# VI-G 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-G-1 Superexcitation and Subsequent Decay of Triatomic Molecules Studied by Two-Dimensional Photoelectron Spectroscopy

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Photoionization and photodissociation processes of  $SO_2$  and  $CS_2$  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 SO<sub>2</sub> 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  $S^+(^2D^0)$ . The precursor molecular states,  $SO_2^*$ , 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  $SO_2^* \rightarrow S^* + O + O$ . The two-dimensional photoelectron spectrum of CS<sub>2</sub> provides tangible evidence for the formation of a dipoleforbidden Rydberg state  $(6\sigma_g)^{-1}(3d\sigma_g)^{1-1}\Sigma_g^+$  at the photon energy of 14.88 eV which autoionizes into the  $v_3$ = 1 vibrational state of the antisymmetric stretch  $v_3$ mode of  $CS_2^+$  ( $X^2\Pi_{g,\Omega}$ ,  $\Omega = 1/2$  and 3/2). This Rydberg state is expected to borrow substantial oscillator strength from the  $(6\sigma_g)^{-1}(5p\sigma_u)^{1-1}\Sigma_u^+$  state through vibronic coupling involving the  $v_3$  vibration.

### VI-G-2 Photoelectron Spectroscopy of Atomic and Molecular Radicals Prepared by RF Atom Source

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There is very little knowledge on the electronic structures of atomic or molecular radicals, though these transient species often play important roles in the elementary reactions in the stratosphere and various plasmas for industrial purposes. Furthermore, studies of superexcited states of such radicals have not yet evolved mainly owing to their low density, short lifetime with respect to fluorescence emission and collisional quenching, and interference with photoelectron bands of other stable or unstable species. To overcome these serious problems we have employed an intense RF radical source that can operate compatibly with our photoelectron spectrometer installed at the beam line BL3B of the UVSOR facility.

Atomic and molecular radicals are produced by an electrical discharge in the resonant cavity (source) which has been tuned so that its load becomes purely resistive. Radicals escape from the source into a vacuum environment through an aperture of 0.5 mm diameter. Under optimal operating conditions, 90% of the molecular H<sub>2</sub>, O<sub>2</sub>, or N<sub>2</sub> leaves the source in dissociated form. The maximum flux of the radical beam is calculated from a gas flow of 0.5 sccm to be *ca*.  $10^{16}$  radicals cm<sup>-2</sup>s<sup>-1</sup> at the ionization region of an electron energy analyzer which is about 30 cm distant from the aperture of the source. As a result, the maximum density at the analyzer position is estimated to be about  $10^{10}$  radicals cm<sup>-2</sup> by assuming the mean translational energy of the radical beam of < 1 eV.

# VI-H Development of a Laser-Synchrotron Radiation Combination Technique to Study Photoionization of Polarized Atoms

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.

## VI-H-1 Laser Photoionization of Polarized Ar Atoms Produced by Excitation with Synchrotron Radiation

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The combination technique is incorporated into an apparatus for two-dimensional photoelectron spectroscopy of atoms and molecules in order to investigate photoionization dynamics of polarized atoms. Ground state Ar atoms are excited with linearly polarized synchrotron radiation to Rydberg states lying below the first ionization potential. Aligned atoms thus formed are ionized by irradiation of laser which is also linearly polarized. Photoelectrons emitted in the direction of the electric vector of synchrotron radiation are sampled and energyanalyzed. Photoelectron angular distribution is measured with respect to the electric vector of the laser (see Figure 1). Derivation is made on the expressions which correlate asymmetric coefficients for the angular distribution with theoretical dynamic parameters involving transition dipole matrix elements. The anisotropy of the present angular distribution can be reasonably explained, assuming that the matrix elements and phase shift differences are essentially independent of the total angular momentum quantum number of the final state and that the spin-orbit interaction in the continuous spectrum is small. In the case of the photoionization of the  $Ar^*(3d[1/2]_1)$  state the ratio of the reduced dipole matrix elements between those for the  $\epsilon p$ and *ɛf* parial waves is evaluated from the observed asymmetry parameter to be 0.60 on the presumption that



the phase shift difference of the two waves is equal to  $\pi/2$ .

