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Dissociative photoionization of CF₄ from 23 to 120 eV

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Using synchrotron radiation as a continuum light source, dissociative photoionization of CF₄ has been studied in the photon-energy region of 23-120 eV. The data were measured at UVSOR, Okazaki. Ion branching ratios were obtained by analyzing time-of-flight (TOF) mass spectra and were converted to the absolute cross sections for the production of singly charged CF₃⁺, CF₂⁺, CF⁺, F⁺, and C⁺ ions as well as doubly charged CF₃²⁺ and CF₂²⁺ ions by using the reported total absorption cross sections¹ of CF₄.

TOF mass spectrometers are widely used to measure the ion branching ratios. However, it is not easy to measure ion branching ratios accurately at excitation energies where molecular and dissociative single and double photoionization take place concomitantly. Usually, the photoelectron signal is used as a start pulse for a time-to-amplitude converter (TAC) and the ion signal provides the stop pulse. With this arrangement, the different numbers of ejected electrons in single and double photoionization cause an overestimation of the number of the ions produced in double photoionization because the probability of forming one output pulse in the electron detector is higher for two electrons hitting simultaneously than that for one electron. This problem was overcome by using the rf signal of the storage ring as the start signal of the TAC.² Another problem is that when dissociative double photoionization occurs (e.g., CF₄²⁺ → F⁺⁺CF₃⁺), the heavier ion (CF₃⁺) is not counted if the ion-detection efficiency is high. This is because the lighter F⁺ ion stops the TAC. Since the ion-detection efficiency in the present study is of the order of a few percent, the heavier ion is detected with almost the same efficiency as the lighter ion.

The ion branching ratios are shown in Fig. 1 and the partial cross sections for the observed ions in Fig. 2. The absolute partial cross sections were obtained by the following equation:

$$\sigma_j(E) = [N_j(E) / \sum N_j(E)] Y(E) \sigma_t(E),$$

where σ_j is the partial cross section for a specific ionization process that produced the ion j , N_j is the number of ions of type j , $N_j(E)/\sum N_j(E)$ is the branching ratio, Y is the ionization yield (the number of ions produced/the number of photons absorbed in unit time), and σ_t is the total absorption cross section. Although the ionization yield in the region of dissociative double ionization is usually greater than unity, the yield in this region is not known at present and was assumed to be unity throughout the energy region studied. The overall agreement between the present data (●) and those of Brion *et al.*¹ (□) is excellent. Ion branching ratios were differentiated with respect to the incident photon energy. The results obtained by this analytical photoion spectroscopy show dissociation pathways of the CF₄⁺ and CF₄²⁺. These pathways will be discussed elsewhere by comparing them with the reported electronic states of the ions.

References

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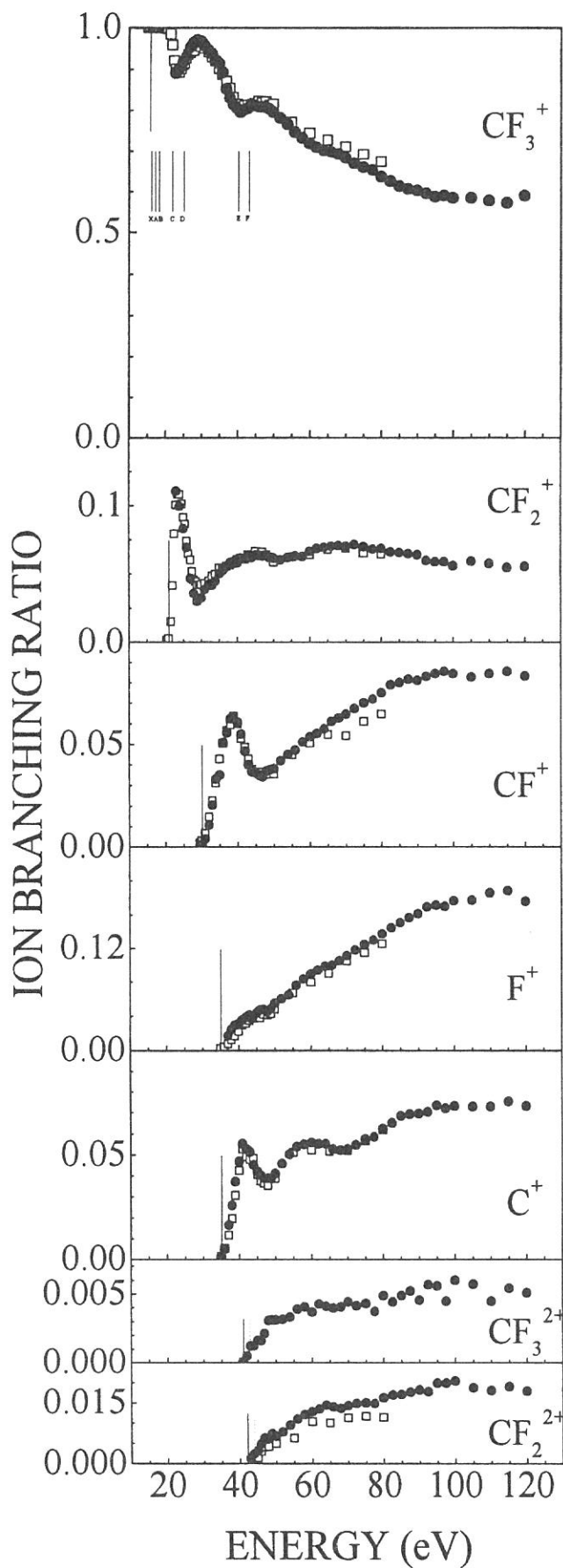


Fig. 1. Ion branching ratios of CF_4 . \bullet , present data; \square from Ref. 1.

