VI-H Photoionization Dynamics Studied by Electron Spectroscopy Combined with a Continuous Synchrotron Radiation Source

Molecular photoionization is a major phenomenon in vacuum UV excitation and provides a large amount of information on fundamental electron-core interactions in molecules. Especially, neutral resonance states become of main interest, since they often dominate photoabsorption cross sections and lead to various vibronic states which are inaccessible in direct ionization. We have developed a versatile machine for photoelectron spectroscopy in order to elucidate dynamical aspects of superexcited states such as autoionization, resonance Auger decay, predissociation, vibronic couplings, and internal conversion. Introduction of a new methodology, two-dimensional photoelectron spectroscopy, allows us to investigate superexcited states in the valence excitation region of acetylene, nitric oxide, carbonyl sulfide, sulfur dioxide and so on. In this method, the photoelectron yield is measured as a function of both photon energy and electron kinetic energy (binding energy). The spectrum, usually represented as a contour plot, contains rich information on photoionization dynamics.

VI-H-1 Autoionization of a Dipole-Forbidden Superexcited State of CS$_2$

MITSUKE, Koichiro; HIKOSAKA, Yasumasa$^1$
($^1$Inst. Mater. Struct. Sci.)

Two-dimensional photoelectron spectroscopy of CS$_2$ has been employed to study excitation and autoionization mechanism of Rydberg states with the aid of analyses of the vibrational branching ratios of the final ions. The photoelectron yield is measured as a function of both photon energy $E_{hv}$ and ionization energy $I_E$. Figure 1 shows a spectrum in the $E_{hv}$ range of 14.6-15.3 eV. The Rydberg state at $E_{hv} = 14.88$ eV shows anomalously intense patterns at $I_E = 10.23$ and 10.28 eV, which are identified as the $v_3 = 1$ vibrational levels of the antisymmetric stretching mode $v_3$ of the two spin-orbit components of CS$_2^+$ [(2$\pi_g$)$^{-1}$ $X^2\Sigma_g^+$, $\Omega = 1/2$ and $3/2$]. Similar enhancement of the $v_3 = 1$ level has also been observed for autoionization of the Rydberg state at $E_{hv} = 14.88$ eV to CS$_2^+$ [(5$\sigma_u$)$^{-1}$ $B^3\Pi_u^+$]. This Rydberg state is considered to be the $v_3 = 1$ level of the two spin-orbit components of CS$_2^+$ [(2$\pi_g$)$^{-1}$ $X^2\Sigma_g^+$, $\Omega = 1/2$ and $3/2$]. The electronic dipole transition is forbidden from the ground state CS$_2$ ($X 1\Sigma_g^+$) to this Rydberg state, but comes to have a substantial oscillator strength through vibronic coupling involving the $v_3$ vibration. Conceivably, the transition to the $v_3 = 1$ vibrionic state borrows the intensity from a nearby dipole-allowed transition. From a broad line profile and a shift in the quantum defect, we conclude that the intensity is borrowed from the transition to the vibrational ground state of (6$\sigma_g$)$^{-1}$(5$p\sigma_u$)$^{1} 3\Sigma_u^+$ observed at $E_{hv} = 14.951$ eV.

**Figure 1.** First band in the two-dimensional photoelectron spectrum of CS$_2$ corresponding to the formation of CS$_2^+$ ($X 1\Pi_{g,1/2}$, $3\Pi_{g,3/2}$). The electron intensity is plotted with eight tones from light to dark on a linear scale. The photon wavelength resolution is 0.8 Å (15 meV at $E_{hv} = 15$ eV) and the overall electron energy resolution is set to 40 meV.

VI-I Laser Photoionization of Polarized Atoms Produced by Excitation with Synchrotron Radiation

