RESEARCH ACTIVITIES VI
Department of Vacuum UV Photoscience

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

This project is being carried out in collaboration with UVSOR, Photon Factory (KEK-PF), Shizuoka University, Osnabrück University, Brazilian Synchrotron Radiation Facility (LNLS), Uppsala University, and Lund University. We are interested in ionic fragmentations and electron emissions via inner-shell excitation of molecules and in their polarization dependence. Last year in high-resolution C1s photoabsorption spectra of acetylene, C_2H_2, we found that the lowest σ_u* state is embedded in the 3sσ_g Rydberg state and is dissociative through interaction with the lowest π* state with bent geometry due to the Renner-Teller effect, that the 3pσ_u and 3pπ_u Rydberg states are clearly resolved and show different vibrational structures, and that the C1s σ_g and σ_u ionization channels show different ionization thresholds, to which the Rydberg series are converging. [For preliminary results, see J. Adachi, N. Kosugi, E. Shigemasa and A. Yagishita, *Chem. Phys. Lett.* **309**, 427 (1999)]. Dr. Jun-ichi Adachi, technical associate, left the Kosugi group for KEK-PF as a research associate in October 1999. Now Dr. Takaki Hatsui has joined the Kosugi group as a new research associate in this field in August 2000. Next year we will extend our experimental and theoretical approaches to several open-shell and unstable molecules.

VI-A-1 Exchange Interaction in the 1s-σ* Resonance of the Triplet Ground State of S_2 in Comparison with O_2

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It is interesting to compare the 1s-σ* resonance of S_2 with that of O_2. The experimental exchange splitting is observed to be ~1 eV in the S 1s-σ* excited states of $^3\Sigma^-$ as shown in Figure 1. It should be noticed that the higher σ* resonance is stronger than the lower σ* resonance in O_2, but in S_2 the lower state is stronger than the higher one. The exchange splitting in the ionized states ΔE_{exch}(ion) is given by $3K_{\mathrm{cx}}$[1] (~1.1 eV for O_2, ~0.2 eV for S_2), where K_{cx} is an exchange integral between the core electron and the π_x* (or π_y*) electron. The exchange splitting in the excited states $\Delta E_{\mathrm{exch}}(\sigma^*)$ is given as follows:[1]

$$\begin{aligned}\Delta E_{\mathrm{exch}}(\sigma^*) &= E\{\sigma^*(^2\Sigma^- \text{ ion core})\} - E\{\sigma^*(^4\Sigma^- \text{ ion core})\}\\ &= 3K_{\mathrm{cx}} - 7/3K_{\mathrm{vx}} - 2/3K_{\mathrm{cv}},\end{aligned}$$

where v denotes the σ* electron. In O_2, K_{cv} and K_{vx} are 1.1~1.2 eV and then $\Delta E_{\mathrm{exch}}(\sigma^*) \sim -2.75$ eV < 0; that is, the σ* state related to the $^4\Sigma^-$ ion core is higher than that related to $^2\Sigma^-$. (Note that this discussion is based on a single electron and frozen orbital picture and if electron correlation is taken into account, $\Delta E_{\mathrm{exch}}(\sigma^*)$ is changed to –1.75 eV from –2.75 eV.[2]) In S_2, K_{cx} is much smaller than in O_2. If so, $\Delta E_{\mathrm{exch}}(\sigma^*) < 0$ and the higher σ* state could be stronger than the lower σ* state. However, this is inconsistent with the present result. This indicates that the picture of the $^4\Sigma^-$ and $^2\Sigma^-$ ion cores and an additional σ* electron does not hold any longer in the S1s-σ* excited states, but the picture of the $^4\Sigma^-$ and $^2\Sigma^-$ valence states and an additional core electron is a good approximation. In this case, the exchange spilitting is give as follows:

$$\Delta E_{\mathrm{exch}}(\sigma^*) = E(^3\Phi_2) - E(^3\Phi_1) = 3K_{\mathrm{vx}} - 7/3K_{\mathrm{cx}} - 2/3K_{\mathrm{cv}} > 0,$$

where the exchange interaction within the valence electrons K_{vx} is much larger than the exchange interaction involving the deep S 1s core, K_{cx} and K_{cv}. The experimental and calculated $\Delta E_{\mathrm{exch}}(\sigma^*)$ are ~ +0.67 eV and ~ +1.15 eV. The experimental and calculated intensity ratios are ~ 1.26 and ~ 1.72.