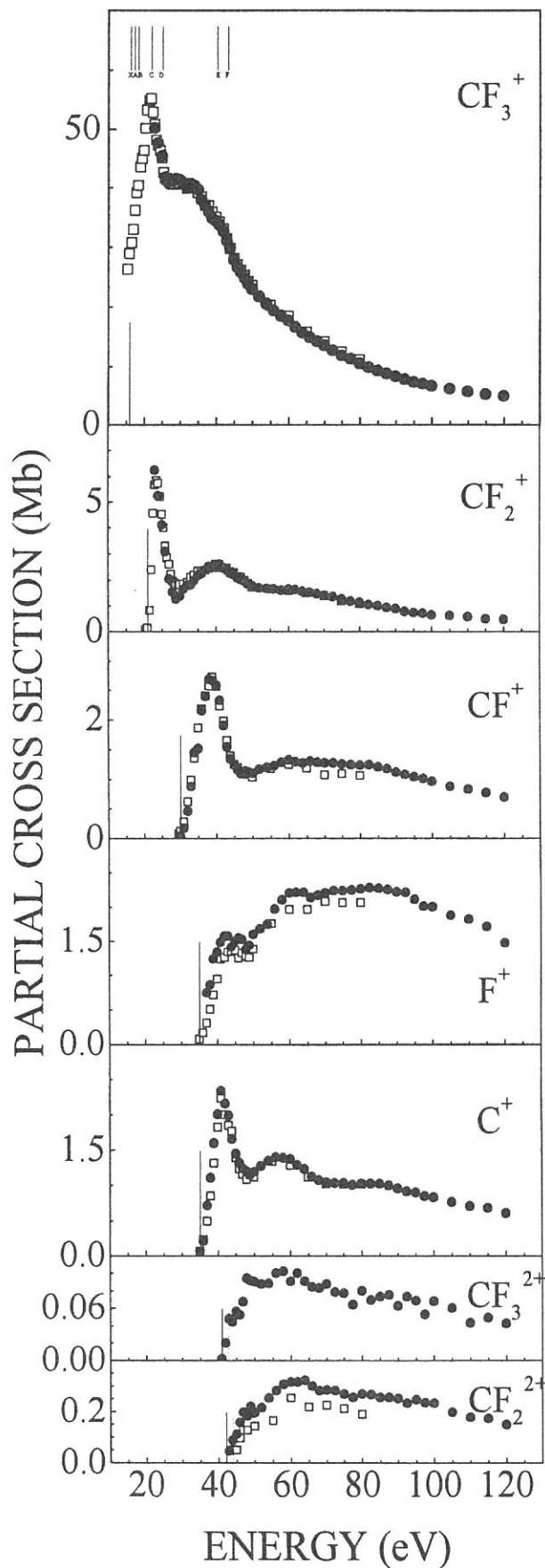


Fig. 2. Partial cross sections for the production of the observed ions.

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Angular Distribution of Ionic Fragments in the Dissociation of SO_2^{2+}

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Photoion-photoion coincidence (PIPICO) technique has been used to measure the angular distributions of $\text{O}^+ + \text{SO}^+$ and $\text{O}^+ + \text{S}^+$ fragments in the dissociative double photoionization of SO_2 in the 37-120eV region with linearly polarized synchrotron radiation.

For electric dipole transitions induced by linearly polarized radiation, the transition probability depends on the orientation of molecules with respect to the direction of polarization of the incident light, consequently this dependence gives rise to the anisotropic orientation of the molecular axes even though the distribution of the ground state molecules is isotropic. Therefore, the angular distributions of ionic photofragments provide detailed information on ionization and dissociation dynamics in terms of the symmetry of the dissociating parent states involved as well as the ejected electrons.

For molecules of cylindrical symmetry, asymmetry parameter β characterizing the angular distribution of the photofragments is given by the expression:

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left(1 + \frac{\beta}{4} [1 + 3p \cos(2\theta)] \right),$$

where σ corresponds to the double ionization cross section, and the molecular axis is oriented along the direction Ω . θ is the angle between the molecular axis and the polarization of the incident light, or equivalently the angle between the direction of photofragment detection and the polarization direction. p is the degree of polarization of the light. In the present case, $p = 0.9$ was assumed.

According to the fact that, even though a molecule dissociates with any value of the asymmetry parameter, the PIPICO spectrum of the fragments detected at the magic angle of 54.7° gives the same profile as that of the isotropic dissociation ($\beta = 0$), the kinetic energy distribution for a given photon energy is derived from the PIPICO spectrum at the detection angle of 54.7° by simulating the spectrum with $\beta = 0$. With the kinetic energy distribution thus obtained, the PIPICO spectra taken at two different detection angles ($\theta = 0^\circ$ and 90°) are simulated by treating β as the fitting parameter. Practically the β value is determined so as to minimize the difference between the measured and calculated profiles. It should be mentioned here that in the present case the detection angle of 55° serves as "pseudo-magic angle" in the measurements where the angular dependence of the cross section almost vanishes. Energy variations of β thus derived are shown in Fig. 1 for $\text{O}^+ + \text{SO}^+$ and in Fig. 2 for $\text{O}^+ + \text{S}^+$.