**Figure 1.** Geometry of the laser-synchrotron radiation combination experiment for investigating photoionization dynamics of polarized atoms. The electric vector  $\vec{E}_{SR}$  of the monochromatized synchrotron radiation is fixed and parallel to the electron sampling direction  $\vec{p}$ . In contrast, the electric vector  $\vec{E}_{laser}$  of the laser can be rotated around its propagation direction. Photoelectron angular distribution is measured as a function of the angle  $\varphi_e$  between  $\vec{E}_{laser}$  and  $\vec{E}_{SR}$ .

## VI-H-2 Development of a New Angle-Resolved Energy Analyzer for Photoelectron Spectroscopy of Polarized Atoms

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A conical electron energy analyzer has been developed to measure the angular distribution of photoelectrons from polarized rare gas atoms excited with synchrotron radiation. Since the photoelectron yield of this type of experiment is quite small, we intend to achieve high angular resolution and wide angular acceptance simultaneously.

Our analyzer consists of a set of an inner and outer conical deflector electrodes, cylindrical lenses, a gas cell and a position sensitive detector (PSD) as shown in Figure 1. Photoelectrons emitted in the gas cell are accelerated between the cell and an extractor electrode, and then focused on an entrance slit by the cylindrical lenses. The electron trajectories between the inner and outer conical electrodes are similar to those expected for a conventional parallel-plate analyzer. However, our conical analyzer has rather larger energy dispersion and larger angular aberration than the parallel-plate analyzer. Energy selected electrons exiting from the conical deflector electrodes are detected with the PSD

$$\frac{\Delta E}{E} = \frac{\Delta R}{1.11R} + k_1 \alpha + k_2 \alpha^2 \approx \frac{1}{30},$$

mounted behind the analyzer. The energy resolution is expressed as

where R denotes the distance between the entrance and exit slits,  $\alpha$  the angular deviation of electrons with respect to the mean trajectory of the incident electrons in the dispersion plane, and  $k_1$  and  $k_2$  angular aberration coefficients. On the other hand, the conical analyzer is incapable of focussing the electron trajectories in the azimuth direction. The azimuth angular resolution is thus estimated to be  $1.5^{\circ}$  from the diameter of the sample volume ( $\phi$  1 mm) and the position sensitivity of the PSD. At a PSD particular position, the angular distribution can be measured in the range of  $0^{\circ}-25^{\circ}$  at the same time. By rotating the PSD about the synchrotron radiation propagation axis, we can obtain the photoelectron angular distribution from  $-5^{\circ}$  to  $95^{\circ}$ with respect to the electric vector of synchrotron radiation.



**Figure 1.** Schematic diagram of the conical analyzer. Principal electrodes of the analyzer are depicted by taking two different views. Left: a cross sectional view on the plane which includes the propagation vectors of the laser and synchrotron radiation. Right: a top view.

# VI-I 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<sup>-1</sup> 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  $N_2^+(X \, {}^2\Sigma_g^+)$  ions produced by synchrotron radiation photoionization of  $N_2$  or  $N_2O$ , and (3) resonance enhanced multiphoton ionization (REMPI) spectroscopy of S( $3s^23p^4 \, {}^3P_{J'}$ , J'' = 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  $N_2^+(X \, {}^2\Sigma_g^+)$ .

VI-I-1 Rotational State Distribution of  $N_2^+$ Produced from  $N_2$  or  $N_2O$  Observed by a Laser-Synchrotron Radiation Combination Technique

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#### [Chem. Phys. Lett. 317, 45 (2000)]

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 of  $N_2$  and  $N_2O$  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 for laser-induced fluorescence (LIF)

spectroscopy of N<sub>2</sub><sup>+</sup>( $X \, {}^{2}\Sigma_{g}^{+}, v, N$ ) cations produced by synchrotron radiation photoionization. Fluorescence was collected in the perpendicular direction to the two light beams, dispersed by another monochromator, and detected with a photomultiplier tube. To increase the number density of ions, we employed a cylindrical ion trap. The collisional quenching of the rotational distribution of ions can be disregarded in the ion trap. We can clearly resolve the rotational structure of the Rbranch resulting from the transition  $(B^2\Sigma_u^+, v' = 0, N +$ 1)  $\leftarrow (X^2 \Sigma_g^+, v^* = 0, N)$  of  $N_2^+$  produced from  $N_2$ . The yield curves for  $N_2^+$  ( $X^2 \Sigma_g^+, v^* = 0, 1$ ) are also measured as a function of the photon energy of the synchrotron radiation. The rotational temperature of N<sub>2</sub><sup>+</sup> ( $X^{2}\Sigma_{g}^{+}$ , v" = 0) produced from N<sub>2</sub>O<sup>+</sup> ( $B^{2}\Pi$ ) is determined from an LIF spectrum to be in the range of 200–230 K. The analysis based on the impulsive model indicates that the equilibrium bond angle of  $N_2O^+(B^2\Pi)$ in the vibrational ground state is much larger than 130°.

