## **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<sub>2</sub>H<sub>2</sub>, we found that the lowest  $\sigma_u^*$  state is embedded in the  $3s\sigma_g$  Rydberg state and is dissociative through interaction with the lowest  $\pi^*$  state with bent geometry due to the Renner-Teller effect, that the  $3p\sigma_u$  and  $3p\pi_u$  Rydberg states are clearly resolved and show different vibrational structures, and that the C1s  $\sigma_g$  and  $\sigma_u$  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- $\sigma^*$ Resonance of the Triplet Ground State of S2 in Comparison with O2

#### **RÜHL, Eckart<sup>1</sup>; FLESCH, Roman<sup>1</sup>; TAPPE, Werner<sup>1</sup>; NOVIKOV, Dimitri<sup>2</sup>; KOSUGI, Nobuhiro** (<sup>1</sup>Osnabrück Univ.; <sup>2</sup>HASYLAB)

It is interesting to compare the 1s- $\sigma^*$  resonance of S<sub>2</sub> with that of O<sub>2</sub>. The experimental exchange splitting is observed to be ~1 eV in the S 1s- $\sigma^*$  excited states of  ${}^{3}\Sigma^{-}$  as shown in Figure 1. It should be noticed that the higher  $\sigma^*$  resonance is stronger than the lower  $\sigma^*$  resonance in O<sub>2</sub>, but in S<sub>2</sub> the lower state is stronger than the higher one. The exchange splitting in the ionized states  $\Delta E_{\text{exch}}(\text{ion})$  is given by  $3K_{\text{cx}}^{11}$  (~1.1 eV for O<sub>2</sub>, ~0.2 eV for S<sub>2</sub>), where  $K_{\text{cx}}$  is an exchange integral between the core electron and the  $\pi_x^*$  (or  $\pi_y^*$ ) electron. The exchange splitting in the excited states  $\Delta E_{\text{exch}}(\sigma^*)$  is given as follows:<sup>1)</sup>

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

where v denotes the  $\sigma^*$  electron. In O<sub>2</sub>,  $K_{cv}$  and  $K_{vx}$  are 1.1~1.2 eV and then  $\Delta E_{exch}(\sigma^*) \sim -2.75$  eV < 0; that is, the  $\sigma^*$  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,  $\Delta E_{exch}(\sigma^*)$  is changed to -1.75 eV from -2.75 eV.<sup>2</sup>) In S<sub>2</sub>,  $K_{cx}$  is much smaller than in O<sub>2</sub>. If so,  $\Delta E_{exch}(\sigma^*) < 0$  and the higher  $\sigma^*$  state could be stronger than the lower  $\sigma^*$  state. However, this is inconsistent with the present result. This indicates that the picture of the  ${}^{4}\Sigma^{-}$  and  ${}^{2}\Sigma^{-}$  ion core and an additional  $\sigma^*$  electron does not hold any longer in the S1s- $\sigma^*$  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:

$$\Delta E_{\text{exch}}(\sigma^*) = E({}^{3}\Phi_2) - E({}^{3}\Phi_1) = 3K_{\text{vx}} - 7/3K_{\text{cx}} - 2/3K_{\text{cv}} > 0,$$
  
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  $\Delta E_{exch}(\sigma^*)$  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- $\sigma^*$ 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<sub>3</sub> 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  $\pi$  or  $\sigma$ character. The  $O_T 1s \rightarrow 7a_1(\sigma^*)$  transition dipole is theoretically estimated to be 7° from the  $O_T^*$ –O bond, being nearly parallel to the O<sub>T</sub>–O bond containing an excited terminal atom (O<sub>T</sub>). 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  $O_T 1s \rightarrow$  $7a_1(\sigma^*)$  excitation by relating the asymmetry parameter  $\beta$  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  $70 \pm 10\%$ . This result is interpreted as a "memory" effect of the initially localized core hole in dicationic states (O<sub>T</sub>–O–O)<sup>2+</sup> 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<sub>2</sub>, and PF<sub>3</sub>