In general, for a molecule undergoing a dipole transition involving a change of orbital angular momentum by +1 (Π transition), the transition moment is perpendicular to the dipole axis, which gives a β value of -1. On the other hand, for a transition involving no change in orbital angular momentum (Σ transition), transition moment is parallel to the dipole axis, which gives a β value of 2. Thus, for a mixed transition where multi-states are involved, each component will contribute to an angular distribution, which in turn means that an experimental value for β provides the intensity ratio between the Σ and the Π components.

The overall feature of β values is a slight change in positive and negative sense around $\beta = 0$ in the whole energy range, indicating that the fragmentation is isotropic in the both cases of $O^{++}SO^+$ and O^++S^+ . This shows a remarkable contrast to the results of CO_2^{2+} where the anisotropic fragmentation is dominant in the low energy range less than 80eV.

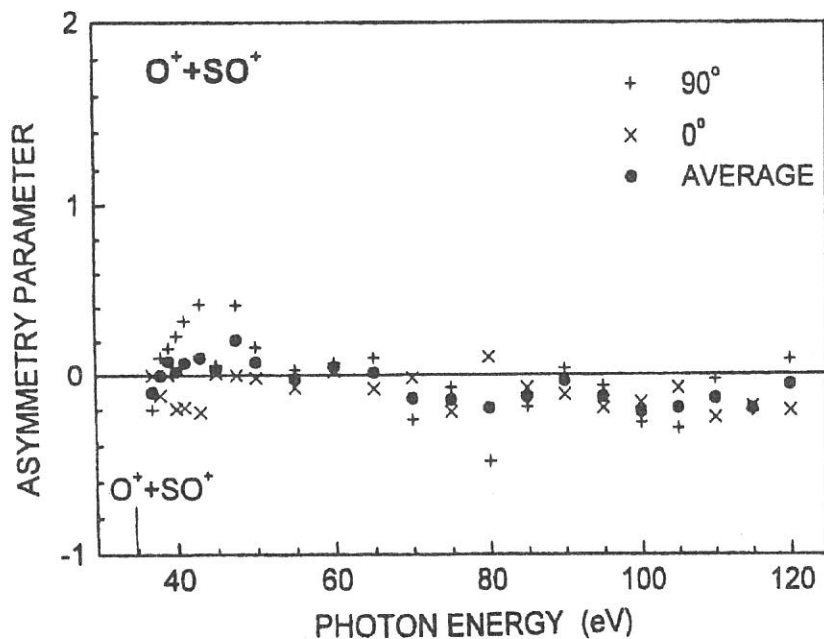


Fig. 1 The asymmetry parameter β for $O^{++}SO^+$ as a function of photon energy. The solid line marks the $\beta = 0$ isotropic reference. The averaged values are derived from the results at two different detection angles of 0° and 90° . See text in more details.

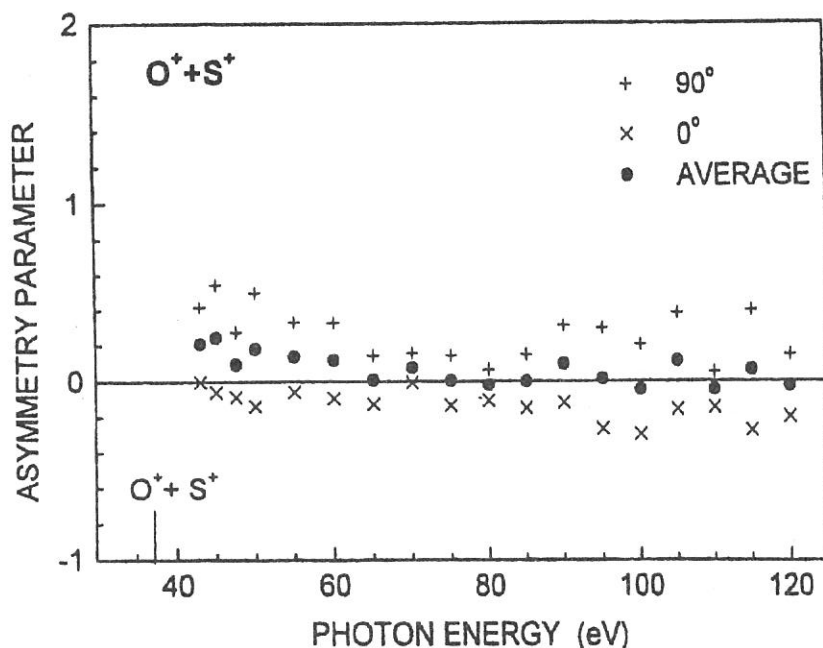


Fig. 2 The asymmetry parameter β for $O^{++}S^+$ as a function of photon energy. The solid line marks the $\beta = 0$ isotropic reference. As in the case of Fig. 1, the averaged values are derived from the results at two different detection angles of 0° and 90° . See text in more details.

