RESEARCH ACTIVITIES VI
Department of Vacuum UV Photoscience

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

In this project, we have two major subjects: (a) resonant photoelectron spectroscopy and (b) resonant inelastic soft X-ray emission spectroscopy following inner-shell excitations of simple molecules and clusters. We have found some spin-forbidden ionized and excited states in (a) and (b). In the spectral assignments, angle(symmetry)-resolved photoion yield techniques and R-matrix/MQDT theoretical approaches are essential.

VI-A-1 Rydberg-Valence Mixing in Core Excitations of C_2H_2. Angle-Resolved Photoion Yield Spectroscopic Study

MASUDA, Suomi[1]; GEJO, Tatsuo[2]; HIYAMA, Miyabi; KOSUGI, Nobuhiro
([1]GUAS; [2]Univ. Hyogo)

[*J. Electron Spectrosc.* in press]

High-resolution angle-resolved ion-yield spectra (ARPIS) are reported for the C1s → Rydberg excitations of acetylene. Vibronic coupling features are found in the energy regions of $3s\sigma_g$ and $3\sigma_u{}^*$ excitation, $3p\sigma_u$ excitation, and near threshold. Figure 1 shows ARPIS of C_2H_2 measured at the C1s → 3s and 3p Rydberg excitation region. To select the fragmentation channels, we varied the retarding potentials for ion detectors. The contributions of the $3s\sigma_g$ Rydberg state and $3\sigma_u{}^*$ valence state were successfully resolved. Consequently, the feature observed in the perpendicular direction is assigned to the C1s → $3\sigma_u{}^*$ valence state coupled with the C1s → π^* state *via cis* bending vibrational mode.

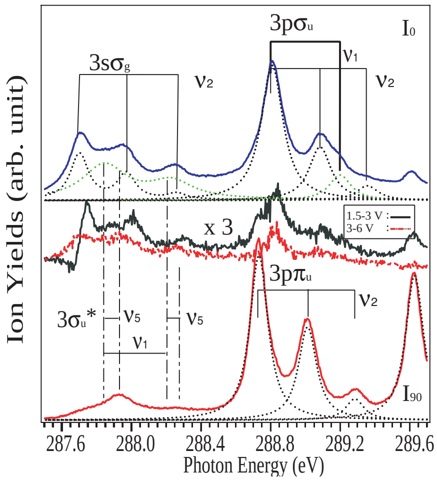

Figure 1. ARPIS of C_2H_2 measured at the C1s → 3s and 3p Rydberg region. Spectra shown on the upper side and lower side correspond to the ion yields measured in the parallel and perpendicular directions, respectively. Spectra shown on the middle are the subtraction spectra measured in the parallel direction with different retarding potentials. : for example, "1.5–3.0 V" means [1.5 V spectra]–[3.0 V spectra].

VI-A-2 Ab Initio R-Matrix/Multi-Channel Quantum Defect Theory Approach to Study Molecular Core Excitation and Ionization: GSCF4R

HIYAMA, Miyabi; KOSUGI, Nobuhiro

[*J. Theor. Comput. Chem.* in press]

Ab initio R-matrix/MQDT approach, which is a combination of *ab initio* R-matrix techniques and the multi channel quantum defect theory (MQDT), has recently been developed by one of the present authors (MH) and Child,[1)] to successfully obtain the potential energy curves of Rydberg states converging to not only the lowest but also the higher ionized states. This approach is also applied to analyze changes in the MQDT scattering matrix arising from the valence state interaction with Rydberg channels.[1)] In the calculations for valence and Rydberg states, the UK molecular R-matrix package developed by Morgan, Tennyson, and Gillan[2)] has been used.

At IMS we extensively study core excitation and ionization of molecules theoretically as well as experimentally. For this purpose we have developed an original *ab initio* polyatomic R-matrix/MQDT code using Gaussian type basis functions (GTFs) for the bound and continuum states with a core hole. Our new program package named GSCF4R is an extension from the conventional *ab initio* SCF-CI (self-consistent field, configuration interaction) package, GSCF3 by one of the present authors (NK), which can be used for both valence and core excitation.[3)]

References

1) M. Hiyama and M. S. Child, *J. Phys. B* **35**, 1337 (2002) ; **36**, 4547 (2003) .
2) L. A. Morgan, J. Tennyson and C. J. Gillan, *Comput. Phys. Commun.* **114**, 120 (1998).
3) N. Kosugi and H. Kuroda, *Chem. Phys. Lett.* **74**, 490 (1980); *Theor. Chim. Acta* **72**, 149 (1987).

