

# RESEARCH ACTIVITIES VI

## Department of Vacuum UV Photochemistry

### VI-A Electronic Structure and Decay Mechanism of Inner-Shell Excited Molecules

This project is being carried out at the Beamline 4B of the UVSOR facility. We have three subprojects: (A) spin-orbit, exchange, and molecular field splittings in S  $2p$  and P  $2p$  excited states, (B) molecules and radicals in condensed phase and in rare gas matrix, and (C) ionic fragmentations following the inner-shell resonance excitation. In (A), we have found some spin-forbidden ionized and excited states in non-radiative (photoelectron emission) and radiative (photon emission) deexcitation spectra in collaboration with the Uppsala University. In (C), we are concentrating on theoretical interpretation of our experimental data measured for last several years.

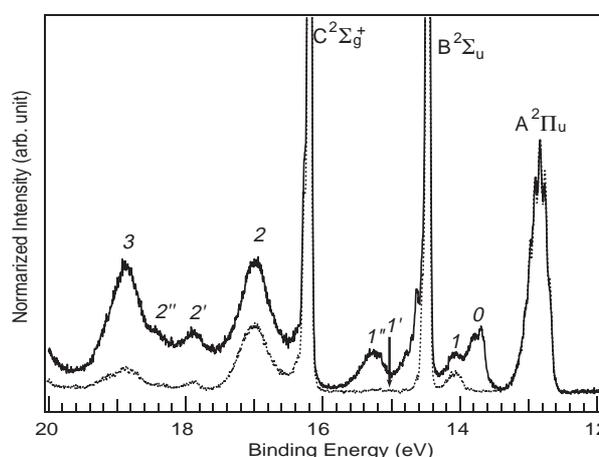
#### VI-A-1 Spin-Forbidden Shake-Up States in the Valence Ionization of CS<sub>2</sub>

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Photoelectron spectroscopy (PES) is widely used to investigate the one-electron energy level in various systems. All lines which have been observed so far in PES are doublet ionized state in the case of molecules with singlet ground state. The shake-up satellites can be enhanced by exciting at resonances. In this report we for the first time demonstrate that invisible (dark) spin-forbidden states in non-resonant PES can be observed by PES at sulfur  $2p$  resonances with strong singlet-triplet mixing *via* spin-orbit coupling of the sulfur  $2p$  core electrons. Figure 1 shows an example of our PES of CS<sub>2</sub>, recorded on the S  $2p_{3/2} \rightarrow 3\pi_u^*$  resonance and below the resonance. Within the (LS) coupling scheme, the excited states are described as strongly mixed states with singlet and triplet components, where the intensity comes from dipole-allowed singlet components. Intermediate states in the resonant PES have triplet components as well, which open up transitions to quartet ionized states in addition to doublet states. Satellite 0 is not observed in the non-resonant spectrum at all. Satellite 1 is assigned to the lowest doublet shake-up state with the  $^2\Pi_u$  symmetry [1] allowed in the non-resonant PES spectra. The satellite 0 is assigned to a transition to the quartet counterpart ( $^4\Pi_u$ ) of the doublet state based on *ab initio* configuration interaction calculations.

#### Reference

1) P. Baltzer *et al.*, *Chem. Phys.* **202**, 185 (1996).



**Figure 1.** PES spectrum of CS<sub>2</sub> recorded at the  $2p_{3/2} \rightarrow 3\pi_u^*$  resonance (163.22 eV) and non-resonant spectrum recorded below the sulfur  $2p$  excitation region (151.2 eV).

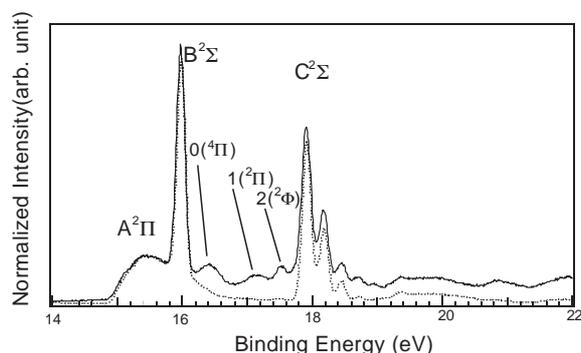
#### VI-A-2 Spin- and Symmetry Forbidden Ionized States of OCS Molecule

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Some satellite structures in the photoelectron spectrum (PES) are enhanced by exciting at the resonances. In this work, we have measured resonant PESs of OCS molecule and successfully found the spin- and symmetry forbidden shake-up states ( $^4\Pi$  and  $^2\Phi$ ) as well as the lowest double shake-up state ( $^2\Pi$ ).

