(⁴S^o) state. These S* atoms are in the singlet Rydberg states converging to S⁺(²D^o). The precursor molecular states, SO₂^{*}, are considered to be multiple-electron excited Rydberg states lying at the photon energy above ~22 eV. The onset of the photoelectron yield due to the atomic autoionization accords with that expected from the thermochemical threshold for the formation of S* through three-body dissociation SO₂^{*} → S* + O + O. The two-dimensional photoelectron spectrum of CS₂ provides tangible evidence for the formation of a dipole-forbidden Rydberg state (6σ_g)⁻¹(3dσ_g)¹ ¹Σ_g⁺ at the photon energy of 14.88 eV which autoionizes into the ν₃ = 1 vibrational state of the antisymmetric stretch ν₃ mode of CS₂⁺ (*X*²Π_{g,Ω}, Ω=1/2 and 3/2). This Rydberg state is expected to borrow substantial oscillator strength from the (6σ_g)⁻¹(5pσ_u)¹ ¹Σ_u⁺ state through vibronic coupling involving the ν₃ vibration.

Reference

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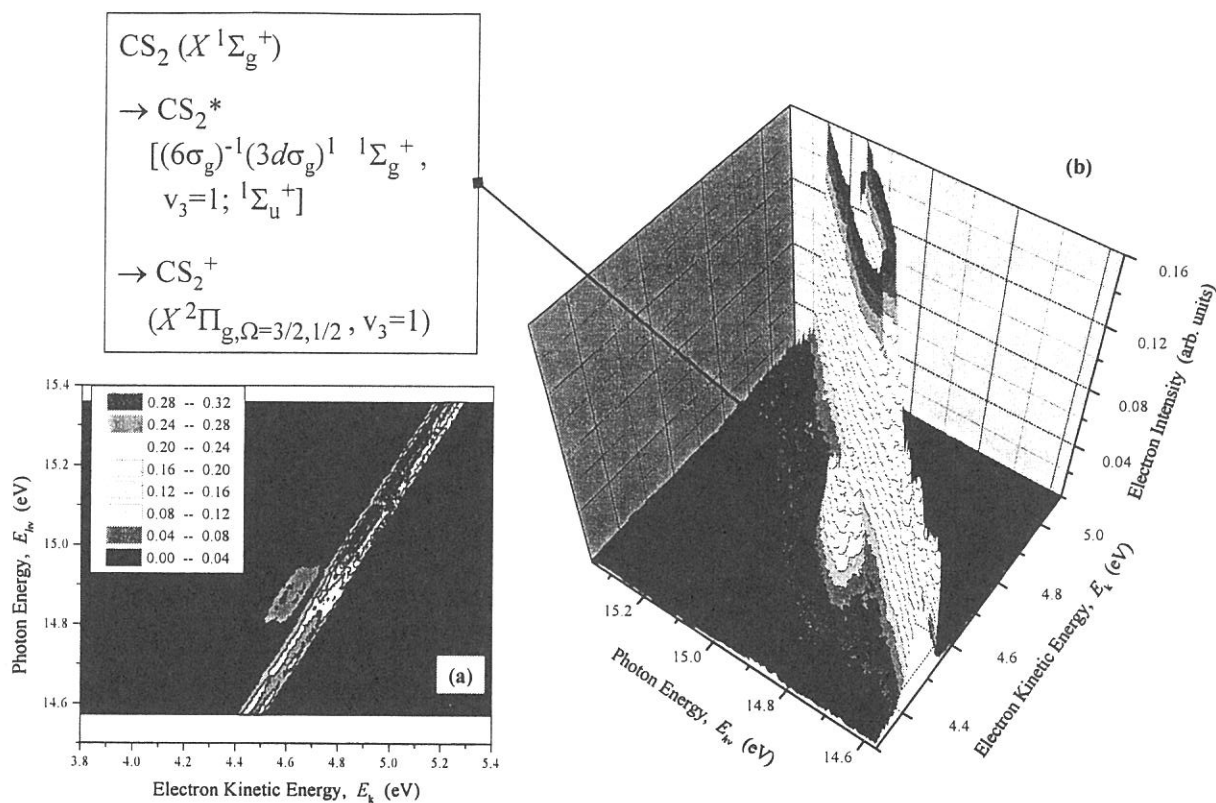


