

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 and at the surface station of the Beamline I-511 of the MAX-II facility in collaboration with the Uppsala University. Dr. Takaki Hatsui has been working as a research associate since August 2000, and Dr. Mitsuru Nagasono as a JSPS postdoctoral fellow since April 2000. We are interested in linear polarization dependence of inner-shell resonant excitations for simple molecules. We have two subprojects: (A) spin-orbit, exchange, and molecular field splittings in S 2p and P 2p excited states and (B) molecules and radicals in condensed phase and in rare gas matrix. In the subproject (A) we are happy to report here a hot result obtained by using a newly-constructed BL4B of UVSOR. In the subproject (B) we have constructed a new apparatus as shown Figure 1. For both the subprojects theoretical investigation is essential and some theoretical approaches are now under development.

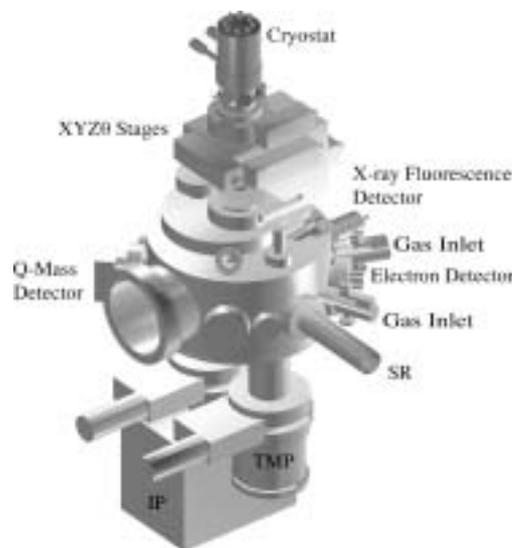


Figure 1. A new apparatus to investigate molecules and radicals in condensed phase and in rare gas matrix.

VI-A-1 Spin-Orbit and Exchange Splittings in the S 2p $\rightarrow \pi^*(b_1)$ Excitation of SO₂

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Figure 1 shows a part of angle-resolved photoion yield spectra (ARPIS) of SO₂, where I₀ (I₉₀) corresponds to ion yields in the direction parallel (perpendicular) to the electric vector of the linear polarized incident light. The photon energy region shown is very narrow, only 3 eV from 164 eV to 167 eV. This region includes only the S 2p excitation to the lowest unoccupied orbital of $\pi^*(b_1)$ symmetry. The S 2p orbitals have a₁, b₂ and b₁ symmetries, resulting in three S 2p- $\pi^*(b_1)$ excited states of B₁, A₂, and A₁ symmetries. The ground state symmetry is A₁ and the A₂ \leftarrow A₁ excitation is dipole-forbidden; that is, the a₁ \rightarrow b₁* (B₁) and b₁ \rightarrow b₁* (A₁) excitations should be observed in Figure 1. Considering the spin-orbit interaction, each singlet excitation is mixed with two triplet excitations, resulting in three dipole-allowed excited states in each symmetry. The transition dipoles to the B₁ states are orthogonal to the molecular plane and these transitions give only I₉₀ yields; on the other hand, the transitions to the A₁ states give both I₀ and I₉₀ yields. In Figure 1, three electronic states of B₁ symmetry show vibrational fine structures, where the lowest electronic state is very weak, and the second (²P_{3/2}) is stronger than the third (²P_{1/2}). On the other hand, Figure 1 shows only two electronic states of A₁ symmetry, where one is located in the ²P_{3/2} manifold,

and the other is in the ²P_{1/2} manifold. The ²P_{1/2} feature seems to be slightly stronger than the ²P_{3/2} feature, though the ²P_{3/2} branch is as twice large as the ²P_{1/2} branch in the case of ionization. This indicates that exchange interaction is essential in the A₁ symmetry. This is reasonable, considering that the 2p_{b1} and π^*b_1 orbitals are oriented parallel. Furthermore, the singlet excited state is quite higher in energy than the triplet excited state, and the lowest state of A₁ symmetry hardly borrows intensity from the singlet component; therefore, the lowest state is invisible in the spectra as shown in Figure 1.