References

1) N. Kosugi, E. Shigemasa and A. Yagishita, *Chem. Phys. Lett.* **190**, 481 (1992).
2) A. Yagishita, E. Shigemasa and N. Kosugi, *Phys. Rev. Lett.* **72**, 3961 (1994).

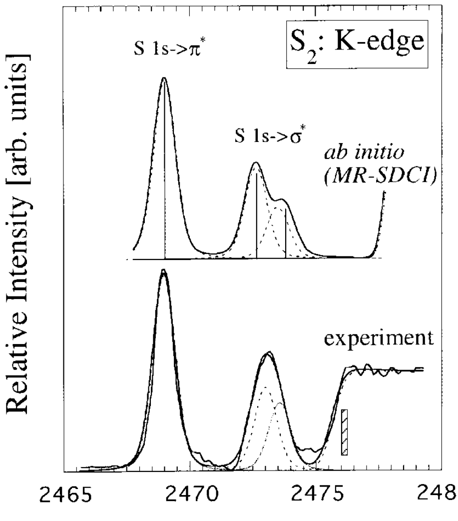

Figure 1. S 1s photoabsorption spectra of S_2 in comparison with theoretical prediction.

VI-A-2 Polarization Dependence of O^+/O_2^+ Fragmentations at the Terminal O1s-to-σ* Excitation of Ozone: A Memory Effect of Core-Hole Localization During the Auger Decay

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[*Chem. Phys. Lett.* in press]

The photoelectron-photoion-photoion coincidence (PEPIPICO) spectra of ozone, O_3 have been measured at the O1s edge for the first time. When an ozone molecule is dissociated after the Auger decay, several different combinations of fragments can be produced. Out of these possibilities, we have chosen to concentrate on the O^+/O_2^+ PEPIPICO spectra. By observing the O^+/O_2^+ ion pair coincidences, we discriminate against possible ultra-fast neutral dissociation before the Auger decay: $O^*–O–O \rightarrow O^* + O–O$. This process cannot produce the fragments $O^+ + O_2^+$, but rather $O^{2+} + O_2$. Due to the local character of the terminal O1s (O 1s) core excitations in O_3, the excitations are considered to take place in the local O–O bond environment, with the unoccupied valence orbitals locally having π or σ character. The $O_T1s \rightarrow 7a_1(\sigma^*)$ transition dipole is theoretically estimated to be 7° from the $O_T^*–O$ bond, being nearly parallel to the $O_T–O$ bond containing an excited terminal atom (O_T). Therefore, we can evaluate preferential fragmentation from $O_T^*–O–O$ to $O_T^+ + O–O^+$ or $O_T–O^+ + O^+$ via $(O_T–O–O)^{2+}$ at the $O_T1s \rightarrow 7a_1(\sigma^*)$ excitation by relating the asymmetry parameter β of the PEPIPICO spectra to the angle between the transition dipole and the bond to be broken. The present analysis shows that photo-induced breaking of the bond closest to the core-excited terminal atom, $O_T^+ + O–O^+$, occurs in high probability of 70 ± 10%. This result is interpreted as a “memory” effect of the initially localized core hole in dicationic states $(O_T–O–O)^{2+}$ after or during the Auger decay.