In conventional photoionization experiments, the most standard method has generally been taken to be measurement of energy and angular distributions of photoelectrons from randomly oriented (unpolarized) atoms or molecules. However, information obtained from these experiments is insufficient, since the initial state constituted of atoms and photons is not selected and the internal properties of final photoions and electrons are not analyzed. In this project, we have performed photoelectron spectroscopy of polarized atoms using linearly-polarized laser light, aiming at complete quantum-mechanical photoionization experiments. Initial excitation with a linearly polarized synchrotron radiation permits ensemble of atoms to be aligned along the electric vector of the light. From an angular distribution of photoelectrons from polarized atoms, we are able to gain insight into the magnitude and phase shift difference of transition dipole matrix elements of all final channels which are allowed by selection rules.
Laser photoionization processes of polarized rare gas atoms have been observed in order to study spin-orbit interactions of many electron systems and exploit the possibility of the complete photoionization experiment. Photoelectrons emitted in the direction perpendicular to both the laser and synchrotron radiation are detected with a 160° spherical electrostatic analyzer. In Figure 1(a), the photoelectron yield for Ar(5s'[1/2]1) → Ar*(2P1/2) + e⁻ (|= 1; j = 1/2, 3/2) is plotted as a function of the angle $\phi_e$ between the electric vector of the laser and the direction of the linear momentum of photoelectrons. The angular distribution should be interpreted in terms of a $p$ partial wave from excited Ar atoms aligned toward the electric vector of synchrotron radiation. We have obtained an asymmetry parameter $\beta$ of 1.7 ± 0.2 from Figure 1(a). The angular distributions have also been measured for photoelectrons produced by the process Ar(3d'[1/2]1) → Ar*(2P J) + e⁻ (|= 1 or 3; j = 1/2, 3/2 or 5/2, 7/2) with $J_f = 1/2$ and 3/2 as illustrated in Figure 1(b). Here, $J_f$ is the total angular momentum quantum number of Ar⁺. The $\beta$ values for these distribution curves were found to be 0.64 ± 0.04 and 0.90 ± 0.07 for the $J_f = 3/2$ and 1/2 states of Ar⁺, respectively. We are planning to perform the complete photoionization experiment to determine dipole matrix elements and phase shift differences for all final open channels.

Figure 1. Angular distributions of photoelectrons: (a) Ar(5s'[1/2]1) → Ar*(2P1/2) + e⁻ (|= 1; j = 1/2, 3/2), (b) Ar(3d'[1/2]1) → Ar*(2P1/2,3/2) + e⁻ (|= 1 or 3; j = 1/2, 3/2 or 5/2, 7/2).
VI-J Vacuum UV Spectroscopy Making Use of a Combination of Synchrotron Radiation and a Mode-Locked or Pulsed UV Laser

An ultraviolet laser system has been developed which synchronizes precisely with the synchrotron radiation (SR) from the storage ring of the UVSOR facility. A mode-locked Ti:sapphire laser is made to oscillate at the frequency of the ring in a multibunch operation mode. The delay timing between SR and laser pulses can be changed from 0 to 11 ns. We have developed another system, a pulsed dye laser pumped by an excimer laser, for SR-laser combination experiments. The second harmonic of the dye laser is tunable at 265–280 nm with a pulse energy of ca. 2 mJ pulse$^{-1}$ at a repetition rate of 10–100 Hz. This laser system is mainly devoted to observing neutral species produced by neutral or ionic photofragmentation induced by SR excitation of molecules. The following three combination studies have been performed: (1) two-photon ionization of helium atoms studied as the prototype of the time-resolved experiment, (2) laser induced fluorescence (LIF) excitation spectroscopy of N$_2^+$($^3\Sigma_u^+$) ions produced by synchrotron radiation photoionization of N$_2$ or N$_2$O, and (3) resonance enhanced multiphoton ionization (REMPI) spectroscopy of S(3$^2p^13P_P$, $J^r$ = 0, 2) dissociated from Rydberg states of OCS. Among these topics LIF spectroscopy of ions is making marked progress in improvements of spectral resolution and fluorescence counts. These improvements are brought about by introducing an RF ion trap and by narrowing the laser band-width. As a consequence, we can obtain reliable rotational distribution curves of N$_2^+$($^{3\Sigma_u^+}$).

VI-J-1 Improvement in the Energy Resolution of Laser Induced Fluorescence Excitation Spectroscopy of Ionic Species Produced by SR Photoexcitation

NIKURA, Hiromichi$^{1}$; MIZUTANI, Masakazu; MITSUKE, Koichiro

$^{(1)}$GUAS

Pump-probe spectroscopy making use of a combination of laser and synchrotron radiation has been performed at the beam line BL3A2 in UVSOR to study ionization and dissociation dynamics in the vacuum UV energy region. The fundamental light emitted from the planar-type undulator was dispersed by a 2.2 m grazing incidence constant deviation monochromator in the photon energy range 15.5–19 eV. The second harmonic of a mode-locked Ti:sapphire laser was used to probe cations produced by SR photoionization. Fluorescence was collected in the perpendicular direction to the two light beams and dispersed by another monochromator and detected with a photomultiplier tube. To increase the number density of ions, we employed a cylindrical ion trap, in which collisional quenching of the rotational distribution of ions can be disregarded. Figure 1 shows an LIF spectrum of N$_2^+$($^{3\Sigma_u^+}$, $v = 0$, N) produced by the photoexcitation of N$_2$ at the SR photon energy of 15.983 eV. This energy is equal to the excitation energy for the formation of the 4d$\sigma_g^{-1}$1$I_g$ Rydberg state converging to N$_2^+$($^2\Pi_o$, $v = 0$). We can clearly resolve the rotational structures of the R-branch resulting from the transition of N$_2^+$($^2\Sigma_u^+$, $v = 0$, N + 1) ← ($^{3\Sigma_u^+}$, $v = 0$, N). The spectral resolution of 1.6 cm$^{-1}$ (0.2 meV) has been achieved.