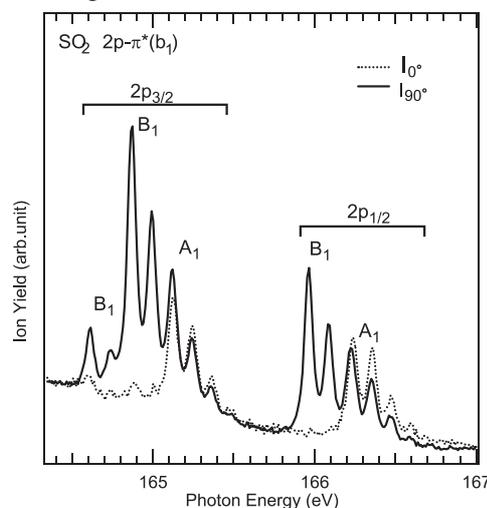


Figure 1. High resolution ARPIS of the spin-orbit split transitions to the S 2p_{a1} $\rightarrow \pi^*b_1$ (B₁) and S 2p_{b1} $\rightarrow \pi^*b_1$ (A₁) excited states of SO₂.

VI-A-2 X-Ray Photoelectron and Absorption Spectra of Fragments from NH₃/Cu(110) Induced by Soft X-Ray Irradiation

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We have studied fragments from NH₃ adsorbed on Cu(110) using N 1s x-ray photoelectron spectroscopy and x-ray absorption spectroscopy in combination with theoretical calculations. As shown in Figure 1, three N 1s photoemission peaks arising under soft x-ray irradiation are assigned to NH_x ($x = 0, 1, \text{ and } 2$) species on Cu(110). These peaks are enhanced in sequence of $x = 2, 1, \text{ and } 0$; *i.e.*, at first the NH₂ species are produced from the NH₃, the NH from the NH₂, and the N from the NH. These fragments are produced by Auger stimulated dissociation (ASD) process and/or x-ray-induced electron-stimulated dissociation (XESD). In the ASD process, fragmentation of NH₃ leads to all NH_x species simultaneously. While in the XESD process, the fragmentation leads to only NH₂ species from NH₃. Therefore the XESD is a dominant process, but the ASD is a minor one. The fragments produced at the early stage correspond to NH₂ anions by considering theoretical predictions. This result suggests a charge transfer process from the Cu substrate to the adsorbed NH₂ radical prepared following the XESD process.

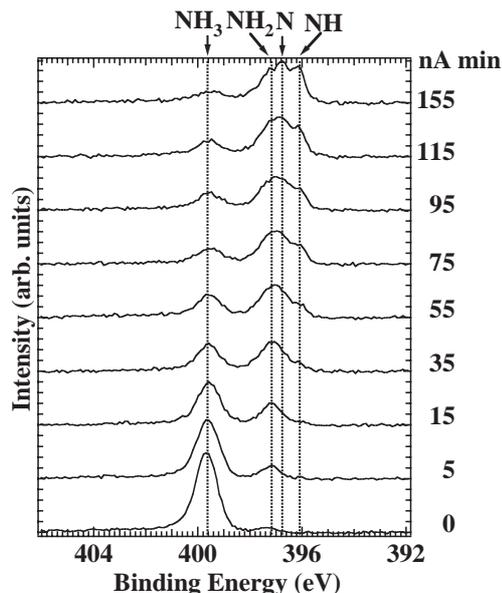


Figure 1. N 1s XP spectra of NH₃/Cu(110) as a function of exposure to x-ray.

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

This project is being carried out by the Kosugi group at the Beamline 1A of the UVSOR facility and at the bulk station of the Beamline I-511 of the MAX-II facility in collaboration with the Uppsala University. 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. We are interested in linear polarization dependence of inner-shell resonant excitations (UVSOR) for planar complex molecules/ions in the single crystal, and in resonantly-emitted photoelectron (UVSOR) and photon (MAX-II) spectroscopies for the same systems by tuning the photon energy to inner-shell resonances. In the UVSOR facility we are using crystal monochromators, which restrict the photon energy to the range higher than the Cu and Ni 2p edge (> 800 eV). Recently, we have decided to move our experimental apparatus to the BL 4B, which is a new beamline covering the lower photon energy (< 800 eV). Next year we hope we will show new results on some interesting materials containing Fe, Mn, and so on.