Photoabsorption spectrum of OCS shows transitions to  $4\pi^*$ ,  $10\sigma^*$  and Rydberg states below the sulfur  $2p$  ionization threshold. Due to the spin-orbit interaction, each transition is split into the  $2p_{3/2}$  and  $2p_{1/2}$  manifolds. Figure 1 shows resonant PES of OCS at the  $2p_{3/2} \rightarrow 4\pi^*$  resonance (solid line) as well as an off-resonance one (dotted line). In the non-resonant PES, a very weak band 1 is clearly observed, which is assigned to the lowest  $^2\Pi$  shake-up satellite, of which the intensity is borrowed from the A state ( $^2\Pi(2\pi^{-1})$ ). In the resonant case, additional strong satellite bands 0 and 2 are found. These satellites are not observed in the non-resonant PES. Based on *ab initio* MRCI calculations, the bands 0

and 1 are assigned to the quartet and doublet  $\Pi$  satellites with the  $(3\pi_x^{-1} 3\pi_y^{-1} 4\pi^{+1})$  electron configuration. The Band 2 is assigned to be the lowest symmetry-forbidden  ${}^2\Phi$  states.

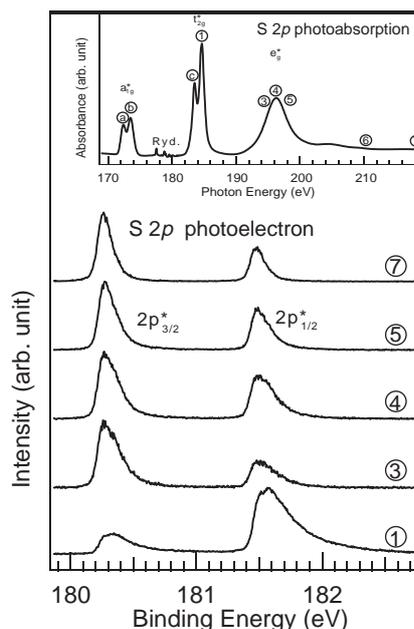


**Figure 1.** Photoelectron spectra of OCS molecule excited at the  $2p_{3/2} \rightarrow 4\pi^*$  resonance (164.4 eV) (solid line) and at off-resonance 10 eV below the  $2p_{3/2} \rightarrow 4\pi^*$  resonance (dotted line).

### VI-A-3 Measurements of Sulfur 2p Photoelectron and Sulfur L-emission of SF<sub>6</sub> at Sulfur 2p Resonances

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The sulfur 2p photoabsorption spectrum of SF<sub>6</sub> molecule shows strong valence excitations and shape resonances as well as very weak Rydberg series (inset in Figure 1), which are characteristic of systems surrounded by electronegative atoms. In this study, sulfur 2p photoelectron spectra and sulfur L-emission spectra have been measured at these resonances. At the resonances below the threshold, triplet valence excited states are found in the soft x-ray emission spectra through singlet-triplet mixed 2p excitations due to the spin-orbit interaction. Above the ionization threshold, dependence upon the excitation energy is generally small in most cases because non-resonant contribution is dominant. In the case of SF<sub>6</sub>, the branching ratio between  $2p_{3/2}$  and  $2p_{1/2}$  photoelectron peaks, however, shows distinct variation upon the excitation energy in photoelectron spectra (Figure 1) and emission spectra. This behaviour has been attributed to the strong exchange interaction between core hole and excited electron at the resonances.