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Laser Induced Fluorescence Excitation Spectroscopy of $N_2^+(X^2\Sigma_g^+, v=0)$ Produced by VUV Photoionization of N_2 — Rotational State-Resolved Spectrum

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The pump-probe experiment combining synchrotron radiation and a laser is expected to be a feasible method for probing ionic and neutral fragments resulting from VUV photoexcitation. We have developed laser induced fluorescence (LIF) excitation spectroscopy of products prepared by VUV excitation of gas phase molecules with synchrotron radiation.^{1,2)} Sample gases, N_2 and N_2O , expanded from a multi-capillary nozzle were photoionized with an undulator radiation supplied from the beam line 3A2. Formed $N_2^+(X^2\Sigma_g^+, v''=0)$ ions were excited to the $B^2\Sigma_u^+, v'=0$ state by irradiation of the second harmonic of a mode-locked Ti:sapphire laser, whose repetition rate is 90.115 MHz, and the fluorescence due to the transition ($B^2\Sigma_u^+, v'=0$) \rightarrow ($X^2\Sigma_g^+, v''=1$) was detected. The rotational temperature of $N_2^+(X^2\Sigma_g^+, v''=0)$ could be evaluated by simulating an LIF excitation spectrum. Previously, it had taken a long time for data acquisition because of an extremely low rate of fluorescence counts. The low count rate was considered to result from the short residence time of produced ions which escape from the laser-irradiation region in a few microseconds. Short residence time decreased the effective number density of N_2^+ ions. In order to lengthen the residence time we newly introduced a quadrupole RF ion trap composed of a central ring electrode and two end electrode.

The undulator radiation monochromatized by a grazing-incidence monochromator is introduced into an ion trap through one of 4 apertures which are equispaced on the side of the central ring electrode. The laser is introduced through the opposite aperture so as to counterpropagate the undulator light. The effusive beam of sample gas is injected through the other aperture and crosses perpendicularly with the two photon beams. The fluorescence from laser-excited N_2^+ is collected through an aperture drilled on the end electrode. A secondary monochromator equipped with a color filter glass is used to eliminate the scattering laser light. An RF voltage with an amplitude of 300 V_{P-P} and a frequency of 1 MHz is applied to the central ring electrode. The fluorescence count rate is 40 times as high as that without the ion trap. Data acquisition time is reduced to one tenth of the previous acquisition time.

Figure 2 shows an LIF excitation spectrum of the ($B^2\Sigma_u^+, v'=0$) \leftarrow ($X^2\Sigma_g^+, v''=0$) transition of N_2^+ which is prepared by photoionization of N_2 at the photon energy of the synchrotron radiation, $E_{SR} = 15.983$ eV. In the report of the fiscal year of 1997, the spectral resolution of the laser was set to about 15 cm^{-1} and the rotational structure of the ($B^2\Sigma_u^+, v'=0$) \leftarrow ($X^2\Sigma_g^+, v''=0$) transition cannot be resolved. In the present spectrum, the pulse duration of the laser is expanded and the spectral resolution is improved to about 1.7 cm^{-1} , though the laser intensity is a tenth as high as the previous set up. The rotational lines at wavelengths shorter than 391.15 nm are well resolved and assigned to transitions for the R branch. In contrast, the lines at longer wavelengths, which comprise the P branch, are overlapped with each other because the band-head lies in the P branch and

spacings between the lines are narrower than the spectral resolution.

The synchrotron radiation energy $E_{SR} = 15.983$ eV is equal to the resonance energy for the formation of $4d\sigma_g^{-1}\Pi_u$ state converging to $N_2^+(A^2\Pi_u, v=0)$. Hence, most N_2^+ ions are considered to be produced by autoionization of this Rydberg state. The LIF excitation spectrum is simulated on the assumption that the rotational temperature of $N_2(X^1\Sigma_g^+, v=0)$ is 300 K and the propensity rule of rotational excitation accompanied by autoionization, $K_{mol} = K_{ion}, K_{ion} \pm 1, \dots, K_{ion} \pm l$, where K_{mol} , K_{ion} and l denotes the total angular momentums apart from spin of neutral superexcited molecule, formed molecular ion and the orbital angular momentum of the ejected electron³⁾. The experimental spectrum is similar to that obtained by the simulation. Details of this simulation will be described in a forthcoming paper.

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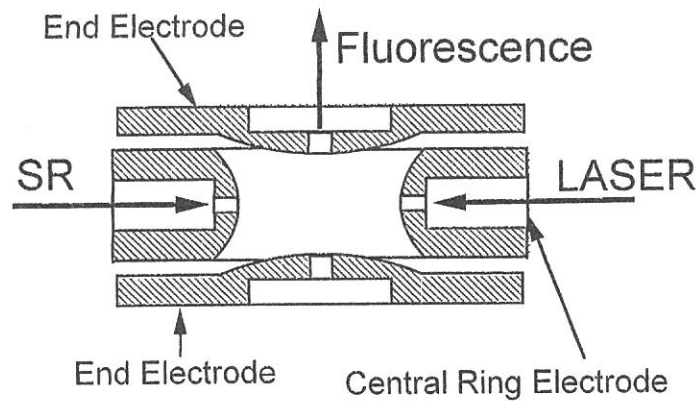


Figure 1. Schematic diagram of the ion trap.