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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,  ${}^{2}P_{3/2}$  and  ${}^{2}P_{1/2}$ . 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 twocomponent spin-orbit Hamiltonian is newly developed to analyze the molecular field splitting (MFS) in the  $^{2}P_{3/2}$  state and the spin-orbit splitting ( $\Delta_{3/2,1/2}$ ), and to get 2p<sup>-1</sup> wavefunctions for three typical molecules, OCS, SO<sub>2</sub> and PF<sub>3</sub>. The BP Hamiltonian is diagonalized by using a minimum number of the  $2p^{-1}$  configurations. The diagonal elements in the  $6 \times 6$  BP matrix are corrected by the 2p hole-state energies calculated with the non-relativistic (2p)<sup>5</sup>-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  $\sigma$  and  $\pi$  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*<sup>2</sup>-dimethylethylenediamine)<sub>2</sub>Cl<sub>2</sub>

OJI, Hiroshi; TAKATA, Yasutaka; HATSUI, Takaki; KOSUGI, Nobuhiro In our previous studies, we found the planar Ni complexes with a 3d<sup>8</sup> 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.<sup>1)</sup> 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)<sub>2</sub>Cl<sub>2</sub> (Ni(DED)<sub>2</sub>Cl<sub>2</sub>) 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  $(\Delta KE/\Delta hv)$  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  $(e.g. \Delta KE/\Delta hv = -0.55 \pm 0.05 \text{ for } K_2[Ni(CN)_4]^{1})$ , 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 AI K-edge XAFS Measurements with a KTP Crystal Monochromator

# TAKATA, Yasutaka; SHIGEMASA, Eiji; KOSUGI, Nobuhiro

#### [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) [2d = 15.965 Å] and quartz (1010) [2d = 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<sub>66</sub> (400) [2d = 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<sub>66</sub> crystal from 1200 eV up to the Y L<sub>III</sub> 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<sub>II,III</sub> 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<sub>4</sub>, [2d = 10.95 Å] crystal can be used in the crystal monochromator. The KTP (011) crystal has a little shorter lattice spacing than YB<sub>66</sub> (400), but it can cover the Mg and Al K-edges and has no absorption edge from 1200 eV up to the P Kedge 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<sub>66</sub>. 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.

### VI-C Observation of Vibrational Coherence (Wavepacket Motion) in Solution-Phase Molecules Using Ultrashort Pulses

With recent remarkable improvements of ultrashort-pulse lasers, we are now able to generate an optical pulse shorter than a few tens of femtoseconds. Owing to its ultrashort duration and broad frequency bandwidth, the ultrashort pulse can excite a molecule 'impulsively' to generate a coherence superposition of a number of vibrational state either in the excited state or in the ground state. This vibrationally coherent state evolves in time, which is called wavepacket motion. The observation and control of the wavepacket motion is one of the most interesting topics in modern spectroscopy. In past years, we have generated ultrashort optical pulses whose duration is ten ~ a few tens of femtoseconds by utilizing several nonlinear optical methods. In this year, we constructed experimental setups using these ultrashort pulses, and performed time-resolved measurements to observe vibrational coherence (wavepacket motion) in the excited state and the ground state.

# VI-C-1 Observation of Vibrational Coherence of S<sub>1</sub> *trans*-Stilbene in Solution by 40-fs-Resolved Absorption Spectroscopy

#### TAKEUCHI, Satoshi; TAHARA, Tahei

#### [Chem. Phys. Lett. 326, 430 (2000)]

Recent remarkable advance in laser technology has made it possible to generate an optical pulse shorter than a few tens of femtoseconds. Owing to its ultrashort duration and broad energy bandwidth, the ultrashort pulse can excite a molecule into a coherent superposition of a number of vibrational states. The coherent properties of the prepared state and its time evolution have been receiving much attention in relation to the exploration of a possible role of the vibrational coherence in photochemical processes.