![LIF excitation spectrum of N$_2$](image)

Figure 1. LIF excitation spectrum of the ($^3\Sigma_u^+$, $v = 0$, N') ← ($^{3\Sigma_u^+}$, $v = 0$, N") transition of N$_2^+$ produced by SR photoionization of N$_2$.

VI-J-2 Rotational State Distribution of N$_2^+$ Produced from N$_2$O

NIKURA, Hiromichi$^{1}$; MIZUTANI, Masakazu; MITSUKE, Koichiro

$^{(1)}$GUAS

We have measured LIF spectra of N$_2^+$($^{3\Sigma_u^+}$, $v = 0$, N) produced by SR excitation of N$_2$O. The spectral resolution of the probing laser was set to 11 cm$^{-1}$. Figure 1 shows a LIF spectrum of N$_2^+$ obtained at the photon energy of 18.556 eV, which value accords with the excitation energy for the formation of the 3$d\pi$ Rydberg state converging to N$_2$O($^{3\Sigma_u^+}$). Auto-ionization to the vibrational manifolds of N$_2$O($^3\Pi$) is followed by the dissociation into N$_2^+$($^{3\Sigma_u^+}$) + O($^3P$). Two maxima centered at 391.54 and 390.8 nm are ascribed to the $P$ and $R$ branches, respectively, for the ($^3\Sigma_u^+$, $v = 0$, N') ← ($^{3\Sigma_u^+}$, $v = 0$, N") transition. The rotational temperature of N$_2^+$ is estimated to be 200–230 K by fitting observed data points with the
theoretical intensity distribution with changing the temperature as a parameter. For the purpose of comparison, the average rotational energy of the $N_2^+(X 3\Sigma^+_g)$ fragment was calculated as a function of the $\angle NNO$ angle on the basis of the modified impulsive model. We assumed a stiff NN bond and no vibrational excitation of the $N_2^+$ fragment. This analysis suggests that the $\angle NNO$ angle of $N_2O^+(B 2\Pi)$ in the equilibrium geometry is larger than 160°.

![Figure 1. LIF spectrum of the $(B 2\Sigma^+_u, v = 0, N') ← (X 3\Sigma^+_g, v = 0, N^')$ transition of $N_2^+$ produced by SR photoionization of $N_2O$. The solid line represents the calculated rotational distribution at the temperature of 220 K.](image)

**VI-K Monochromator Newly Developed on the Beam Line BL2B2 in UVSOR**

A grazing incidence monochromator has been constructed which supplies photons in the energy region from 20 to 200 eV. This monochromator will bridge the energy gap between the beam lines BL3A2 and BL8B1, thus providing for an accelerating demand for the high-resolution and high-flux photon beam from the research field of photoexcitation of inner-valence electrons or L-shell electrons in the third-row atom.

**VI-K-1 First Performance Test of the 18 m-Spherical Grating Monochromator**

ONO, Masaki; HATTORI, Hideo; YOSHIDA, Hiroaki; MITSUKE, Koichiro (1Hiroshima Univ.)

This monochromator of Dragon type has been designed to cover the energy range of 20-200 eV with three gratings (G1, 80-200 eV; G2, 40-100 eV; G3, 20-50 eV). The resolving power ($E/\Delta E$) of 5000 and the photon flux of more than $1 \times 10^{10}$ photons s$^{-1}$ are expected at a 100 mA ring current. The performance is now being examined by measuring photoionization efficiency curves of rare gas samples introduced into a differentially pumped chamber at the end station.

Figure 1 shows a He$^+$ efficiency curve in the region of the $2snp \pm 2pns$ series resulting from doubly excitation of He. The widths of the entrance and exit slits of the monochromator were set to 50 µm. The members up to $n = 14^+$ of the series are clearly observed. The spectral width of the $14^+$ line is about 6.5 meV (FWHM). We therefore evaluate that $E/\Delta E$ of approximately $10^4$ has been achieved at 65 eV. When $E/\Delta E$ is lowered to 6500 by changing the slit widths to 100 µm, the photon flux at 65 eV is estimated to be $1 \times 10^{10}$ photons s$^{-1}$. Next, the photon energy is tuned at 91.2 eV which agrees with the excitation energy of the $5p ← 3d_{5/2} 5p[3/2]$ state of Kr. From the band width of its resonance peak, $E/\Delta E$ is estimated to be 4500 with the slit widths of 50 µm.

**Reference**


**Figure 1.** Photoionization efficiency curve exhibiting the $2snp \pm 2pns$ series of the doubly-excited He atom measured with the slit widths of 50 µm. Inset shows an enlarged spectrum in the region of $n \geq 9^+$. 

![Reference](image)