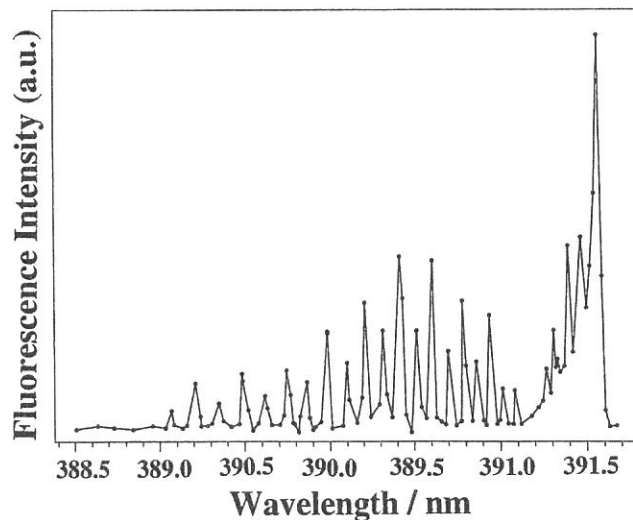


Figure 2. Laser induced fluorescence excitation spectrum of the $(B^2\Sigma_u^+, v'=0) \leftarrow (X^2\Sigma_g^+, v''=0)$ transition of N_2^+ which is prepared by photoionization of N_2 at $E_{SR} = 15.983$ eV. The monitored fluorescence is ascribed to the transition $(B^2\Sigma_u^+, v'=0) \rightarrow (X^2\Sigma_g^+, v''=1)$.

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Laser Spectroscopy of Neutral Fragments from Superexcited States Prepared by Synchrotron-Radiation Photoexcitation

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We have developed pump-probe spectroscopy making use of the combination of UV laser and synchrotron radiation to investigate the dynamics of neutral dissociation of superexcited molecules. For detecting neutral species, a resonance enhanced multiphoton ionization (REMPI) technique is invoked. The schematic experimental setup is shown in Fig. 1. Undulator radiation emitted from beamline BL3A2 of UVSOR is crossed perpendicularly with a molecular beam discharged from a pulsed nozzle. Produced ions are extracted toward electrode 1 by a retarding field between electrodes 1 and 2. A part of neutral fragments produced by VUV excitation are sampled through an aperture of electrode 2 and ionized by a frequency-doubled dye laser (1 - 2 mJ pulse⁻¹) focused with an $f = 500$ mm lens on the space between electrodes 2 and 3. Ions produced by (2+1)-REMPI of neutral fragments are detected with a quadrupole mass filter equipped with a channeltron electron multiplier.

We have measured a REMPI spectrum of $S(3s^23p^4\ ^3P_{j''},\ J'' = 0, 2)$ dissociated from superexcited states of OCS prepared by photoexcitation with undulator radiation (BL3A2, UVSOR) whose photon energy ranges from 13 to 17 eV. The spectral resolution of the second harmonic of a probe laser was estimated to be 0.003 nm. Figure 2 shows a REMPI spectrum of $S(3s^23p^4\ ^3P_2)$ atom as a function of the probe laser wavelength in the region including the two-photon transition, $S(3s^23p^35p\ ^3P_j) \leftarrow S(3s^23p^4\ ^3P_2)$. The undulator photon energy was fixed at 16.5 eV. The maximum at 269.290 nm is considered to comprise two peaks resulting from transitions from $S(3s^23p^4\ ^3P_2)$ to $S(3s^23p^35p\ ^3P_1$ and $^3P_2)$, though they are not separated because of a low signal-to-background ratio. As well as $S(3s^23p^4\ ^3P_2)$, we have observed the REMPI signal of $S(3s^23p^4\ ^3P_0)$ at 271.375 nm; this wavelength corresponds to a two-photon transition from $S(3s^23p^4\ ^3P_0)$ to $S(3s^23p^35p\ ^3P_0)$. Next, we fixed the laser wavelength at the maximum of the curve in Fig. 2, *i.e.*, 269.290 nm, and measured the REMPI signal intensity as a function of the energy of the undulator radiation in the range of 13 - 17 eV. The resultant spectrum is considered to represent a relative photodissociation cross section curve for the formation of $S(3s^23p^4\ ^3P_2)$ from OCS. Peak features existing at 13 - 16 eV and

16 - 17 eV are ascribed to the Rydberg series converging to the $B^2\Sigma^+$ and $C^2\Sigma^+$ states, respectively, of OCS^+ . In summary, we can obtain direct evidence for the first time for the formation of nonfluorescing and non-autoionizing neutral species dissociated from molecular superexcited states, by means of pump-probe spectroscopy combining synchrotron radiation and laser.

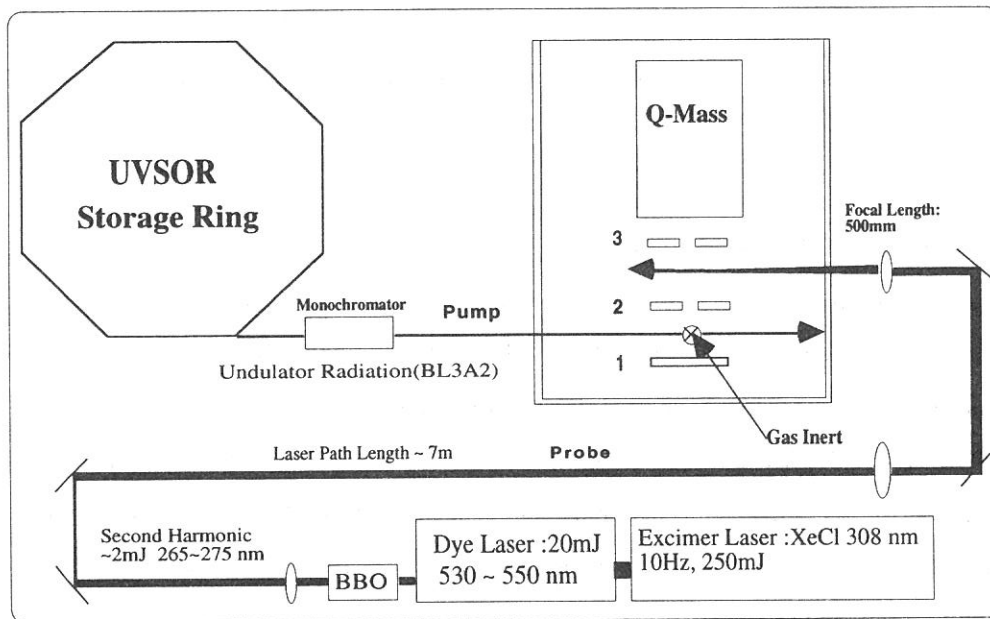


Figure 1. Schematic experimental setup for the REMPI spectroscopy of neutral fragments produced by synchrotron radiation excitation.