Fig. 1. (a): Two-dimensional photoelectron spectra of CS_2 in the photon energy range of 14.57 – 15.36 eV. The photoelectron yield, measured as a function of both photon energy $E_{h\nu}$ and electron kinetic energy E_k , is presented by the contour plots filled with 8 different colors according the photoelectron intensity on the plot. The photon wavelength resolution is 0.8 Å, which corresponds to 15 meV at $E_{h\nu}=15.0$ eV. The energy resolution of the analyzer is set to 40 meV. The spectrum is taken at wavelength intervals of 0.3 Å. The diagonal stripes at $I_E = E_{h\nu} - E_k = 10.08$ and 10.13 eV are identified as direct ionization and/or autoionization into the spin-orbit components ($\Omega=3/2$ and $1/2$, respectively) of the vibrational ground state of $\text{CS}_2^+ (X^2\Pi_{g,\Omega})$.

(b): Surface plot mapped with 16 differently-colored bands according the electron intensity on the surface. This plot is gained by converting the contour plot in panel (a).

(BL4B)

Symmetry resolved photoabsorption spectra of N₂ in the K-shell excitation region

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In order to identify the symmetries of molecular inner-shell excited states, polarization dependent studies have been widely applied to both chemisorbed and free molecules. The photodissociating molecules produced by a subsequent Auger decay of the K-shell vacancy are not isotropically distributed in relation to the exciting radiation, because the absorption probability is greatest when the transition dipole moment is aligned with the electric vector of the incident radiation. Since the lifetime of the molecular inner-shell excited state is much shorter than the molecular rotation period, the angular distribution of the fragments should show a corresponding anisotropy. For diatomic molecules, the measurements of the energetic fragment ions emitted parallel and perpendicular to the electric vector of the incident light achieve complete symmetry resolution between the $\Delta\Lambda=0$ (parallel) and $\Delta\Lambda=1$ (perpendicular) transitions [1].

The angle-resolved photoion measurements were performed on the newly constructed beamline BL4B, equipped with a varied-line-spacing plane grating monochromator. Two identical ion detectors with retarding grids were used to detect energetic photoions (>5 eV) emitted at 0° and 90° relative to the electric vector of the incident light. The $\Delta\Lambda=0$ component spectrum (I_0) and $\Delta\Lambda=1$ component spectrum (I_{90}) were obtained by counting the signals from the 0° and 90° positioned detectors, as a function of the photon energy, respectively.

The symmetry-resolved nitrogen K-edge photoabsorption spectra of N₂ measured with a monochromator bandpass of 0.4 eV are shown in Fig. 1. It is clear that the obtained I_0 and I_{90} spectra nicely demonstrate the symmetry decomposition of the conventional photoabsorption spectrum. Fig. 2 shows the high-resolution symmetry-resolved photoabsorption spectra, with a monochromator bandpass of 0.08 eV, in the so-called double excitation region. The I_{90} spectrum exhibits three broad bands centered around 411, 415, and 419 eV, which have not been of interest so far. The strongest band displays fine structures, which have been attributed to the double excitations tentatively. The structure just above the threshold has recently been found [2] and assigned to the double excitations. No special attention has been paid to the band detected at the shape resonance position in the I_{90} spectrum. In the I_0 spectrum, a very weak shoulder on the left-hand side of the shape resonance enhancement can be seen, which may be due to the double excitations having Σ symmetries. The detailed theoretical analyses on such double excitations are now in progress.

