

# RESEARCH ACTIVITIES VI

## Department of Vacuum UV Photoscience

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

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 succeeded in development of a next-generation soft X-ray emission spectrometer. In the spectral assignments, angle(symmetry)-resolved photoion yield techniques and R-matrix/MQDT theoretical approaches are essential.

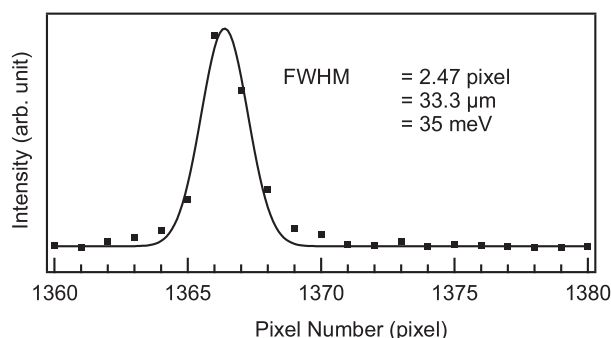
#### VI-A-1 Development of a Transmission-Grating Spectrometer for Soft-X-Ray Emission Studies

HATSUI, Takaki; HORIGOME, Toshio; KOSUGI, Nobuhiro

Last year we reported our new design of a transmission-grating spectrometer (TGS) for high resolution soft X-ray emission studies. This spectrometer will realize a resolution  $E/\Delta E$  up to 5000 in the energy region of 50–600 eV. Here we report the first results using a prototype setup. The spectrometer has a Wolter type I mirror, a free-standing transmission grating, and a back-illuminated charge coupled device (CCD). A high collection angle up to  $1.5 \times 10^{-3}$  sr is achieved by introducing the Wolter mirror as a prefocusing system. The developed Wolter mirror<sup>1)</sup> shows a slope error less than 0.4 arcsec. A SiC transmission grating with a groove density of 6250 l/mm is also developed.<sup>2)</sup> The CCD is mounted at 1.5 m downstream of the grating on a Rowland torus mount with a radius of 0.75 m. Diffracted x-rays are detected in the normal incidence geometry, resulting in high detection efficiency. Ray-trace simulations indicate that aberrations do not practically degrade the energy resolution as high as 5000. It is limited by the figure errors of the optical elements and the spatial resolution of the detector. The energy resolution of TGS was examined by measuring the diffuse scattering of a tungsten wire with a diameter of 3  $\mu\text{m}$  illuminated. Figure 1 illustrates a line profile along dispersion direction of the CCD detector image. The results indicate that the energy resolving power is above 3100 at 110 eV. Further evaluation of the performance by introducing the entrance slit is now under progress.

#### References

- 1) In collaboration with A. Ohba *et al.* (Hamamatsu Photonics K.K.).
- 2) Manufactured by NTT-ATN.



**Figure 1.** Line profile along dispersion direction of the CCD detector image. Full width at half maximum of 33.3  $\mu\text{m}$ , which corresponds to energy resolution of 35 meV ( $E/\Delta E = 3100$ ), has been obtained.

#### VI-A-2 Application of R Matrix/MQDT Method to both Valence and Core Excitations in NO

HIYAMA, Miyabi; KOSUGI, Nobuhiro

Both valence and core excitations of NO molecule are studied using the R matrix/Multi-channel Quantum Defect Theory<sup>1)</sup> program code, GSCF4R.<sup>2)</sup> In the case of valence excitation, the quantum defects and the coupling constant between  $\pi\text{-Rydberg}$  state and  ${}^2\Pi$  state of NO were calculated. The theoretical quantum defects for  ${}^2\Sigma$ ,  ${}^2\Pi$ , and  ${}^2\Delta$  are in good agreement with the experimental values. The theoretical coupling constants not only for B( ${}^2\Pi$ ) but also for L( ${}^3\Pi$ ) are also in good agreement with the experimental values. In the case of core excitation, the potential curves above the N 1s ionization threshold of NO were calculated. There may be six potential energy curves corresponding to the resonances around 412 eV. Finally, the twin local maxima near 412 eV in the absorption spectra of NO may be assigned to the resonances whose characters are  $\sigma^*$  excitation and the mixture of  $\sigma^*$  and doubly excitations, respectively.

#### References

- 1) M. Hiyama and M. S. Child, *J. Phys. B* **35**, 1337–1351 (2002); **36**, 4547–4559 (2003).
- 2) M. Hiyama and N. Kosugi, *J. Theor. Comput. Chem.* **4**, 35–47 (2005).

## 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 Wuerzburg University. 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 in some matrix phases 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 Photoionization of Small Krypton Clusters in the Kr 3d Regime: Evidence for Site-Specific Photoemission

HATSUI, Takaki; SETOYAMA, Hiroyuki;  
KOSUGI, Nobuhiro; WASSERMANN, Bernhard<sup>1</sup>;  
BRADEANU, Ioana<sup>2</sup>; RÜHL, Eckart<sup>2</sup>  
(<sup>1</sup>Berlin Frei Univ.; <sup>2</sup>Würzburg Univ.)

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

Kr 3d ionization energies of small, variable size krypton clusters are investigated by photoelectron spectroscopy, where the size regime of clusters with an average size  $\langle N \rangle \leq 30$  is studied. Characteristic shifts in Kr 3d ionization energies to lower binding energies are found compared to the bare atom. These are also different from those of large krypton clusters. Moreover, we find evidence for photoionization of the krypton dimer. Its 3d ionization energy is barely shifted relative to the atomic value. Results from model calculations considering different isomers and cluster sizes as well as defect sites give evidence that the experimental results can be related to photoionization from different surface sites in variable size krypton clusters. This can be related to site-specific photoemission in small Kr clusters. The results are compared to size effects in Kr 3d near-edge features of variable size Kr clusters as well as recent results on Kr 3d photoionization of large Kr clusters.

### VI-B-2 Core Excitation in O<sub>3</sub> Localized to One of Two Symmetry-Equivalent Chemical Bonds – Molecular Alignment through Vibronic Coupling

WIESNER, Karoline<sup>1</sup>; NAVES DE BRITO, Arnaldo<sup>2</sup>; SORENSEN, Stacey<sup>3</sup>; KOSUGI, Nobuhiro; BJORNEHOLM, Olle<sup>1</sup>  
(<sup>1</sup>Uppsala Univ.; <sup>2</sup>LNL; <sup>3</sup>Lund Univ.)

[*J. Chem. Phys.* **122**, 154303 (2005)]

Core excitation from terminal oxygen O<sub>T</sub> in O<sub>3</sub> is shown to be an excitation from a localized core orbital to a localized valence orbital. The valence orbital is localized to one of the two equivalent chemical bonds. We experimentally demonstrate this with the Auger Doppler effect which is observable when O<sub>3</sub> is core-excited to the highly dissociative O<sub>T</sub> 1s<sup>-1</sup>7a<sub>1</sub><sup>+1</sup> state. Auger electrons emitted from the atomic oxygen frag-

ment carry information about the molecular orientation relative to the electromagnetic field vector at the moment of excitation. The data together with analytical functions for the electron-peak profiles give clear evidence that the preferred molecular orientation for excitation only depends on the orientation of one bond, not on the total molecular orientation. The localization of the valence orbital “7a<sub>1</sub>” is caused by mixing of the valence orbital “5b<sub>2</sub>” through vibronic coupling of anti-symmetric stretching mode with b<sub>2</sub>-symmetry. To the best of our knowledge, it is the first discussion of the localization of a core excitation of O<sub>3</sub>. This result explains the success of the widely used assumption of localized core excitation in adsorbates and large molecules.