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 Fritz-Haber Institute, McMaster University, University of Alberta, and Photon Factory. We are experimentally interested in ionic fragmentation and electron emission via inner-shell excitation of molecules and in their linear polarization dependence. Recently we are also developing a theoretical approach based on quantum chemistry for inner-shell spectroscopy and dynamics.

VI-A-1 Partial Electron Yield Spectrum of N_2: Doubly Excited States at the K-Shell Threshold

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

Doubly excited states have been revealed both below and immediately above the core ionization threshold in N_2 by measuring a partial electron yield spectrum at the kinetic energy corresponding to the Auger decay of the double excitations. In this partial yield spectrum the core-to-Rydberg transitions and the σ^* shape resonance are absent from this absorption spectrum. The calculated potential energy curves suggest a strongly dissociative nature of the molecular-type double excitations. This agrees well with the observed width of the absorption feature in the partial yield spectrum.

VI-A-2 Inner-Shell Excitation of PF_3, PCl_3, PCl_2CF_3, OPF_3 and SPF_3

NEVILLE, John J.[1]; JÜRGENSEN, Astrid[2]; CAVELL, Ronald G.[2]; KOSUGI, Nobuhiro; HITCHCOCK, Adam P.[1]
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[*Chem. Phys.* **238**, 201 (1998)]

Total ion yield spectra of PF_3, PCl_3, PCl_2CF_3, OPF_3 and SPF_3 were recorded in the region P 2p, P 2s, S 2p, S 2s and halogen (Cl 2p, F 1s) excitation using synchrotron radiation. The theoretical calculations indicate that several of the discrete states are best described as LS-coupled states because the core-valence electron exchange is very large and thus the singlet-triplet splitting is larger than the spin-orbit splitting. Aspects of partial ion yield measurements support this interpretation by revealing isolated single states without a corresponding partner at the spin-orbit splitting. The partial ion yields help clarify spectral interpretation by removing interference from overlap with adjacent states having the normal (j,j)-coupled ion core character.

VI-A-3 The Sulphur 2p Photoabsorption Spectrum of NSF_3

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[*Chem. Phys.* in press]

The Sulfur 2p photoabsorption spectrum of gaseous NSF_3 has been measured at high resolution using synchrotron radiation. Similar to isoelectronic OPF_3 and other pyramidal phosphorus compounds there exist two states, best described as LS-coupled because of a very large core-valence electron exchange. The post-edge features, corresponding to outer well p and d shape resonances, were assigned.

VI-A-4 Jahn-Teller Effect and Rydberg-Valence Mixing in the C1s → 3pt_2 and 3dt_2 Rydberg Excited States of CH_4

ADACHI, Jun-ichi; TAKATA, Yasutaka; SHIGEMASA, Eiji; KOSUGI, Nobuhiro; YAGISHITA, Akira[1]
([1]KEK-PF)

Figure 1 shows angle-resolved photoion-yield spectra for the C1s excited states of CH_4 using linearly polarized synchrotron radiation. The angular distributions of fragment ions emitted from the C1s → 3pt_2 and 3dt_2 Rydberg excited states of CH_4 are anisotropic; the anisotropy parameter β_{3V} deviates from zero. This means that the bond angle on the fragmentation is distorted. The anisotropic photoabsorption is attributed to the Jahn-Teller effect in the excited states with $^1T_2$ symmetry. The bond angle distortion on the fragmentation is related to the Jahn-Teller distortion along the bending modes (ν_2 and ν_4). The Jahn-Teller effect in the Rydberg excited states is expected to be so weak that the T_d geometry is hardly changed. We have to take into accout the Rydberg-valence mixing in order to explain the present result, that is, the 2t_2* valence orbital may be mixed with the 3pt_2 and 3dt_2 Rydberg orbitals in the distorted geometry.