VI-A-3 Molecular Field and Spin-Orbit Splittings in the 2p Ionization of Second-Row Elements: A Breit-Pauli Approximation Applied to OCS, SO_2, and PF_3

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[*Chem. Phys. Lett.* in press]

Angular distribution of photoelectrons is one of fundamental properties in the inner-shell photoionization process in addition to the photon energy dependence of the photoionization cross sections. The angular distribution of 1s electrons has been investigated for fixed-in-space molecules by utilizing linear polarization of synchrotron radiation. We expect this technique will also be applicable to the photoionization dynamics study in the 2p electron of second-row elements, by combining with theoretically predicted wavefunctions of the spin-orbit split 2p ionized states, $^2P_{3/2}$ and $^2P_{1/2}$. The most accurate approach to take into account the spin-orbit interaction is a four-component method based on the Dirac-Fock configuration interaction calculations, but this is very complicated and is not generally used. In the present work, an ab initio Breit-Pauli (BP) approach as a two-component spin-orbit Hamiltonian is newly developed to analyze the molecular field splitting (MFS) in the $^2P_{3/2}$ state and the spin-orbit splitting ($\Delta_{3/2,1/2}$), and to get $2p^{-1}$ wavefunctions for three typical molecules, OCS, SO_2 and PF_3. The BP Hamiltonian is diagonalized by using a minimum number of the $2p^{-1}$ configurations. The diagonal elements in the 6×6 BP matrix are corrected by the 2p hole-state energies calculated with the non-relativistic $(2p)^5$-SDCI calculations, resulting in good agreement with the experimental energy separations due to MFS. The $(2p)^5$-SDCI is configuration interaction with single and double substitutions from reference states with five electrons in the 2p manifold. On the other hand, to reproduce $\Delta_{3/2,1/2}$ the relaxation in the 2p orbital itself is essential. The bond angle effect is important to determine MFS due to σ and π character in the 2p orbital and to determine the spin-orbit wavefunction. A similar BP Hamiltonian calculation to interpret “linearly polarized” 2p photoabsorption spectra of molecules containing second-raw elements such as HCl is now under way.

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

This project is being carried out in collaboration with UVSOR, Photon Factory (KEK-PF), and Uppsala University. We are measuring Ni 2p photoabsorption, and resonantly emitted photoelectron and soft X-ray spectra of molecular Ni complexes with planar geometry. Dr. Yasutaka Takata, who was a research associate in charge of this project in the Kosugi group, left for Spring-8 as a research associate of RIKEN (IPCR) in May 2000. Now Dr. Hiroshi Oji has joined the Kosugi group as a postdoctoral IMS fellow in this field in April 2000.

VI-B-1 Ni 2p Photoabsorption and Resonant Photoelectron Spectroscopy of High-Spin Ni Complex, Ni(*N*,*N*’-dimethylethylenediamine)$_2$Cl$_2$

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In our previous studies, we found the planar Ni complexes with a $3d^8$ low-spin ground state show characteristic resonant behavior in the Ni 3p and 3s resonant photoelectron spectra, which form a contrast to these of Ni metal and Ni oxide.[1] The kinetic energy of Ni 3p satellite peaks decrease as the photon energy increases, indicating the one electron, or excitonic, feature of the excited states in the planar Ni complexes. In the present work, we measured soft X-ray Ni 2p absorption and resonant Ni 3s and 3p photoelectron spectra of a $3d^8$ high-spin Ni complex, Ni(*N*,*N*'-dimethylethylenediamine)$_2$Cl$_2$ (Ni(DED)$_2$Cl$_2$) to clarify the effect of the spin state on the core-excited states of the system. Figure 1 shows the kinetic energy of the Ni 3p main and satellite photoelectron peaks (a, b, c) as a function of the photon energy. Figure shows a nearly linear relationship between the kinetic energy of the these satellite peaks and the photon energy with the slope ($\Delta KE/\Delta h\nu$) of +1. This dependence of satellite peaks on the photon energy is different from that of the low-spin complexes where the slope becomes negative (*e.g.* $\Delta KE/\Delta h\nu = -0.55 \pm 0.05$ for K$_2$[Ni(CN)$_4$]$^{1)}$), but is similar to that of NiO, where the correlation and multiplet interaction are important.