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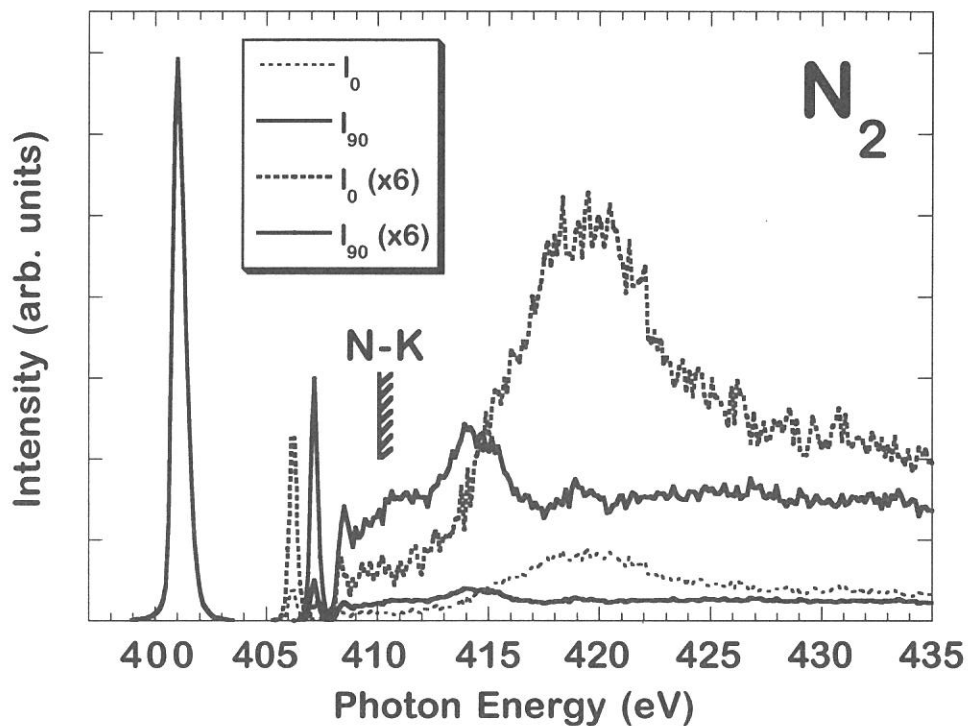


Fig. 1. Symmetry-resolved *K*-shell photoabsorption spectra of N₂.

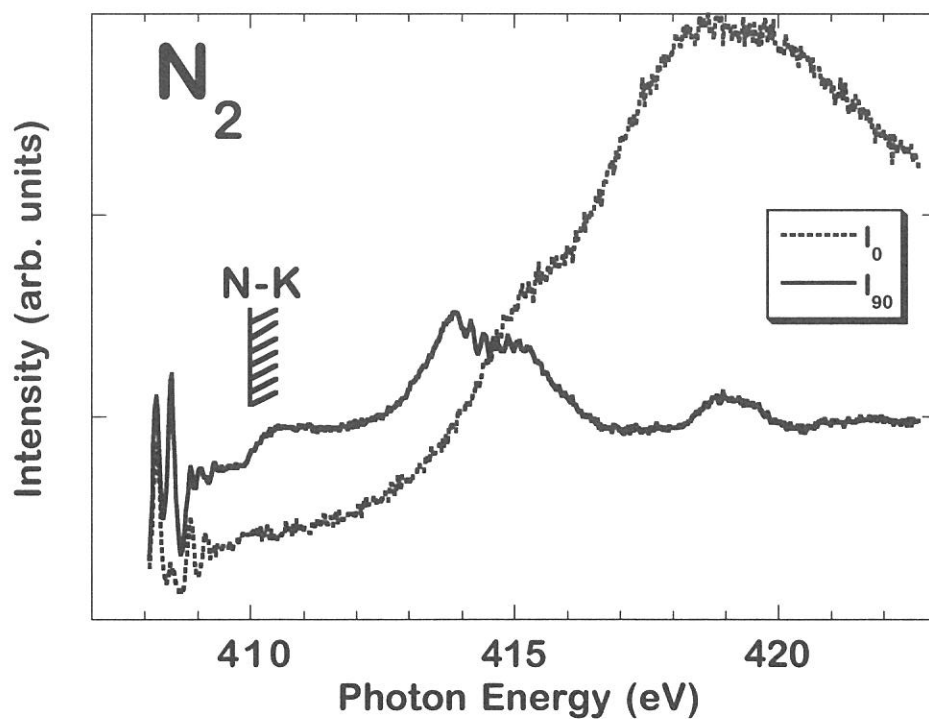


Fig. 2. High-resolution symmetry-resolved *K*-shell photoabsorption spectra of N₂.