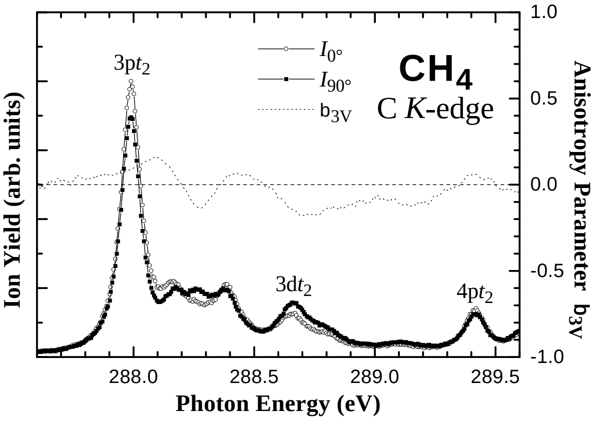

Figure 1. Angle-resolved ion-yield spectra for the C1s → $3pt_2$ and $3dt_2$ Rydberg excited states of CH_4.

VI-A-5 Renner-Teller Spliting in the 1s → $1\pi_g$* Excited States of C_2H_2

ADACHI, Jun-ichi; TAKATA, Yasutaka; SHIGEMASA, Eiji; KOSUGI, Nobuhiro; YAGISHITA, Akira[1]
([1]KEK-PF)

Figure 1 shows high-resolution angle-resolved photoion-yield spectra for the C1s → $1\pi_g$* excited states of C_2H_2. The π* peak shows fine structures on the lower energy side with a spacing of about 0.11 eV. The fine structures of the lower eneryg side are dominated by the bending modes (cis- and trans-bending modes), which are induced by the Renner-Teller effect. The fragment ions at the π* peak are observed not only in the 90° direction but also in the 0° direction ($I_{0°}$) respective to the electric vector of the incident light ($I_{90°}$); the anisotropy parameter β_{3V} deviates from –1. In addition, the $I_{0°}$ yield is slightly enhanced on the lower energy side of the peak. The result agrees with the Renner-Teller splitting, that is, the lower π* excited state has a stable bent structure. The π* peak has a clear shoulder structure on the higher energy side with its spacing of about 0.46 eV. This shoulder is mainly attributed to the C-H stretching mode.

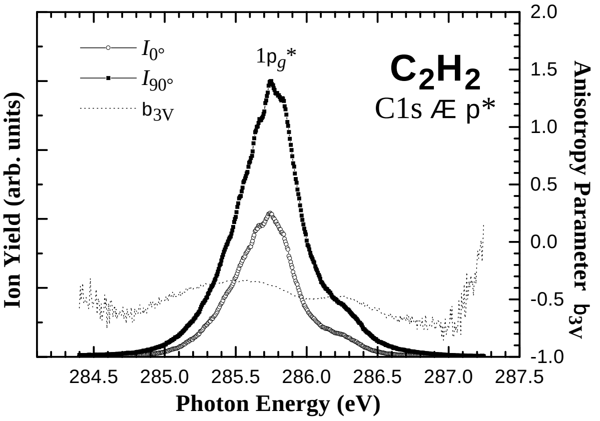

Figure 1. Angle-resolved ion-yield spectra for the C1s → π* states of C_2H_2.

VI-A-6 Enhancement of the O1s → $ns\sigma_g$ Rydberg Series of CO_2 through the $5\sigma_g$-Valence Mixing

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We have measured high-resolution angle-resolved ion-yield spectra for the O1s excited states of CO_2 using linearly polarized synchrotron radiation. The spectra show the $2\pi_u$* peak at 535.4 eV, the Rydberg series between 536 and 540.8 eV, the broad peak just above the O1s ionization threshold, and the shape resonance ($4\sigma_u$*) at 559 eV. It is found that the O1s → $3s\sigma_g$ Rydberg peak overlaps with the higher energy-side component of the π_u* peak. The present spectra show that the $ns\sigma_g$ Rydberg series is the stronger than the other Rydberg series. In addition, the intensity of the $4s\sigma_g$ Rydberg peak is stronger than that of the $3s\sigma_g$ Rydberg peak. These results are explained by the $ns\sigma_g$ Rydberg-$5\sigma_g$* valence mixing as in the case for the terminal N and O1s excited states of N_2O.[1] On the other hand, the $5\sigma_g$* valence excited state may raise its energy just above the O1s ionization threshold through the mixing.

Reference

1) J. Adachi *et al.*, *J. Chem. Phys.* **102**, 7369 (1995).