# VI-J 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-J-1 Performance of the Dragon-Type Monochromator at UVSOR

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A Dragon-type monochromator has been newly constructed at the bending-magnet beamline BL2B2 of the UVSOR facility. The monochromator has been designed to cover the energy range 20–200 eV with three gratings (G1: 80–200 eV, G2: 40–100 eV, G3: 20–50 eV). A resolving power,  $E/\Delta E$ , of 5000 and a photon flux more than  $1 \times 10^{10}$  photons s<sup>-1</sup> at a 100-mA ring current are expected. The optical alignment and performance test have been finished.

The resolving power is evaluated from the ion yield spectra of the rare gas atoms: the  $3d_{5/2}^{-1}5p$  line of Kr (91.2 eV, exploited for G1 and G2), 2snp + 2pns series of He (60–65 eV, for G2) and  $3s^{-1}np$  series of Ar (25–30 eV, for G3). Moreover, the photon flux is estimated by measuring the photocurrent of a gold mesh which is put in the path of the photon beam. Figure 1 summarizes the resolving power and photon flux at a 100-mA ring current when both the entrance and exit slits are set to 100 µm wide. The solid line in Figure 1(b) shows the expected values derived theoretically.<sup>1)</sup> By adjusting the slit widths, we can attain the resolving power of 2000–8000 and the photon flux of 1 × 10<sup>10</sup> photons s<sup>-1</sup> simultaneously at a 100-mA ring current.

The second-order contribution is inspected on the basis of the ion yield spectrum of Kr around 45.6 eV. The peak of the  $3d_{5/2}^{-1}5p$  line at 91.2 eV appears due to the contaminating second-order light. The percentage of the second-order light at 45.6 eV is estimated to be 7% from the ratio between the absorption cross sections at 45.6 and 91.2 eV.

#### Reference

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**Figure 1.** (a) The photon flux at a 100-mA ring current and (b) resolving power when the entrance and exit slit widths are set to  $100 \ \mu$ m. The solid lines in panel (b) indicate the expected values.

### VI-J-2 Anisotropy of the Fragment lons from Small Molecules Excited with Synchrotron Radiation

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In order to make assignments of core-electron excited states and study their decay dynamics, an apparatus for symmetry-separated absorption spectroscopy has been developed at the end-station of the beam line BL2B2. The spectrometer contains two ion detectors each of which comprises a grid made of copper mesh followed by a ceratron electron multiplier. Two ion detectors are placed in the parallel and perpendicular direction to the electric vector of synchrotron radiation. Retarding voltages were applied to the grids so that only fragment ions with high kinetic energy were allowed to reach the entrance of the ceratron multiplier. The difference in the collection efficiency and sensitivity of the ceratron multiplier between the two ion detectors were corrected by measuring the spectrum of  $SF_6$ . From the  $O_h$  symmetry it is predicted that the fragment ion yield via core excited states of SF<sub>6</sub> should be isotropic.

Figure 1 shows preliminary results of ion yield spectra of the fragment ions from SF<sub>6</sub> and the calculated asymmetry parameter  $\beta$ , when the retarding voltage is set to 5 V. In the ion yield spectra the prominent peaks in the region of > 170 eV are due to the resonance excitation of a sulfur 2*p* electron. The  $\beta$  parameter is almost 2 at low photon energies below 30 eV, which manifests that fragmentation occurs faster than the molecular rotation. There exist several features around 20–60 eV and a broad peak centered at ~ 100 eV in the yield spectra. The interpretation of these features is now in progress. The artificial structures around 110 eV arise from an imperfect photon-flux normalization process involving photocurrent measurements at the gold mesh (see the preceding theme VI-J-1).



**Figure 1.** Ion yield spectra and the asymmetry parameter of the fragment ions from  $SF_6$ . A retarding voltage of 5 V is applied to the two copper grids.