VI-B-1 Photoabsorption and Resonant Photoelectron Spectroscopy of a Rare-earth Borocarbide LaB₂C₂

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Rare-earth borocarbides RB_2C_2 (R : rare-earth (RE) metals) are intercalation compounds in which rare-earth metal cations are intercalated in the planar BC sheets. These compounds show interesting electronic and magnetic properties, such as superconducting behavior

($T_c = 2.4$ K for LuB_2C_2 ¹). Therefore it is important to know their electronic structure in order to clarify the mechanism of these properties. In this study, the La 3d photoabsorption ($h\nu \sim 830$ eV) and resonant valence-band photoelectron spectra of lanthanum borocarbide (LaB_2C_2) were measured to reveal the partial density of states at the core-excited atom is enhanced in resonant photoelectron spectra. Use of the relatively high energy photons of BL1A at UVSOR facility allows us to perform the bulk-sensitive measurements. The off- ($h\nu = 826.4$ eV) and on- (834.3 eV) resonant photoelectron spectra of LaB_2C_2 in the valence region are shown in

Figure 1. Abscissa represents the binding energy relative to the Fermi level (E_F). La 3d-4f photoabsorption spectrum of LaB_2C_2 is also indicated in the inset. A La 5p band (~ 20 eV) and some bands near to the E_F (0–7 eV) are significantly enhanced in the on-resonant spectrum. The latter resonant enhancement suggests that some valence states near to E_F are localized on La atom. This does not support the complete donation of the three valence electrons of La to the BC sheet, but means that some valence electrons (according to the theoretical band calculation,²⁾ La 5d-derived electrons) of La atom are participating to the formation of the valence band of LaB_2C_2 . The number of La 5d derived-valence electron localized on a La atom is roughly estimated to be 0.3.

References

- 1) J. van Duijn *et al.*, *Phys. Rev. B* **62**, 6410 (2000).
- 2) H. Harima and M. Shirai, *J. Phys. Soc.* submitted.

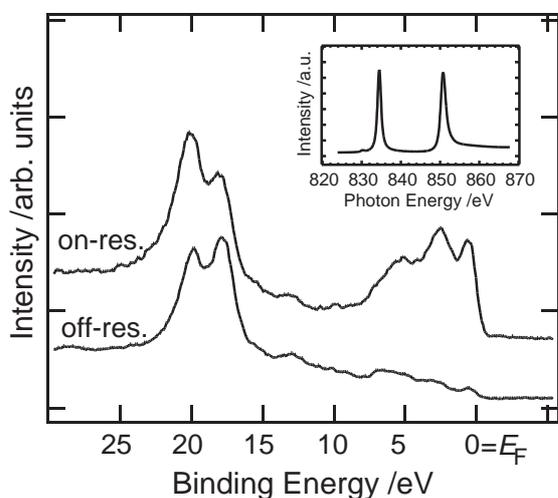


Figure 1. Off- and on-resonant valence-band photoelectron spectra of LaB_2C_2 . La 3d-4f photoabsorption spectrum of LaB_2C_2 is also indicated in the inset.

VI-B-2 Cu L-Edge X-Ray Absorption Spectra of $(\text{Me}_2\text{-DCNQI})_2\text{Li}_{1-x}\text{Cu}$

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Cu L-edge X-ray absorption spectra for $(\text{Me}_2\text{-DCNQI})_2\text{Li}_{1-x}\text{Cu}_x$ alloys (Me₂-DCNQI: 2,5-dimethyl-N,N'-dicyanoquinonediimine) were measured at room temperature in order to investigate the local electronic structure around Cu atoms. Total electron yield mode was used except for the alloyed sample with $x < 0.1$, which was obtained by measuring the partial fluorescence yield. Both in the Cu L₃- and L₂-edge regions of $(\text{Me}_2\text{-DCNQI})_2\text{Cu}$ ($x = 1$) shows a characteristic higher-energy broad band B in addition to a lowest sharp band A associated with the transitions to the Cu 3d hole, while $\text{K}_3\text{Cu}(\text{CN})_4$ with Cu 3d¹⁰ shows only a higher-energy band E (Figure 1). The broad band B arise from the transitions to the lowest unoccupied molecular orbital (LUMO) of Me₂-DCNQI molecules,

where the intensity comes from the Cu 3d components through strong hybridization with Cu. The spectral feature does not change even if the x value (the Cu content) is reduced to less than 0.1. This indicates that these alloys have nearly the same covalent bond between Cu and Me₂-DCNQI as $(\text{Me}_2\text{-DCNQI})_2\text{Cu}$ ($x = 1$).