In this project trying to examine the mechanism for the excited-state vibrational coherence, we carried out time-resolved absorption measurements for transstilbene in solution with use of a setup based on 10-fs pulses (Figure 1). We measured a temporal behavior of the  $S_n \leftarrow S_1$  absorption signal around 640 nm following the 320-nm excitation with a time-resolution as good as 40 fs (Figure 2). In the obtained data, an underdumped oscillation due to the S<sub>1</sub> vibrational coherence was observed in the early times. The Fourier-transform analysis showed that the  $S_1$  in-plane deformation mode  $(v_{25}, 200 \text{ cm}^{-1})$  predominantly gives rise to the oscillatory signal. We considered the mechanism for this mode-specificity, and found that the amplitude of the vibrational coherence signal can be related to the S<sub>n</sub>  $\leftarrow$  S<sub>1</sub> resonance-Raman activities of the S<sub>1</sub> vibronic levels and their Franck-Condon activities in the  $S_1 \leftarrow S_0$ excitation process. With reference to the reported  $S_1$ vibrational spectra, we evaluated the relative amplitude of the  $v_{25}$  component against that of the  $v_{24}$  mode (285  $cm^{-1}$ ) that appears strongly in the S<sub>1</sub> Raman spectra, and obtained the ratio consistent with the experimental data. It was concluded that the substantial contribution of the  $v_{25}$  mode in the pump-probe data results from significant displacements among the S<sub>0</sub>, S<sub>1</sub>, and S<sub>n</sub> potentials along the corresponding vibrational coordinate.



**Figure 1.** Spectral properties of *trans*-stilbene in the S<sub>0</sub> and S<sub>1</sub> states. (a) Steady-state absorption spectrum of *trans*-stilbene in heptane. (b) S<sub>n</sub>  $\leftarrow$  S<sub>1</sub> transient absorption spectrum of *trans*-stilbene in heptane measured at 1 ps after 267-nm photoexcitation. Spectra of the pump (c) and the probe (d) pulses used in the 40-fs-resolved absorption measurements are also shown.



**Figure 2.** Time-resolved absorption signal of *trans*-stilbene in heptane (10<sup>-2</sup> M). (a) Temporal behavior of the  $S_n \leftarrow S_1$  absorption (640 nm) measured with excitation at the reddest edge of the ground-state absorption (320 nm). (b) Oscillatory component depicted in a magnified scale.

#### VI-C-2 Generation of Two Independently-Tunable Pulses for Extremely-Fast Pump-Probe Absorption Spectroscopy

#### TAKEUCHI, Satoshi; TAHARA, Tahei

Time-resolved absorption spectroscopy using ultrashort pump and probe pulses has been widely employed for the studies of the dynamical properties of photoexcited molecules. With increasing progresses in laser technology, the time-resolution of these measurements has also been improved drastically, which gives us a chance to even observe new phenomena occurring within a few tens of femtoseconds. In order to achieve such a good time-resolution in molecular spectroscopy, we previously reported the construction of a timeresolved absorption spectrometer utilizing 10-fs pulses generated from a high-power optical parametric amplifier (OPA). In this setup, the second harmonic of the 10-fs pulse was used as a pump pulse in the uv region, while the 10-fs fundamental pulse in the visible region was used as a probe pulse. Consequently, the pump wavelength changed with the tuning of the probe wavelength. This restriction placed on the combination of the pump and probe wavelengths has so far limited the applicability of this spectrometer. Although we successfully applied the spectrometer to the observation of the vibrational coherence of  $S_1$  trans-stilbene,<sup>1)</sup> it is apparently highly desirable that the pump and probe wavelengths can be tuned *independently* in the pumpprobe measurements. For this purpose, we modified the