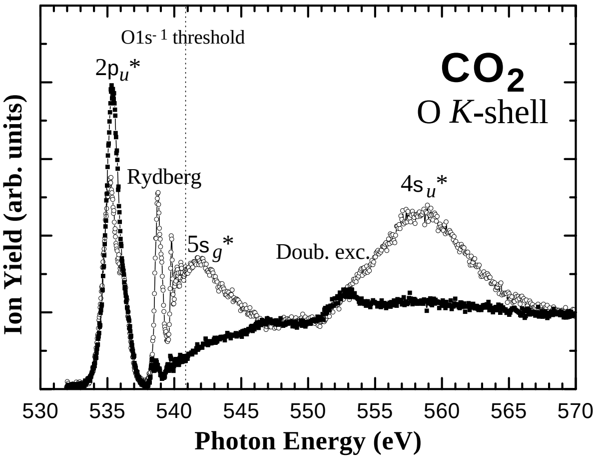

Figure 1. Angle-resolved ion-yield spectra for the O1s excited states of CO_2.

VI-A-7 Vibronic Coupling and Valence Mixing in the 1s → Rydberg Excited States of C_2H_2 in Comparison with N_2 and CO

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

The angle-resolved ion-yield spectra are reported for the C1s → Rydberg excitations of linear acetylene, C_2H_2, in comparison with N_2 and CO. The $3\sigma_u$* valence state is observed in the $3s\sigma_g$ Rydberg region with no mixing. The $3p\sigma_u$ state is found in the same region as the $C1s\sigma_g$ → $3p\pi_u$ state, which shows only totally symmetric vibrations. This is the first to observe that the Rydberg state in C_2H_2 keeps gerade and ungerade symmetries without vibronic coupling through antisymmetric stretching vibrations related to core hole localization. On the other hand, the lowest $1\pi_g$* valence state induces vibronic coupling through bending vibrations in the $3\sigma_u$* and $3s\sigma_g$ states.

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

We are investigating electronic structure of molecular Ni complexes with planar structure by means of inner-shell photoabsorption and photoelectron spectra at the soft X-ray double crystal monochromator beamline BL1A of the UVSOR facility. We have found that a one-electron picture is appropriate to interpret the Ni 2p photoabsorption and resonant photoelectron spectra of the molecular Ni complexes, and that the metal-to-ligand charge transfer (MLCT) is essential to describe the photoexcited states. This year, we extend our study to resonant X-ray emission spectra, and also to another Ni compounds with Ni-Ni bonding.

VI-B-1 Ni 2p-3d Photoabsorption and Strong Charge Transfer Satellites in Divalent Ni Complexes with Molecular Ligands. Evaluation of π-Back Donation Based on the DFT Approach

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

Density functional theory within a transition potential approach (DFT-TP) is applied to interpret remarkably strong π-type MLCT (metal-to-ligand charge transfer) satellites in the Ni 2p photoabsorption of planar low-spin Ni^{II} complexes, $K_2Ni(CN)_4 \cdot H_2O$ and bis(dimethylglyoximato)nickel. The MLCT intensities calculated with DFT-TP are in good agreement with experiment, whereas the HF-STEX (Hartree-Fock based static exchange approximation) approach underestimates the intensities. The DFT-TP approach gives more reasonable π-back donation due to a better description of the strong covalency hybridization of the ligand π* orbitals with the occupied 3d orbitals. The DFT analysis indicates that we can evaluate π-back donation qualitatively by experimentally examining the MLCT satellites.

VI-B-2 Ni-Ni Chemical Bond in $[Ni_2(napy)_4Br_2]$-$[B(C_6H_5)_4]$ Studied by Linearly Polarized Ni 2p Photoabsorption