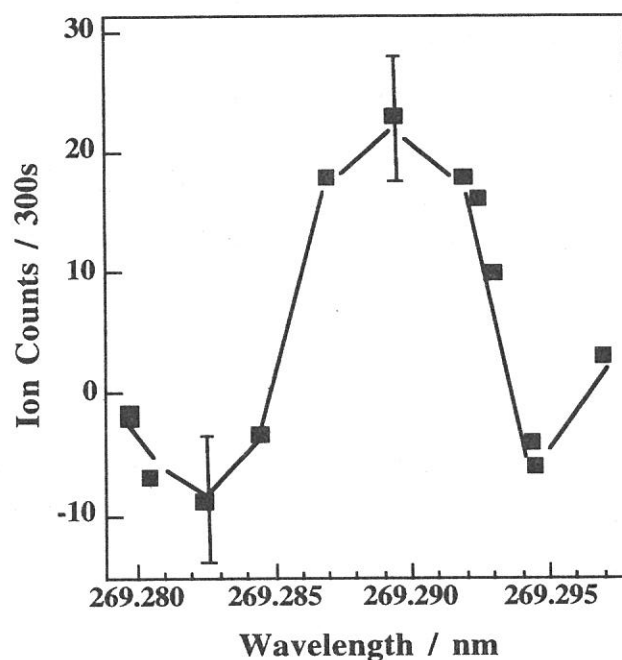


Figure 2. Laser REMPI spectrum of $S(3s^2 3p^4 \ ^3P_2)$ produced by photoexcitation of OCS at the undulator photon energy of 16.5 eV.

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Rotational and Vibrational Distributions of N_2^+ Produced from Superexcited States of N_2 and N_2O

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Vibrational Distribution of $N_2^+(X^2\Sigma_g^+)$ from N_2

The electronically ground state of N_2^+ is produced from N_2 or N_2O by direct ionization or autoionization using synchrotron radiation and observed by laser induced fluorescence (LIF) excitation spectroscopy. The experimental setup and procedures have been described in the preceding report of Mizutani *et al.* Figure 1 shows the yield curves of $N_2^+(X^2\Sigma_g^+, v'', N'')$ for (a) $v'' = 0$ and (b) $v'' = 1$, measured as a function of the photon energy of the synchrotron radiation. The spectral resolution was set to 2.4 \AA . The wavelength of the probe laser were tuned to 391.54 nm and 388.53 nm in Panels (a) and (b), respectively, where the transitions ($B^2\Sigma_u^+, v' = 0 \leftarrow (X^2\Sigma_g^+, v'' = 0)$ and ($B^2\Sigma_u^+, v' = 1 \leftarrow (X^2\Sigma_g^+, v'' = 1)$), respectively, give rise to the band head in the *P* branch of concomitant rotational structures. The fluorescence was dispersed and detected by a second monochromator with a maximum transmission at 427 and 423 nm, in agreement with the central wavelengths in the rotational distributions of the transitions ($X^2\Sigma_g^+, v'' = 1 \leftarrow (B^2\Sigma_u^+, v' = 0)$ and ($X^2\Sigma_g^+, v'' = 2 \leftarrow (B^2\Sigma_u^+, v' = 1)$), respectively. Resonance peaks in Fig. 1 can be identified to Rydberg states converging to the ionization threshold of $N_2^+(A^2\Pi_u)$; their assignments are given in Fig.1. The two spectra in Fig. 1 exhibit similar peak features, though obvious differences in the relative peak intensity are recognized. One of the most marked features is that the relative intensity of the $4d\delta g^1\Pi_u, v = 1$ state at 771.6 \AA is enhanced in Panel (b). This result is consistent with the relative partial photoionization cross sections for the formation of $N_2^+(X^2\Sigma_g^+, v = 0$ and 1) from N_2 reported by Haworth *et al.*¹⁾ They have concluded that 75 % of Rydberg molecules in the $4d\delta g^1\Pi_u, v = 1$ state undergo autoioniation into $N_2^+(X^2\Sigma_g^+, v = 1)$.