(BL8B1)

Study on dissociation dynamics of core-excited acetonitrile using Auger electron-photoion-photoion coincidence measurements

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Auger electron-photoion(-photoion) coincidence (AEPI(PI)CO) measurement is a powerful tool to investigate dissociation dynamics of core-excited molecules. However, few AEPI(PI)CO results for complex organic molecules have been reported. We have measured AEPI(PI)CO spectra of acetonitrile- d_3 (CD_3CN) for the $N1s \rightarrow \pi^*$ excitation ($h\nu \sim 400$ eV) at the soft X-ray beamline BL8B1 of UVSOR by using a cylindrical mirror analyzer (CMA) and a high-resolution time-of-flight mass spectrometer. Electrons and ions are extracted by a weak electrostatic field (40 V/cm). Energy resolution ($E/\Delta E$) of the CMA is about 40.

The resonant Auger spectrum of CD_3CN obtained under the present experimental conditions has two broad maximum at around 378 and 360 eV and a shoulder at around 345 eV. A remarkable dependence on Auger-electron energy is observed for the formation of CD_2CN^{2+} , which is only one doubly charged ion among observed ion species. The AEPICO yield spectrum of CD_2CN^{2+} as a function of the Auger-electron energy has a maximum well coincide with the second maximum (~ 360 eV) of the resonant Auger spectrum. This unique doubly-charged CD_2CN^{2+} ion may be produced efficiently by autoionization and subsequent D atom elimination from the singly-charged parent ions in Auger-final states with ~ 40 eV binding energy, because this energy is slightly higher than the threshold of doubly-charge parent ion (CD_3CN^{2+}) which is estimated to be ~ 33 eV from the normal AEPICO spectrum.

A part of the AEPICO 2D-coincidence maps of CD_3CN at $N1s \rightarrow \pi^*$ excitation for different Auger-electron energies ($E_{AE} = 360$ eV and 345 eV) are shown in Fig. 1. As shown in Fig. 1(a), the resonant-Auger-final states with low binding energy (~ 40 eV) mainly lead to dissociation into ($\textcircled{1}C_2D_3^+ + N^+$) and ($\textcircled{2}CD_3^+ + CN^+$) by single bond-cleavage. Two-body dissociation to ($\textcircled{3}CD_2^+ + DCN^+$) with rearrangement is also observed. On the other hand, for the higher binding energy (~ 55 eV, Fig. 1(b)) multiple bond-cleavage is enhanced, and ion-pairs like ($\textcircled{4}CD_3^+ + C^+$) and

(C₂⁺+N⁺) are formed. The slope of the contour of coincidence peaks for the two-body dissociations (①~③) is -1, while that of (④CD₃⁺+C⁺) peak is about -2. This value is in good agreement with the calculated value of -2.17 for the assumed sequential dissociation process as following.