**Figure 1.** Photoelectron spectra of SF<sub>6</sub> recorded at the sulfur 2p resonances (shown in inset).

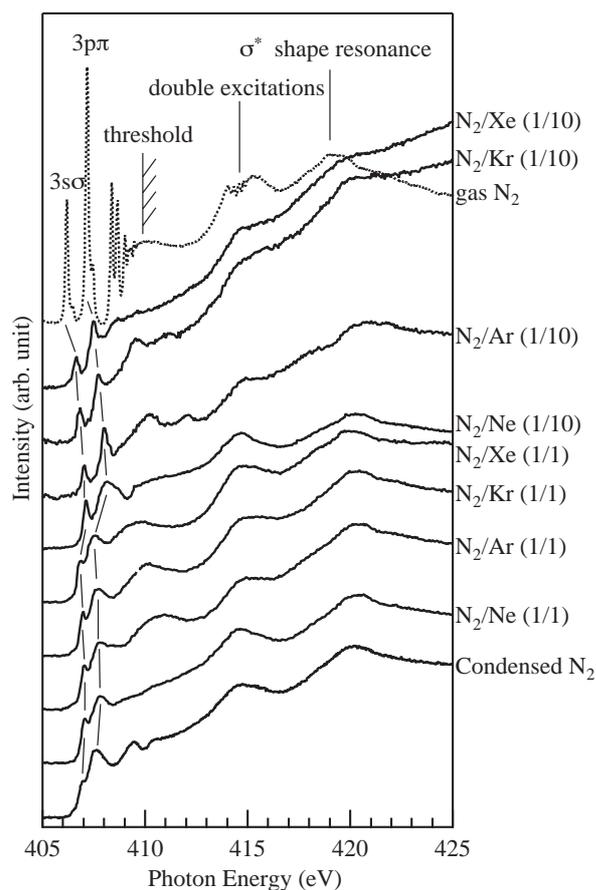
### VI-A-4 N 1s Photoabsorption of N<sub>2</sub> Trapped in Rare Gas Matrices

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The gaseous N<sub>2</sub> spectrum shows complex structures in the N 1s threshold region, resulting from resonances by transitions into  $\pi^*$ ,  $\sigma^*$ , Rydberg and multiple-electron excited states. Some of them have diffuse character and should have environmental effects around the molecule. In the present work, we have measured N 1s excitation spectra of N<sub>2</sub> trapped in rare gas matrices.

On a new beamline BL4B at UVSOR, N 1s photoabsorption spectra were measured with an electron yield method for rare-gas matrix isolated and condensed N<sub>2</sub>, and with a transmission method for gaseous N<sub>2</sub>. Samples were prepared by mixing gaseous N<sub>2</sub> with rare gas, Ne, Ar, Kr or Xe, in a vacuum vessel and evaporated on an Au coated Cu plate. The temperature of the plate was below 6.5 K by a cryostat. The ratios N<sub>2</sub> to rare gas were 1/10 and 1/1.

Figure 1 shows that 3s and 3p Rydberg-like excited states exhibit blue shifts in photon energy in the matrix phase. The shift of the Rydberg excitation energy is determined by competition between the shifts of the ionization potential and the term value. The ionization potential becomes smaller as the distance between the N<sub>2</sub> and the neighbors, or the cage size, smaller. On the other hand, the term value is related to the antibonding character in the Rydberg state, and the antibonding character depends on the overlap of the Rydberg orbital with the valence orbital of the neighbor species; that is, the term value becomes smaller as the cage size smaller. Thus, the observed matrix effect indicates that the variation of the term value for the 3s and 3p Rydberg is larger than that of the ionization potential.



**Figure 1.** The N  $1s$  photoabsorption spectra near the N  $1s$  ionization threshold region for the N<sub>2</sub> in gaseous phase, rare gas matrix phases and condensed phase.

#### VI-A-5 Ab Initio CI Calculation for O $1s \rightarrow \sigma^*$ Core-Excited States of Ozone: Difference in Direction between Transition Dipole Moment and Photodissociation