VI-A-3 Ab Initio R-Matrix/Multi-Channel Quantum Defect Theory Applied to Molecular Core Excitation and Ionization

HIYAMA, Miyabi; KOSUGI, Nobuhiro

[*J. Electron Spectrosc.* in press]

Very recently we have completed an original ab initio polyatomic R-matrix/MQDT program package, GSCF4R[1] based on Gaussian type basis functions (GTFs) for the bound and continuum states, to extensively study molecular excitation and ionization in the X-ray region as well as in the VUV region. Calculated results for core excitation and ionization of NO show that the R-matrix/MQDT method is indispensable to describe the core-to-Rydberg states with the higher quantum number and the continuum states which cannot be described by using GTFs in the outer region of an appropriate boundary. In the inner region the close-coupling approximation augmented with the correlation term in GSCF4R is proved to be powerful to obtain the potential energies of valence and Rydberg-valence mixed states and the interchannel couplings between several core-ionized states.

Reference

1) M. Hiyama and N. Kosugi, *J. Theor. Comput. Chem.* in press.

VI-A-4 Valence in the Rydberg/Continuum Region in Molecular Inner-Shell Spectroscopy

KOSUGI, Nobuhiro

[*J. Electron Spectrosc.* in press]

Using schematic potential energy curves and molecular orbitals, we have discussed where the 1s → σ* excited state is located in the 1s excitation of N_2, O_2, CH_3F, and C_2H_2, and how we know evidence for the 1s → σ* excited state in photoabsorption spectra of CH_4, CO_2, and N_2O. In the former molecules, the σ* state is identified in the Franck-Condon region from the ground state; in the latter molecules, the σ* state is not clearly identified but its evidence is observed through the Rydberg-valence mixing in the Franck-Condon region. In N_2, the σ* state is located above the ionization threshold and is autoionizing. In O_2, the σ* state is mainly mixed with the 3pσ* Rydberg state converging to the $^4\Sigma$ ionized state. In CH_3F, the σ* state is observed below the 3s Rydberg state. In C_2H_2, the σ* state and the 3s Rydberg state are observed in the same energy region and the σ* state has an effect of the conical intersection with the lowest π* state, where the σ* state is lower than the π* state for a longer HCC–H distance. On the other hand, in CH_4, the Jahn-Teller distortion of the 3p Rydberg transition induces contribution from the σ* state. In the 1s excitations from the terminal atoms in CO_2 and N_2O, some lower s-type Rydberg states get intensities from the σ* state. In the 1s excitations from the central atoms, the σ* state is a dark state (not exactly in N_2O). In the C1s excitation of CO_2, the 3s Rydberg states are vibronically enhanced through mixing with the π* state.

VI-A-5 Spin-Orbit and Exchange Interactions in Molecular Inner-Shell Spectroscopy

KOSUGI, Nobuhiro

[*J. Electron Spectrosc.* **137-140**, 335 (2004)]

In recent high-resolution and sophisticated soft X-ray molecular spectroscopies, small exchange interaction (EX) involving the core electron has been revealed. Interatomic core-core EX is generally small; therefore, it is considered that even the core electron described as $1s\sigma_g$ and $1s\sigma_u$ in homonuclear systems is localized on an atom. However, small but appreciable interatomic core-valence EX in N_2 and C_2H_2 results in observable *g*-*u* splittings in the core ionization, which are experimentally evaluated from extrapolation of the $1s\sigma_g^{local} \rightarrow np\sigma_u, np\pi_u$ and $1s\sigma_u^{local} \rightarrow nsd\sigma_g, nd\pi_g$ Rydberg series. Due to intermolecular Rydberg-valence EX, blue shifts in low-lying core-to-Rydberg excitations in N_2 and Ar are experimentally identified from gas phase to surface, from surface to bulk, and from large to small cage size of rare gas matrixes. EX involving the 2p core electron is anisotropic, depending on the relation between the 2p orbital direction and molecular structure. In some sulfur containing molecules, it is experimentally revealed that the S2p and excited electrons have EX compatible to the 2p spin-orbit interaction (SO) for parallel 2pπ → π* transitions and EX smaller than SO for perpendicular 2pσ → π* transitions. In other words, the *jj* coupling scheme is not applicable to the parallel transitions. Furthermore, it is revealed that, in resonant photoelectron and soft X-ray emissions on the S2p excitation of CS_2 and SF_6, spin-forbidden shake-up valence ionizations with quartet spin couplings and spin-forbidden valence excitations with triplet spin couplings are observable *via* triplet components mixed in intermediate core-excited states.