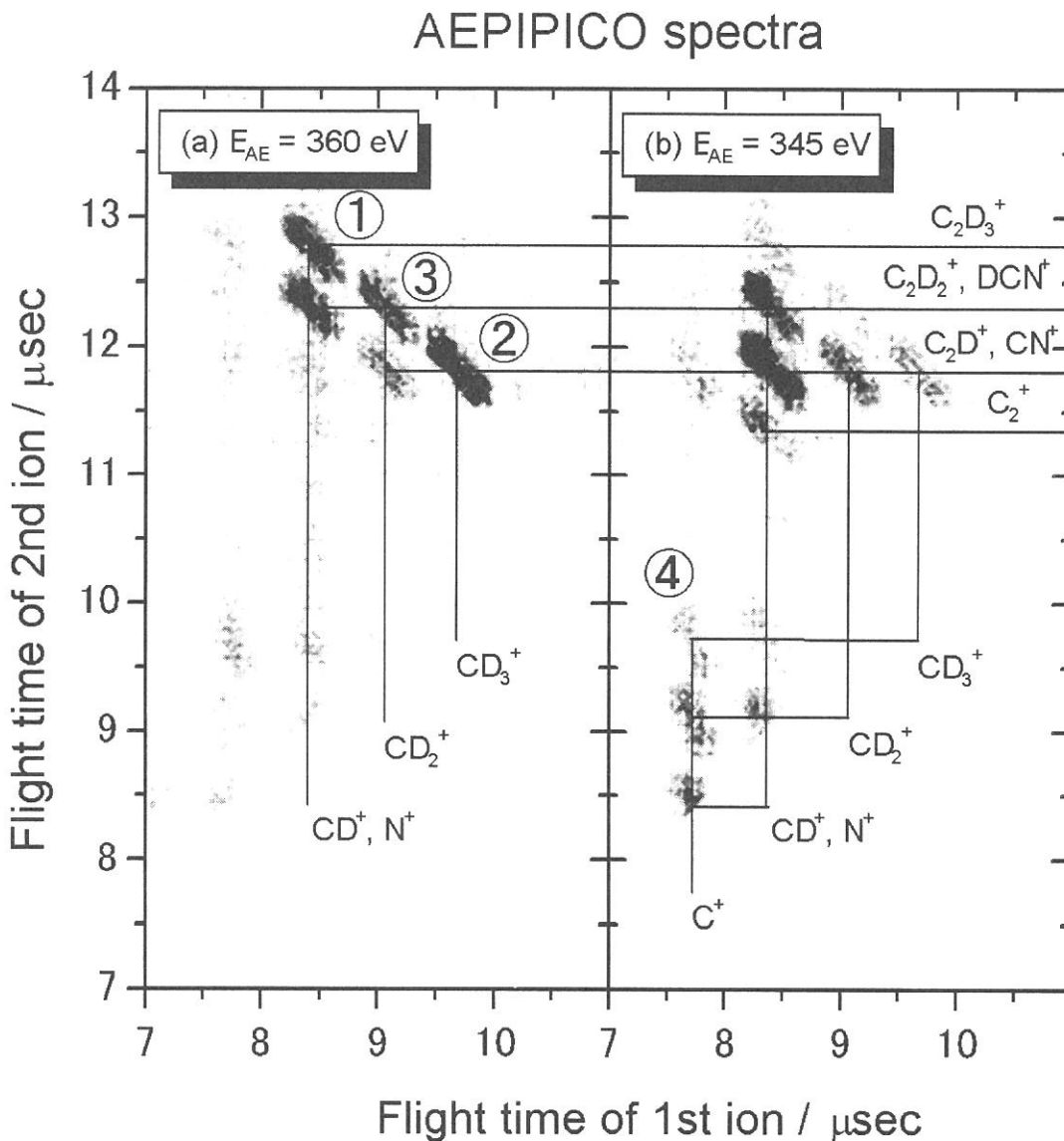


Fig.1 AePIPICO 2D-coincidence maps of CD₃CN at N1s π^* excitation for different Auger-electron energies ((a)E_{AE} = 360 eV and (b)345 eV).

(BL8B1)

Angle-, energy- and mass-resolved photofragmentation of the N and C *K*-shell excited CF₃CN molecule

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When an inner-shell electron of a molecule is photoexcited, a multiply ionized molecule is formed through Auger decays. The Coulomb explosion in this multiply charged molecular ion follows the loss of bonding electrons. One of the goals in the studies of inner-shell photoexcitation dynamics is to develop a more detailed understanding of the electronic relaxation and fragmentation processes and, applicably, to take advantage of the localized nature of the core hole to induce a specific bond rupture in a molecule. Inner-shell electrons of an atom in a specific chemical environment can be selectively excited with a monochromatized soft x-ray synchrotron radiation, because the energy levels of the inner-shell electrons differ from one atom to another. The dynamics can be probed by the measurement of mass, angular, and kinetic energy distributions of the fragment ions [1].

Trifluoroacetonitrile (CF₃CN) is one of the intriguing molecules in two respects. Firstly, we can selectively excite a specific atom (F, N or either C). Fluorine is the most electronegative atom and induces the largest chemical shift around it in a molecule. Secondly, we can investigate the fragmentation dynamics of the inner-shell excited molecule noticing the linearity of the C–C≡N skeleton. Whether anisotropic fragmentation can be observed in the polyatomic molecule is our concern here. Thus, in the present study we investigate the angle-resolved time-of-flight (TOF) mass spectra of the N and C *K*-shell excited CF₃CN molecule.