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The Ni-Ni bonding is not well characterized in contrast to the metal-metal bonds of early transition metals. In order to elucidate the character of Ni-Ni bonding, linearly polarized Ni 2p photoabsorption spectra of $[Ni_2(napy)_4Br_2][B(C_6H_5)_4]$ (napy: 1,8-naphthyridine) were measured (Figure. 1). For $[Ni_2(napy)_4Br_2]^{1+}$ cation with Ni atoms of the formal oxidation number +1.5, there are 3 holes in σ–, δ–, and π–symmetry orbitals produced mainly by Ni 3d orbitals. The lowest band A is strong in the E ⊥ z direction, and very weak in the E // z direction, where E and z denote the electric vector of the incident photon and the molecular axis parallel to the Ni-Ni bond, respectively. This indicates that some holes are located in δ orbitals. On the contrary, band B is strong in the E // z direction and weak in the E ⊥ z direction, indicating that the other holes are located in the σ* orbital. The intensity ratio of band A to B is estimated to be about 2 from the spectrum of the powder sample. Therefore, one hole is located in the σ* orbital and two holes in δ-symmetry orbitals, though we cannot distinguish between $\delta^3\delta^{*3}$ and $\delta^4\delta^*$ configurations.

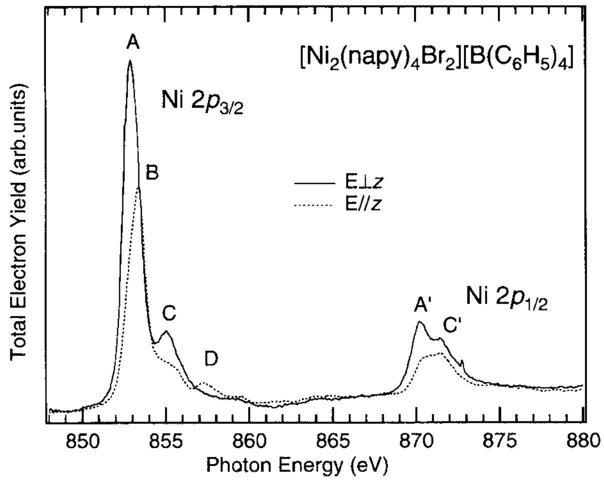

Figure 1. Linearly polarized Ni 2p photoabsorption spectra of a single crystalline $[Ni_2(napy)_4Br_2][B(C_6H_5)_4]$ for the E // z and E ⊥ z directions, where E and z denote the electric vector of the incident photons and the molecular axis z parallel to the Ni-Ni bond, respectively.

VI-B-3 Valence Band Excitation Observed in Resonant Soft X-Ray Emission Spectra of $K_2Ni(CN)_4 \cdot H_2O$ at the Ni 2p Edge

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In order to investigate the valence band structure of a planar nickel complex $K_2Ni(CN)_4 \cdot H_2O$, which shows characteristic MLCT (metal-to-ligand charge transfer) bands in the Ni 2p photoabsorption spectra, resonant soft X-ray emission spectra at the Ni 2p edge have been measured. The experiments were performed at the undulator beamline BW3 in HASYLAB (Germany).

Soft x-ray emission spectra of $K_2Ni(CN)_4\cdot H_2O$ at some Ni 2p resonant excitation are plotted in Figure 1 as a function of the energy difference between excitation and emission energies. At resonance A assigned to the intra-atomic Ni 2p → 3d* excitation, three structures are observed in addition to the elastic peak at 0 eV. These peaks correspond to the d → d* valence excitation with different symmetry. On the other hand, at t resonances B and C, the spectra drastically changed and give the single peak with narrow band width. We have assigned resonances B and C to the excitation to ligand π* orbitals with different symmetry; therefore, the emiision peaks correspond to the d → π* or π → π* valence excitation.