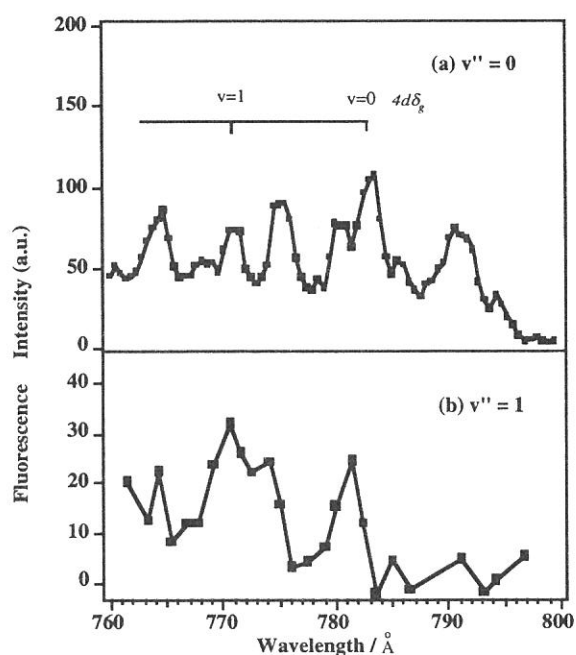


Figure 1. Yield curves of $N_2^+(X^2\Sigma_g^+, v'', N'')$ for (a) $v'' = 0$ and (b) $v'' = 1$.

Rotational Distribution of $N_2^+(X^2\Sigma_g^+, v=0)$ from N_2O

Figure 2 shows an LIF spectrum of $N_2^+(X^2\Sigma_g^+, v''=0)$ produced from N_2O by synchrotron radiation photoexcitation at 18.987 eV. The two maxima centered at 391.54 nm and 390.8 nm are ascribed to the *P* and *R* branches, respectively, for the $(B^2\Sigma_u^+, v'=0, N') \leftarrow (X^2\Sigma_g^+, v''=0, N'')$ transitions. Since the spectral resolution of the laser was approximately 15 cm^{-1} , the rotational lines are heavily overlapped. The rotational temperature of $N_2^+(X^2\Sigma_g^+, v''=0)$ can be roughly estimated by comparing the ratio between the peak heights of the *P* and *R* branches, as long as the relative intensities of the rotational levels of N_2^+ produced by autoionization obey the Boltzmann distribution. The obtained value is 200 - 300 K. The solid line in Fig. 2 represents a spectrum at 250 K calculated by using the theoretical intensity distribution of rotation bands convoluted with a laser spectral width of 13 cm^{-1} .

¹⁾ A. Haworth, D. G. Wilden and J. Comer, J. Electron Spectrosc. Relat. Phenom. **37** (1985) 291.

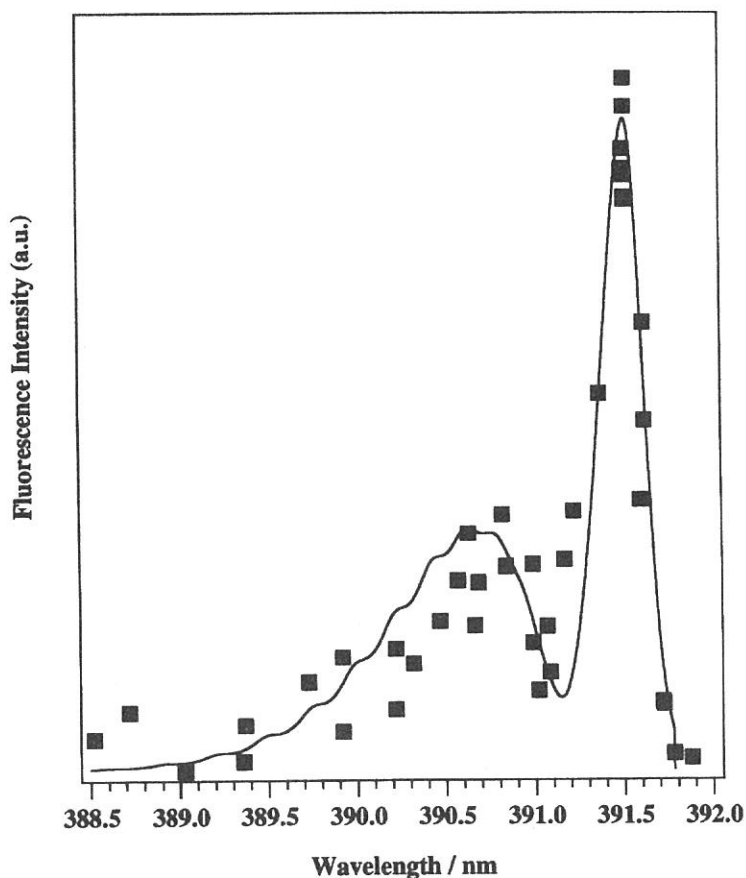


Figure 2. LIF spectrum of $N_2^+(X^2\Sigma_g^+, v''=0)$ produced from N_2O . Photon energy of synchrotron radiation is fixed at 18.987 eV.

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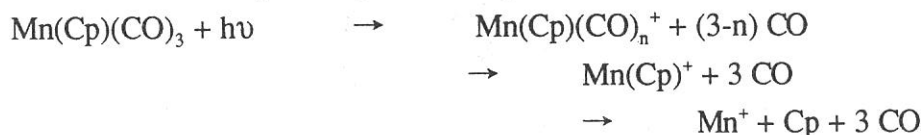
Dissociative Photoionization of $\text{Mn}(\text{C}_5\text{H}_5)(\text{CO})_3$ in the Mn 3p Inner-Valence Region.

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In previous X-ray absorption and electron energy loss measurements on various transition metal compounds, it has been suggested that a strong photoionization resonance can be found in the vicinity of metal np ionization threshold, which can be attributed to the transition from metal np orbital to an unoccupied molecular orbital. However, there has been little information about ion fragmentation following such resonance transition. We are performing a series of detailed studies of dissociative photoionization of various transition metal compounds in the inner valence region by use of the TOF mass spectrometry and photoion-photoion coincidence (PIPICO) technique.^{1,2} In the present work, the dissociative photoionization of $\text{Mn}(\text{C}_5\text{H}_5)(\text{CO})_3$ is studied in the vicinity of Mn 3p inner-valence region (55eV).