OJI, Hiroshi; KOSUGI, Nobuhiro

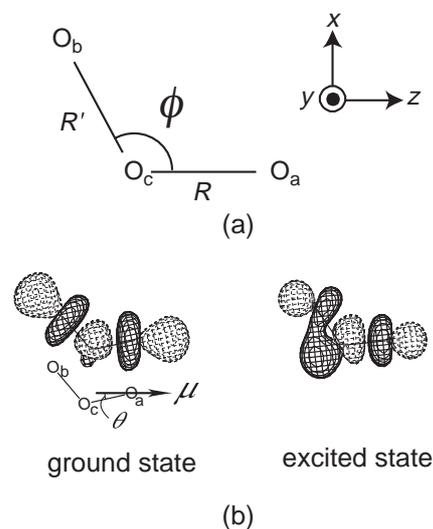
The transition dipole moment ( $\mu$ ) for the O $1s \rightarrow \sigma^*(7a_1)$  excitation of O<sub>3</sub> were calculated by *ab initio* configuration interaction (CI) method. Accurate evaluation of  $\mu$  is necessary to investigate detailed dynamics of photodissociation of polyatomic molecules following the core-excitation, since the direction of  $\mu$  with respect to the bond axis acts as an essential factor in determining the anisotropy parameter for fragment species. We have examined molecular structure dependence of  $\mu$  by changing the length of one bond in O<sub>3</sub>.

The molecular structure of O<sub>3</sub> with the definitions of bond-length  $R$ ,  $R'$ ,  $\phi$  and the axes of coordinates are illustrated in Figure 1(a). The MO patterns for ground and core-excited states at the equilibrium structure ( $R = R' = 0.127$  nm,  $\phi = 118^\circ$ ) obtained by one electron approximation are shown in Figure 1(b). In the ground state, the shape of MO reflects its  $C_{2v}$  symmetry and there is some deviation between the direction of  $\mu$  and that of O<sub>a</sub>–O<sub>c</sub> bond axis. In the core excited state, the shape is strongly distorted by core excitonic effect, but  $\mu$  is not still parallel with the bond. The results of CI calculation was  $\theta = 8.34^\circ$ , as seen in Table 1. If the

length of  $R$  is shortened,  $\theta$  becomes larger. On the other hand, when  $R$  is lengthened,  $\theta$  gradually decreases, but does not become almost 0 until  $R = 0.25$  nm. The present results indicate that the direction of the  $1s \rightarrow \sigma^*$  transition dipole  $\mu$  is not always parallel to the  $\sigma$  bond and more or less affected by the neighboring atoms that are not directly connected with the core-excited atom.

**Table 1.** Results of the CI calculation for the components of  $\mu$  ( $\mu_x$ ,  $\mu_z$ ) and the angle between the directions of  $\mu$  and O<sub>a</sub>–O<sub>c</sub> bond ( $\theta$ ) as functions of  $R$ , when the terminal O (O<sub>a</sub>) core is excited.

$R$ / nm	$\mu_x$ / a.u.	$\mu_z$ / a.u.	$\theta$ / deg
0.120	0.013663	-0.038903	19.35
0.125	0.019042	-0.050656	12.19
<b>0.127</b>	<b>0.007505</b>	<b>-0.051173</b>	<b>8.34</b>
0.140	0.004682	-0.054426	4.92
0.170	0.003143	-0.054332	3.31
0.200	0.002290	-0.055824	2.35
0.250	0.000128	-0.057585	0.13



**Figure 1.** (a) The structure of O<sub>3</sub>. The axis of coordinate used in the calculation is also illustrated. (b) MO patterns of  $\sigma^*(7a_1)$  of O<sub>3</sub> in the ground and excited states when the terminal oxygen (O<sub>a</sub>) core is excited. The definition of the angle  $\theta$  is illustrated.

## VI-B Soft X-Ray Photoelectron-Photoabsorption Spectroscopy and Electronic Structure of Transition Metal Compounds

In this project, we were using the crystal monochromator Beamline 1A of the UVSOR facility, which restrict the photon energy to the range higher than the Ni  $2p$  edge ( $> 800$  eV), but now are using Beamline 4B, covering the lower photon energy ( $< 800$  eV). We can excite the first row elements to their  $1s$  resonance states. We are interested in linear polarization dependence of inner-shell resonant excitations for planar complex molecules/ions in the single crystal, and in resonantly-emitted photoelectron by tuning the photon energy to inner-shell resonances. Dr. Hiroshi Oji has been working as a postdoctoral IMS fellow since April 2000, and Dr. Takaki Hatsui as a research associate since August 2000.