The experiments were performed on the beamline BL8B1 at UVSOR facility. Photoabsorption spectra were observed at room temperature in the N and C *K*-shell regions with the typical energy resolution $E/\Delta E$ of 2000–4000. An ion chamber with two 10-cm long electrodes was used. The photon beam entered through an Al thin filter. The ion current was fed to a picoammeter and stored in a personal computer, together with the pressure of the sample CF₃CN gas monitored with a capacitance manometer. The photon energy was calibrated using the published soft x-ray peaks, i.e., the π^* resonance transitions of N₂ and CO at 401.0 and 287.3 eV, respectively [2].

The TOF mass spectra were also measured at the several prominent resonance peaks observed. An energy resolution of about 1 eV was employed for the measurement. The sample gas was introduced into the main experimental chamber as an effusive molecular beam through a gas nozzle which is mounted orthogonal to both the photon beam axis and the TOF mass spectrometer tube. An Al thin filter was inserted upstream in order to suppress the scattered stray light. The pressures in the chamber during the measurements were kept 1×10^{-5} Torr. The spectrometer was operated under a Wiley–McLaren space-focusing condition [3] with an extraction field of –250 V/cm. This extraction field results from a proper compromise between the sensitivity to the angular distributions and the moderate coincidence count rate of the photofragment ions. Detection of an electron defines the time zero of the TAC for the TOF mass

spectrum. The TOF mass spectra were acquired at 0° and 90° angles with respect to the linearly polarized electric vector of the incident photon. The sample gas for the present study was purchased from SynQuest Laboratories, Inc. and was used without further purification.

The earlier studies of inner-shell photoexcitation dynamics of diatomic molecules have clearly shown that an anisotropic photofragmentation is characteristically observed at the photon energy corresponding to the excitation of a $1s$ electron into the π^* unoccupied molecular orbital. Figure 1 shows the enlarged TOF mass spectra recorded at the $\pi^* \leftarrow C_N(1s)$ resonance excitation of CF_3CN . In these spectra the contribution of background originating from the ionization of valence electrons was subtracted by the measurement of the spectra at around 283 eV. It is noteworthy that the peaks of CN^+ and CF_3^+ observed at the 90° angle distinctly split into triplets: The central peak is formed by the ions with almost zero or small kinetic energies, while the wings in the lower- and the higher-mass regions arise from the fragment ions with kinetic energies initially toward and away from the TOF tube, respectively. Similar spectra were obtained at the $\pi^* \leftarrow N(1s)$ excitation.

The profiles of CN^+ , CF^+ , and CF_3^+ peaks were reproduced by the fitting method developed by Saito and Suzuki [4]. The results are also shown in Fig. 1. The CN^+ and CF_3^+ ions are produced by typical $\Pi-\Sigma$ transition, which means that the symmetry basically holds also for the relatively large CF_3CN molecule. The anisotropy parameters for CN^+ were found to be +0.10, -0.57 , and -0.85 for kinetic energies 0.01–0.41, 0.67–3.61, and 4.33–6.86 eV, respectively. More distinct results were obtained for the $N(1s)$ excitation.

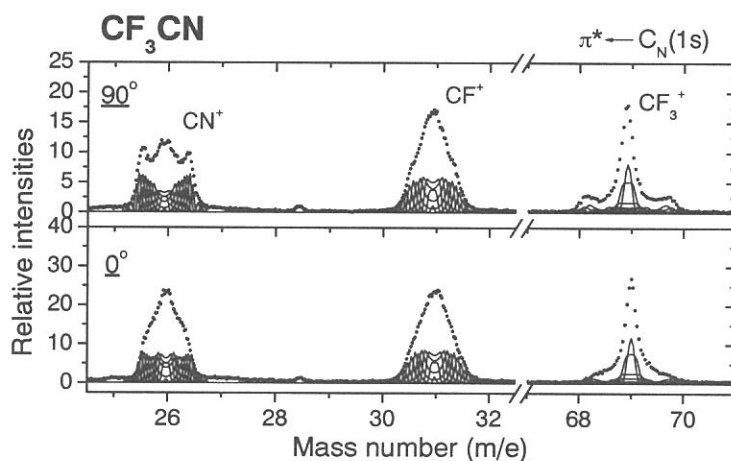


Fig. 1: Experimental and simulated angle-resolved TOF mass spectra recorded at the $\pi^* \leftarrow C_N(1s)$ resonance excitation of CF_3CN . The dots indicate the experimental data. The solid curves are the simulated profiles for the kinetic energy components of 0.01–6.86, 0.01–6.86, and 0.01–3.17 eV for CN^+ , CF^+ , and CF_3^+ ions, respectively.