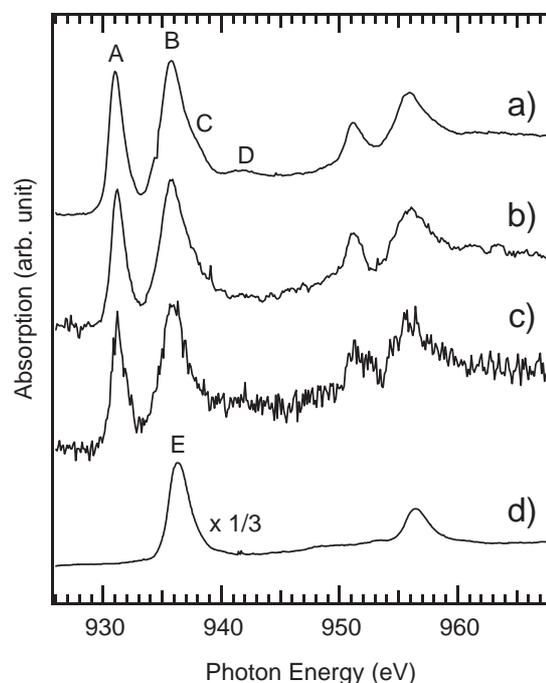


Figure 1. Cu L-edge X-ray absorption spectra of $(\text{Me}_2\text{-DCNQI})_2\text{Li}_{1-x}\text{Cu}_x$ with $x = 1$ (a), $x = 0.15$ (b), and $x < 0.1$ (c). Spectrum of $\text{K}_3\text{Cu}(\text{CN})_4$ is presented for comparison (d).

VI-B-3 Resonant Inelastic X-Ray Scattering of Ni Dimethylglyoxime

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In our previous study, we found two metal-to-ligand charge transfer (MLCT) transitions in the Ni L-edge X-ray absorption spectrum of a planar Ni complex, Ni dimethylglyoxime $[\text{Ni}(\text{Hdmg})_2]$. The MLCT transition was proved to have close correlation with the π -backbonding. The presence of core hole in the final states of x-ray absorption, however, makes it difficult to obtain quantitative information on the bonding between metal and ligand. On the other hand, the final states of resonant x-ray inelastic scattering (RIXS) correspond to valence-excited states without core hole. In the present study, we have measured RIXS of $\text{Ni}(\text{Hdmg})_2$ in order to clarify the bonding nature quantitatively.

Figure 1 shows RIXS spectra (a) and (b) at the higher-energy MLCT excitation. In the $E_{\text{in}} // k_{\text{out}}$ (E_{in} : electric vector of incident x-ray, k_{out} : wavevector of emitted x-ray) geometry, the band at 860 eV is very weak in accordance with the selection rule, where the direct recombination is symmetry forbidden. The spectrum (c), obtained at the excitation far above the

ionization threshold, is similar to the resonant spectra (a) and (b). Compared with the $E_{in} // k_{out}$ spectrum, peak position of the strongest peak in the $E_{in} \perp k_{out}$ spectrum (a) is shifted toward lower energy side. Based on the consideration of the selection rule and the electronic structure, the shift arises from different one-electron excitations, and the most intense peak in spectra (a) and (b) is revealed to have final states with $(Ni\ 3d)^{-1}(\text{ligand}\ \pi^*)^1$.

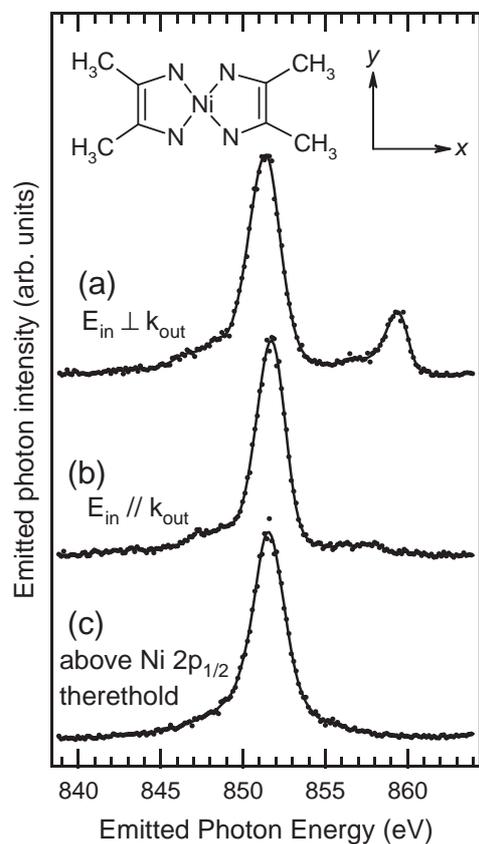


Figure 1. Resonant inelastic X-ray scattering of $Ni(Hdmg)_2$ at the excitation of MLCT band with the $E_{in} \perp k_{out}$ (a) and $E_{in} // k_{out}$ (b) geometries. A non resonant spectrum is shown for comparison (c).