VI-B Soft X-Ray Photoelectron-Photoabsorption Spectroscopy and Electronic Structure of Molecular Solids and Clusters

This project has been carried out in collaboration with Würzburg University and RIKEN. We have two subprojects: (a) molecules and radicals in condensed phase and in rare gas matrix, and (b) ionic fragmentations of atomic and molecular clusters following the inner-shell resonance excitation. In (a), we have measured excitation spectra of some matrix phases and of some bases in DNA duplexes at the bending-magnet beamline BL4B of the

UVSOR facility. In (b), we have developed a new cluster source for photoelectron measurements on a newly constructed undulator beamline BL3U.

VI-B-1 Temperature Dependence of the Bulk Ar $2p_{3/2}$-4s Excited State of Argon Solid

HATSUI, Takaki; SETOYAMA, Hiroyuki; KOSUGI, Nobuhiro

[*J. Electron Spectrosc.* in press]

Core excitons of rare gas solid have been studied extensively in order to elucidate their character. In the present study, the Ar $2p_{3/2}$-4s excited state for bulk argon solid has been investigated at 8 and 16 K (Figure 1). Careful energy calibration of the monochromater has demonstrated that the peak position at 16 K shows a red shift of 4.2 ± 0.9 meV compared with that at 8 K. The increase of the temperature from 8 to 16 K results in the elongation of the lattice constant of the argon solid from 5.290 to 5.294 Å. The larger lattice constant is expected to cause a blue shift in ionization threshold caused by the weaker stabilization through polarization interaction (PL) of the surrounding atoms/molecules, and a red shift by the weaker exchange interaction (EX) between the excited electron and the electrons of neighboring atoms/molecules. In order to quantitatively examine the observed temperature dependence, *ab initio* theoretical calculations has been carried out for Ar_{19} cluster. The calculations predict the red shift to be 2.7 meV as a sum of the blue shift of 1.1 meV through PL and the red shift of 3.8 meV through EX. The agreement of the theory with the experiment implies the reliability of the calculations. The mean radius of the 4s excited orbital is predicted to be 5.80 Å.

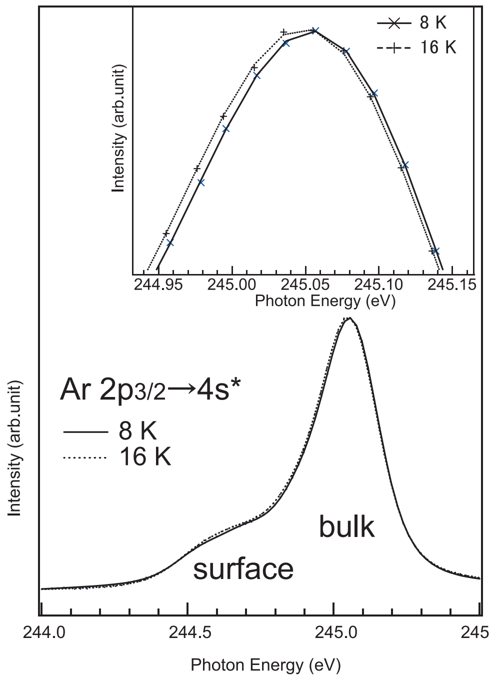

Figure 1. Photoabsorption spectra for argon solid around the Ar $2p_{3/2}$-4s bands at 8 and 16 K. Enlarged spectra around the peak of the bulk Ar $2p_{3/2}$-4s band are shown in inset.