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(BL8B1)

Study on dissociation dynamics of core-excited acetone using Auger electron-photoion-photoion coincidence measurements

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To elucidate the detail of the core-excited dissociation processes of organic molecules, especially those from the dicationic states produced after Auger decay, Auger electron-photoion-photoion coincidence (AEPIPICO) method has been applied to acetone. Correlations between different ions produced by an Auger process are recorded in a fast multiscaler, by using the signal of an energy-selected resonant Auger electron as a start signal and the ion signals as multi-stop signals. AEPIPICO signals at the O 1s to π^* resonance, from where only singly charged ionic states is formed by Auger decays, were observed at the lower Auger electron energy side. When the energy of resonant Auger final state is higher than the threshold of dication formation, autoionization channels to form dication states and therefore dissociation to form ion-pairs become possible. By selecting the energy of Auger electron, it is found that only a unique ion-pair CH_3^+ and CH_3CO^+ is produced from the ground state of acetone whereas various ion-pairs such as " $\text{H}_3\text{C}_3^+ - \text{O}^+$ " and " $\text{CH}_3^+ - \text{CH}_3\text{C}^+$ " are produced from the excited states (see Fig.1).

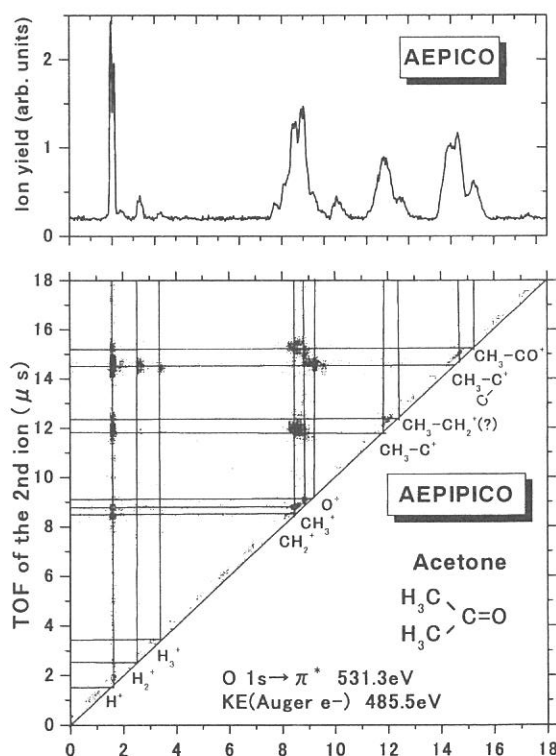


Fig.1 AEPIPICO spectra of $(\text{CH}_3)_2\text{CO}$ at O1s π^* excitation for the Auger-electron energy of 485.5 eV.

(BL8B1)

Details of H_3^+ Formation from Core-Excited Methanol Revealed by Electron-Ion-Ion Coincidence (PEPIPICO) Measurements.

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A number of researches on the dissociation processes of core-excited molecules have been carried out extensively. In those studies, PEPIPICO (Photoelectron-Photoion-Photoion Coincidence) technique was used as the powerful tool to investigate the ionic dissociation from doubly or highly charged molecular ions. However, there are only a few reports applying this technique to complex organic molecules [2]. To investigate ionic dissociation processes of core-excited organic molecules, especially the molecular elimination process to form H_3^+ , high mass-resolution PEPIPICO measurements were performed for methanol CH_3OH and CD_3OH .

Measurements were carried out at BL8B1 of UVSOR using the reflectron time-of-flight (RTOF) mass spectrometer [1], which is featured by a high-mass resolution for fragment ions with kinetic energies of several eV while preserving kinetic energy information of the fragment ions.

Figure 1 shows the PEPIPICO and PEPIPICO spectra of methanol- d_3 (CD_3OH) measured at 544 eV, 4.9 eV above the O 1s ionization threshold (539.1 eV) [5], with using a moderate extraction field (200 V/cm) and the linear TOF mode. In the PEPIPICO spectrum, D_3^+ is clearly observed with partial yield of 0.6 %, while D_2H^+ is not discernible. From the present result for CD_3OH , it can be concluded that the dominant reaction pathway to form H_3^+ from core excited $CH(D)_3OH$ is the $H(D)_3$ elimination from the methyl group.