### VI-B-1 B $1s$ - and La $4d$ -Edge Photoabsorption and Resonant Photoelectron Spectroscopy of Rare-Earth Borocarbide $\text{LaB}_2\text{C}_2$

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(<sup>1</sup>Yokohama Natl. Univ.)

Last year we reported the La  $3d$ -edge X-ray absorption spectroscopic (XAS) and valence-band resonant photoelectron spectroscopic (RPES) studies of lanthanum borocarbide ( $\text{LaB}_2\text{C}_2$ ) at UVSOR-BL1A, where we could obtain the information about the degree of charge transfer between La atoms and BC sheets. In the present work, B  $1s$ -edge ( $\sim 200$  eV) and La  $4d$ -edge ( $\sim 100$  eV) XAS and valence-band RPES were measured at the BL4B soft X-ray beamline of the UVSOR facility to obtain further information about the electronic structure of  $\text{LaB}_2\text{C}_2$ .

La  $4d$ -edge XAS spectrum of  $\text{LaB}_2\text{C}_2$  is shown in Figure 1. The assignments of the peaks are indicated in the figure.<sup>1)</sup> The valence- and inner-valence RPES spectra of  $\text{LaB}_2\text{C}_2$  at various photon energies (indicated by numbers) are shown in Figure 2. Abscissa corresponds to the binding energy relative to the Fermi level ( $E_F$ ). La  $5p$  bands ( $\sim 20$  eV) are significantly enhanced in the on-resonant (La  $4d$ ) spectrum. Especially, an anomalous change of the photoemission branching ratio between  $5p_{3/2}$  and  $5p_{1/2}$  intensity can be seen. Actually, this anomaly is also observed in other La compounds. Ogasawara *et al.* attributed this to the multiplet dependence of the Auger transition probabilities.<sup>1)</sup> The intensity of the all valence- and inner-valence band begins to decrease from the photon energy of "5," and almost no structure can be observed at "10." Such a phenomenon was not observed in the RPES spectra at B  $K$ -edge (not shown here).

#### Reference

1) H. Ogasawara *et al.*, *Solid State Commun.* **81**, 645 (1992).

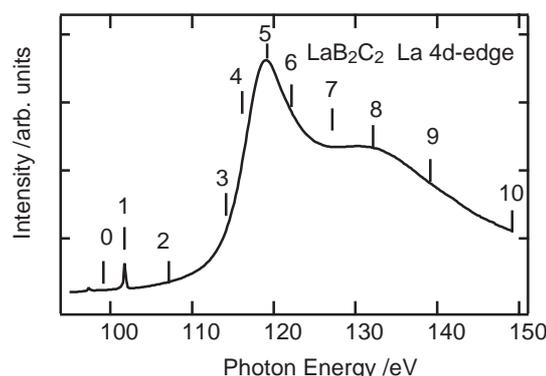


Figure 1. La  $3d$ -edge XAS spectrum of  $\text{LaB}_2\text{C}_2$ .

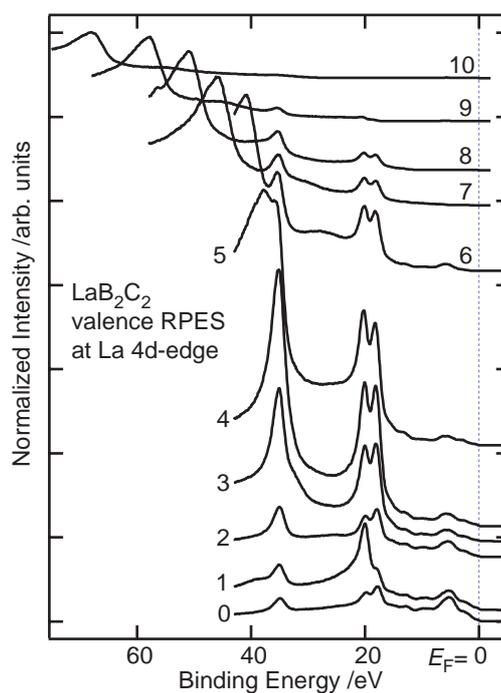


Figure 2. The valence and inner-valence RPES spectra of  $\text{LaB}_2\text{C}_2$  of various photon energies.