VI-B-2 Sulfur 2p Excited States of OCS in Rare Gas Matrices

SETOYAMA, Hiroyuki; HATSUI, Takaki; KOSUGI, Nobuhiro

[*J. Electron Spectrosc.* in press]

Sulfur 2p x-ray absorption spectra have been measured for OCS solid and for the mixture of OCS and Ar, Kr or Xe in order to study effects of surrounding molecules on the S 2p excited states of OCS. Figure 1 shows S 2p photoabsorption spectra of OCS solid and Xe matrices for different concentration ratios, OCS:Xe = 1:0, 1:1, and 1:7/3. Bands 1 and 2 are assigned to the S $2p_{3/2}$- and S $2p_{1/2}$-4π* core-to-valence transitions, respectively. Bands 3, 4, 5 and 6 are assigned to the $2p_{3/2}$-4s, $2p_{1/2}$-4s, $2p_{3/2}$-“d”, and $2p_{1/2}$-“d” transitions with Rydberg character, respectively. The core-to-valence excited states (bands 1 and 2) do not change their positions upon the mixing, whereas the excited states originating from Rydberg 4s and “d” states show energy shifts. The observed dependence of the shifts on the mixing concentration and on the rare gas element were explained in terms of the polarization stabilization of the ionization threshold and the exchange repulsion of the excited electron by the electrons of the neighboring atoms/molecules. At the same mixing ratio, the polarization stabilization was found to be independent of the rare gas element.

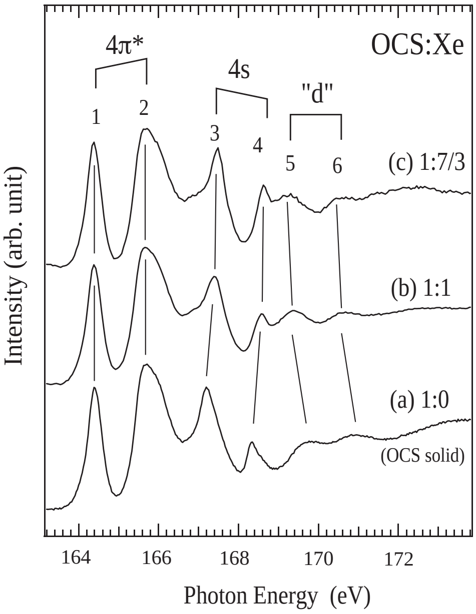

Figure 1. Soft X-ray absorption spectra for OCS and OCS/Xe matrices with different ratios, 1:1 and 1:7/3.

VI-B-3 Cluster Size Effects in Core Excitons of 1s-Excited Nitrogen

FLESCH, Roman[1]; KOSUGI, Nobuhiro;

BRADEANU, Ioana[1]; NEVILLE, John[2]; RÜHL, Eckart[1]
([1]Würzburg Univ.; [2]Univ. New Brunswick)

[*J. Chem. Phys.* **121**, 8343 (2004)]

Cluster size effects in core excitons below the N 1s ionization energy of nitrogen clusters are reported in the energy regime 405–410 eV. These results are compared to the molecular Rydberg states as well as the corresponding bulk excitons of condensed nitrogen. The experimental results are assigned using *ab initio* calculations. It is found that the lowest excitons (N 1s → 3sσ and N 1s → 3pπ) are blueshifted relative to the molecular Rydberg transitions, whereas others (N 1s → 3dπ and N 1s → 4pπ) show a redshift. Results from *ab initio* calculations on $(N_2)_{13}$ clearly indicate that the molecular orientation within a cluster is critical to the spectral shift, where bulk sites as well as inner- and outer-surface sites are characterized by different inner-shell absorption energies. These results are compared to the experimental spectra as well as previous work on site-selectively excited atomic van der Waals clusters, providing an improved spectral assignment of core exciton states in weakly bound molecular clusters and the corresponding condensed phase.