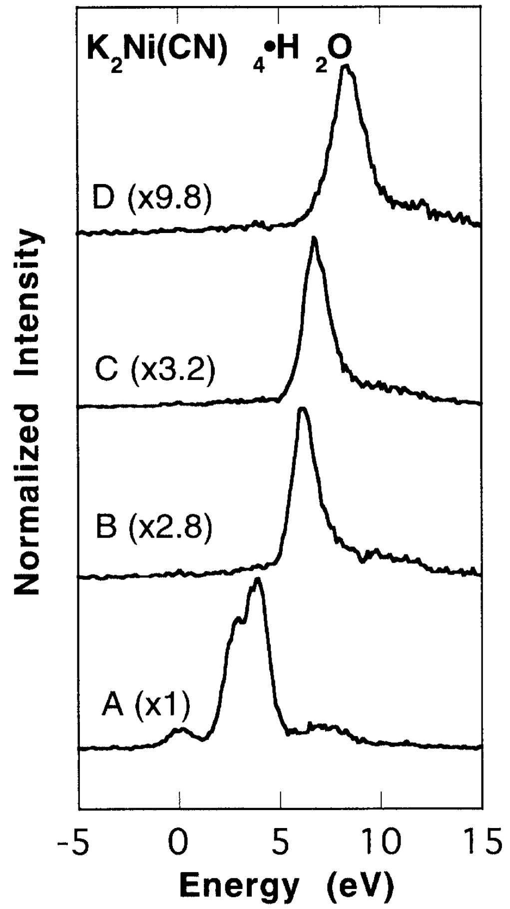

Figure 1. Soft x-ray emission spectra of $K_2Ni(CN)_4\cdot H_2O$ at some Ni 2p resonant excitation The energy (lateral axis) is obtained by subtracting the emission energy from the excitation energy.

VI-B-4 Resonant X-Ray Emission Spectra of $K_2Ni(CN)_4\cdot H_2O$ at the Ni 1s Edge

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([1]GUAS; [2]Univ. Tokyo; [3]KEK-PF)

Recently, we have reported that the electronic structure of nickel planar complexes can be described within a one-electron picture from the Ni 2p photoabsorption and resonant photoelectron spectra. This is different from the interpretation for the strongly correlated system such as NiO. In order to confirm our interpretation experimentally, resonant X-ray emission spectra of $K_2Ni(CN)_4\cdot H_2O$ at the Ni 1s edge were measured at the beamline BL-8B in Photon Factory.

Figure 1 shows resonant X-ray emission spectra at the Ni 1s excitation. The spectrum A was measured at a quadrupole transition to Ni $3d_{x2\text{-}y2}$, and B, C are at dipole transitions to Ni 4pπ*. The elastic peak is shifted to the higher energy side with increase of the excitation energy. Nearby the peak, no extra feature with energy loss was observed. This is quite different from the results for NiO. In NiO, two peaks with the energy loss of 4.9 and 7.8 eV were observed and assigned to the deexcitation to an LMCT (ligand-to-metal charge transfer) state $3d^9\underline{L}$ ($\underline{L}$: ligand hole). The absence of the energy loss feature clearly indicates that LMCT is not important and the one-electron picture is appropriate for the nickel planar complexes. For the Ni K_β line, the energy shift is observed, depending on the photoexcited states. Narrowing of the peak width due to the Raman effect was observed.

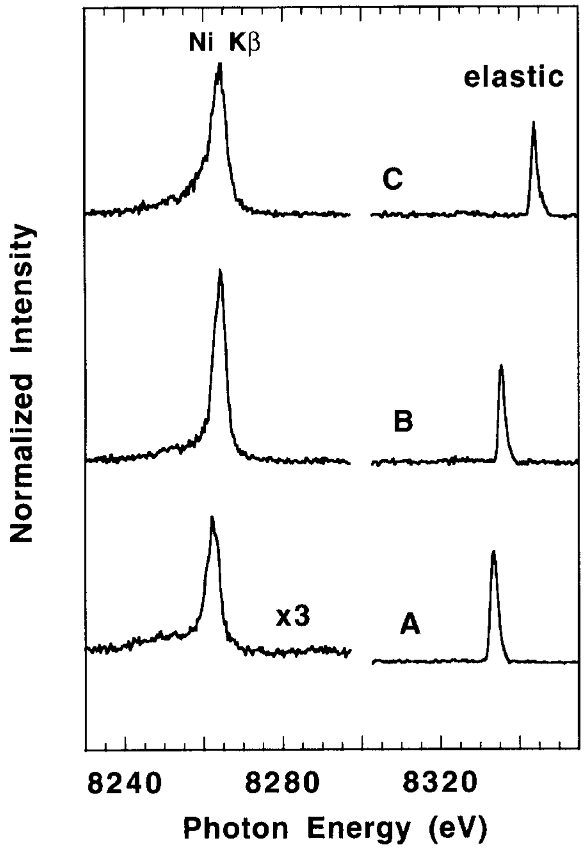

Figure 1. X-ray emission spectra of $K_2Ni(CN)_4\cdot H_2O$ at Ni 1s edge.