Figure 1 shows an example of TOF mass spectrum of $\text{Mn}(\text{Cp})(\text{CO})_3$ ($\text{Cp} = \text{C}_5\text{H}_5$) at 58eV of incident photons and with 20.0cm of flight tube length. The most intense fragment ion is Mn^+ . Ions having a formula $\text{Mn}(\text{Cp})(\text{CO})_n^+$ ($n=0,1,3$) also show high abundance. On the other hand, the fragment ions having a formula $\text{Mn}(\text{CO})_n^+$ are seldom observed. This fact shows that the Mn-CO bond cleavage occurs before the Mn-Cp bond cleavage. These results indicate that ion fragmentation dominantly proceeds by primary loss of the CO molecules. The CO elimination is followed by cleavage of Mn-Cp bond, and finally, Mn^+ is formed.



The fragment ions Cp^+ and C_3H_m^+ are also abundant. This observation is in good agreement with the results of the previous investigation of ferrocene.¹ However, the abundance of CO^+ is relatively small and those of C^+ and O^+ are almost null in the ion fragmentation of $\text{Mn}(\text{Cp})(\text{CO})_3$. This result contrasts strikingly with that of ion fragmentation in the transition-metal carbonyl compounds.² It may indicate that the positive hole created in a CO ligand is quickly filled by electron transfer from $\text{Mn}(\text{Cp})$ before CO^+ elimination or C-O bond cleavage.

As the photon energy increases from below to above the Mn 3p ionization threshold (55eV), the intensities of the doubly charged ions of the formula $\text{Mn}(\text{Cp})(\text{CO})_n^{2+}$ show an increase. However, these ions amount to only a few percent in the mass spectra and thus the variation of these ions are very small. We can not find any remarkable variation in ion mass spectra when photon energy is tuned at the Mn 3p ionization threshold.

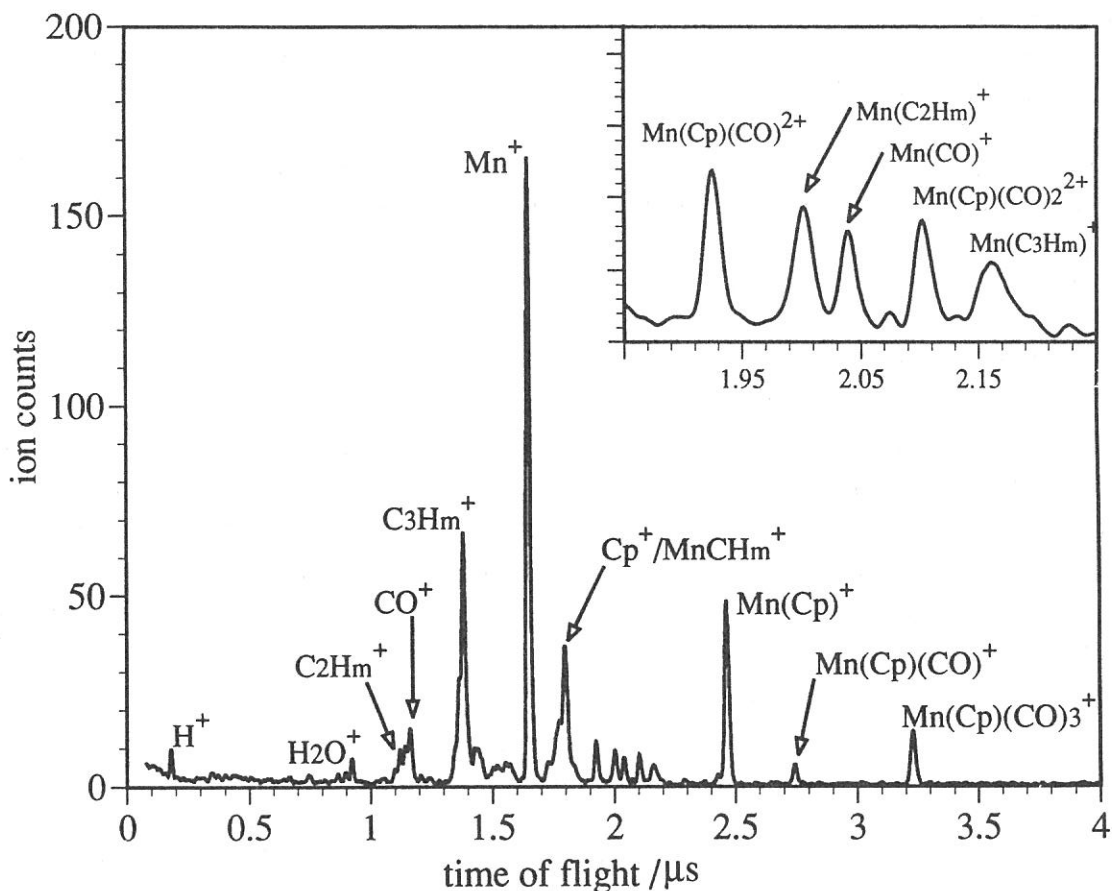


Figure 1; A PEPICO (TOF mass) spectrum of $\text{Mn}(\text{Cp})(\text{CO})_3$ taken at 58eV of incident photon energy and 20.0cm of flight tube length.

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