VI-B-4 Metal-to-Ligand Charge Transfer in Polarized Metal L-Edge X-Ray Absorption of Ni and Cu Complexes

HATSUI, Takaki; KOSUGI, Nobuhiro

[*J. Electron Spectrosc.* **136**, 67 (2004)]

Metal L-edge X-ray absorption spectra for Ni and Cu complexes are discussed by investigating their linear polarization dependence. The origin of the characteristic bands is revealed to be one-electron transitions to ligand-centered molecular orbitals carrying metal-to-ligand charge transfer (MLCT). We have shown that the strong bands B and C in $K_2[Ni(CN)_4]\cdot H_2O$ and $Ni(Hdmg)_2$ are definitely assigned to the MLCT transitions by examining the linear polarization dependence and by carrying out *ab initio* molecular orbital calculations. The MLCT transitions are also found in metal $L_{2,3}$-edge X-ray absorption spectra of $[(n\text{-}C_4H_9)_4N]_2[Ni(mnt)_2]$, $(Me_2\text{-}DCNQI)_2Cu$, $K_3Cu(CN)_4$, and $[(C_2H_5)_4N][Ni(mnt)_2]$. It is shown that the intensity of the MLCT transitions is directly correlated to the strength of the back-donation, in which the excited orbital is involved. The linear polarization dependence is also useful to reveal the symmetry of the holes in doped systems and to characterize the Ni–Ni chemical bonding.

VI-B-5 Electronic Structure of Bases in DNA Duplexes Characterized by Resonant Photoemission Spectroscopy near the Fermi Level

KATO, Hiroyuki S.[1]; FURUKAWA, Masashi[1]; KAWAI, Maki[1,2]; TANIGUCHI, Masaki[3]; KAWAI, Tomoji[3]; HATSUI, Takaki; KOSUGI, Nobuhiro
([1]RIKEN; [2]Univ. Tokyo; [3]Osaka Univ.)

[*Phys. Rev. Lett.* **93**, 086403 (2004)]

The electronic structure of bases in DNA duplexes was investigated by resonant photoemission spectroscopy near the Fermi level, in order to specify charge migration mechanisms. Figure 1(A) shows an N K-edge XA spectrum of poly(dG)·poly(dC) and DNA. In the XA spectrum, two 1s → π* resonant peaks at 399.7 eV and 401.9 eV and a broad 1s → σ* resonant peak at 407 eV were observed. This spectrum is in good agreement with the previously reported XA spectra of poly(dG)·poly(dC) DNA,[1)] in which the first (energetically lower) and the second (higher) 1s → π* resonant peaks have been assigned to resonance at imine (–N) and amine (–NH–) site orbitals, respectively. The off-and-on-RPE spectra near the Fermi level of poly(dG)·poly(dC) DNA are shown in Figure 1(B) as a function of kinetic energy. The Auger signals can be extracted from the on-RPE spectra by subtracting the off-RPE spectra, as indicated by the dotted lines. A kinetic energy shift of N-KLL Auger electrons and an intensity enhancement of valence electrons on the resonant photoemission spectra are clearly observed. Similar behaviors are also found for poly(dA)·poly(dT) DNA. These directly show the localized unoccupied states of the bases. We conclude that the charge hopping model is suitable for electric conduction in DNA duplexes rather than the charge transfer model *via* delocalized states when electrons pass through the π* states of DNA bases.

Reference

1) S. M. Kirtley *et al., Biochim. Biophys. Acta* **1132**, 249 (1992).

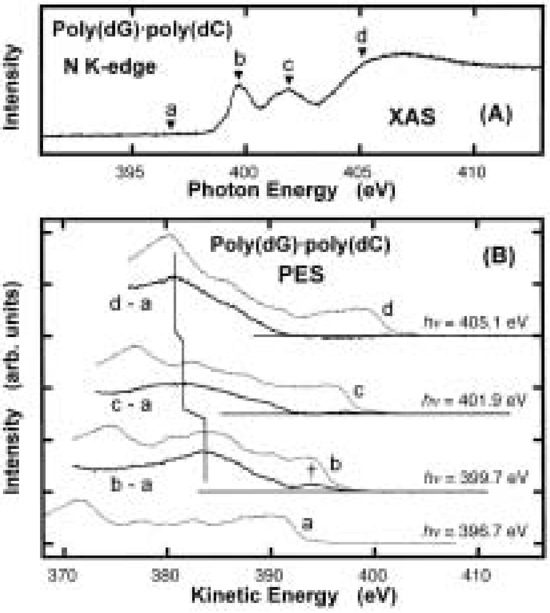

Figure 1. N K-edge XA spectrum of poly(dG)·poly(dC) DNA (A), and its off- and on-RPE spectra as functions of kinetic energy (B). Excitation enegies are shown as arrows a–d in Figure 1(A). The differential spectra based on the off-RPE spectrum in binding energy show resonant Auger signals.