PEPIPICO spectra of methanol plotted as the correlation of second-ions to each first-ions are shown in Fig. 2. The spectra reveal that H_3^+ ion is formed exclusively with COH^+ , and CH_3^+ with OH^+ . Another strong correlation is observed for CH_x^+/OH_y^+ ion pairs ($x=0-3, y=0,1$), in which x and y has negative correlation. This results suggests that the two type of ion-pairs, CH_3^+ and OH^+ ion-pair formed by single C-O bond scission without further C-H bond scissions and completely cracked (C^+ and O^+) ion-pair formed with further C-H bond scission(s), originate from different dissociation channels, possibly different Auger final states.

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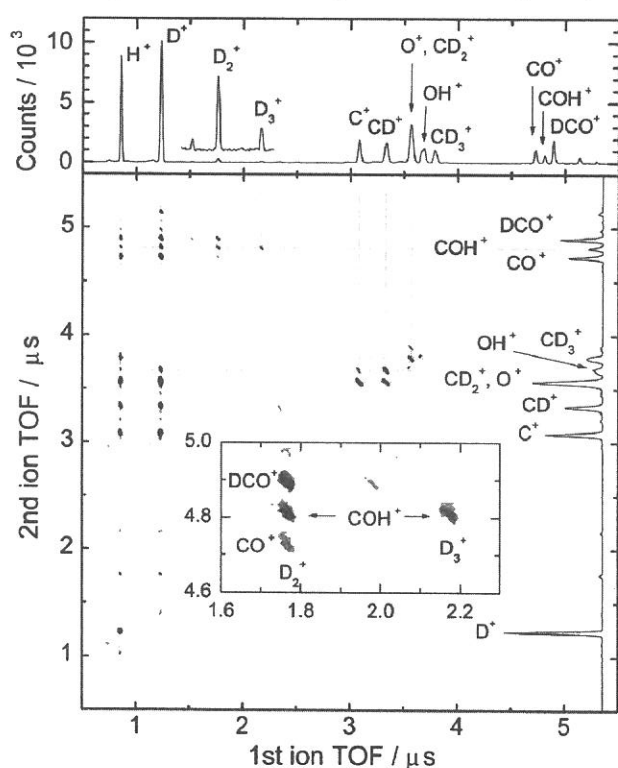


Fig. 1. PEPIPICO (top) and PEPIPICO spectra of CD_3OH measured at the O1s ionization. Inset shows the mass region of the first ions $D_2^+ - D_3^+$ and the second ions $CO^+ - DCO^+$.

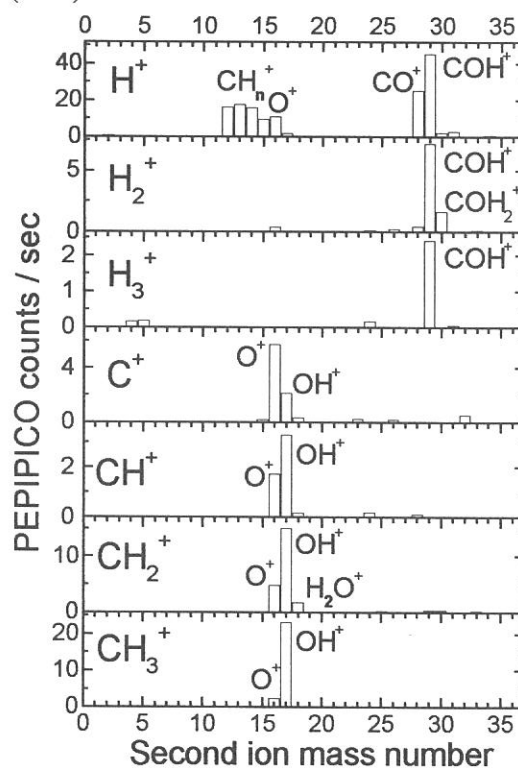


Figure 2. Electron-ion-ion correlation spectra plotted for each first-ion, obtained by the O1s excitation to the ionization continuum of CH_3OH .