Reference

1) Y. Takata, T. Hatsui and N. Kosugi, *J. Electron Spectrosc. Relat. Phenom.* **88**, 235 (1998).

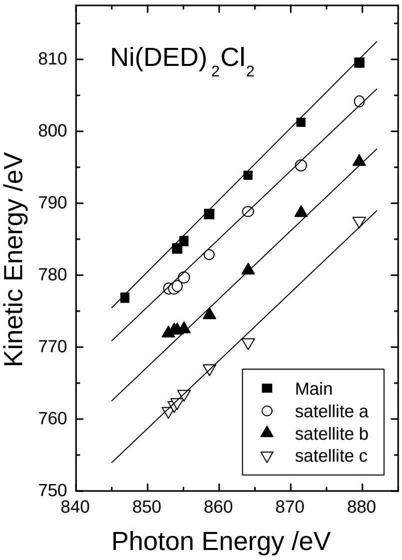

Figure 1. Photon energy dependence of the kinetic energy of Ni 3p main and satellite photoelectron peaks.

VI-B-2 Mg and Al K-edge XAFS Measurements with a KTP Crystal Monochromator

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[*J. Synchrotron Radiat.* in press]

There has been a strong demand for monochromator crystals with a larger lattice spacing than the Si, Ge and InSb crystals widely used in the soft X-ray region, especially in order to get a wide energy range covering the Mg (1305 eV) and Al (1560 eV) K-edges and their EXAFS region. As crystal monochromators to get these near-edge spectra, beryl (1010) [2*d* = 15.965 Å] and quartz (1010) [2*d* = 8.512 Å] have been used, respectively; however, the energy range (*k* range) is limited because beryl and quartz contain Al and Si, respectively. Recently, a YB$_{66}$ (400) [2*d* = 11.72 Å] crystal monochromator has been introduced to measure EXAFS for the Mg, Al and Si K-edges. There is no absorption edge originating from the elements contained in the YB$_{66}$ crystal from 1200 eV up to the Y L$_{III}$ edge of 2080 eV. However, this crystal has a serious problem; two positive glitches at 1386 and 1438 eV are caused by sharp increase in reflectivity of the (600) reflection at the Y L$_{II,III}$ edges. Although to solve such a problem, a cut-off mirror is employed, it is still hard to completely exclude these glitches.

The KTP (011), KTiOPO$_4$, [2*d* = 10.95 Å] crystal can be used in the crystal monochromator. The KTP (011) crystal has a little shorter lattice spacing than YB$_{66}$ (400), but it can cover the Mg and Al K-edges and has no absorption edge from 1200 eV up to the P K-edge of 2145 eV. We have introduced the KTP (Crystal Laser Co., France) crystal at the soft X-ray double crystal beamline BL1A of the UVSOR facility and examined its performance and applicability to the EXAFS measurement in the energy range between 1200 and 2000 eV. The KTP crystal monochromator at the BL1A proves to supply stable photon beams and the energy resolution is estimated to be about 0.5–0.8 eV. The KTP has two excellent advantages in comparison with YB$_{66}$. First, there is no absorption structure originating in the elements contained in KTP in the energy range to be measured. Secondly, a higher throughput is available. By use of the KTP monochromator, reliable EXAFS spectra for the Mg and Al K-edges have been observed for a wide *k* range. The UVSOR storage ring is being operated at a rather low energy (750 MeV), and the BL1A utilizes radiation from a bending magnet, whose critical energy is 424 eV. The radiation damage proves to be less serious for beryl and quartz crystals; therefore, we can expect a small radiation damage to the KTP crystal.