previous apparatus by adding another low-power OPA with a single-pass amplification scheme (Figure 1). In this modified setup, the entire output of the high-power OPA (10-20 fs, 10 µJ, 1 kHz) is frequency-doubled to generate the pump pulse ( $\approx 0.3 \ \mu$ J) tunable in the range of 250-375 nm. On the other hand, the output of the low-power OPA in the visible region (500-750 nm) is used as a probe and a reference pulse that are tunable independently of the pump wavelength. The timeresolution of this apparatus is typically ca. 40 fs, as evaluated by the FWHM of a cross-correlation trace between the two pulses. The independent tunability as well as the good time-resolution achieved in this spectrometer is highly suitable to extremely-fast molecular spectroscopy. Making the most use of these advantages, we are now investigating the coherent properties of molecules during ultrafast chemical reactions.

#### Reference

<sup>1)</sup>S. Takeuchi and T. Tahara, *Chem. Phys. Lett.* **326**, 430 (2000).



Figure 1. Experimental apparatus of the extremely-fast time-resolved absorption spectrometer using independently-tunable pump and probe pulses.

VI-C-3 Measurement of Impulsive Stimulated Raman Scattering Using Ultra-Short Pulses Generated by a Krypton Gas-Filled Hollow Fiber

FUJIYOSHI, Satoru<sup>1</sup>; TAKEUCHI, Satoshi; TAHARA, Tahei (<sup>1</sup>GUAS) Impulsive stimulated Raman scattering (ISRS) spectroscopy is one of the third-order nonlinear spectroscopy suitable to the study of the low-frequency molecular vibrations. The frequency region to which this technique is sensitive depends on the duration of the pulse used in the measurements. Therefore, we need to use short pulses in order to obtain the information about the molecular vibrations in the wide frequency region.

We generated ultra-short pulses ( $\tau \sim 35$  fs, 800 nm) by using a Kr gas-filled hollow fiber (the autocorrelation is shown in inset of Figure 1) and applied it to the ISRS measurement. The homodyne ISRS signal obtained from liquid CS<sub>2</sub> is shown in figure 1. In addition to the electric response (sharp peak around 0 ps) and nuclear response (collective motion, broad peak around 0.2 ps), a beating signal with a period of 51 fs can be recognized. This beating signal corresponds to the intramolecular vibration at 655 cm<sup>-1</sup>, which becomes observable with use of optical pulses as short as 35 fs.



Figure 1. Impulsive stimulated Raman scattering signal of liquid  $CS_2$ . Inset: The autocorrelation of ultra short pulses that are used in this measurement.

#### VI-C-4 Construction of an Apparatus for Optical Heterodyne Detected Impulsive Stimulated Raman Scattering Measurement Using a Phase Mask

#### FUJIYOSHI, Satoru<sup>1</sup>; TAKEUCHI, Satoshi; TAHARA, Tahei

 $(^{I}GUAS)$ 

Femtosecond optical heterodyne detected impulsive stimulated Raman scattering (OHD-ISRS) spectroscopy is one of the time-domain spectroscopies that can afford information about the low-frequency molecular vibrations. In order to achieve stable heterodyne detection, the relative optical phase between the signal light and the local oscillator (LO) light needs to be accurately controlled. We previously reported OHD-ISRS measurements, in which the phase control was attained by active adjustment of the optical path length.<sup>1)</sup> Recently, a diffractive optics (phase mask) was reported to be applicable in this spectroscopy, which does not require active path-length stabilization<sup>2,3)</sup> and hence facilitate heterodyne detection. We constructed an apparatus with use of the phase mask and the diagram is shown in Figure 1a.

In this apparatus, the visible femtosecond pulse is first divided into two pluses. Each pulse is diffracted into two first-order pulses. The first pair is used as pump pulses and the second pair is used as probe and LO pulses. Figure 1b shows OHD-ISRS signal obtained from liquid carbon tetrachloride with this setup using 75-fs femtosecond pulses (700 nm). The relative phase between the signal light and the LO light was kept stable over a span of one hour even without any active feed back.

#### References

1)S. Matsuo and T. Tahara; Chem. Phys. Lett. 264, 636 (1997).

2) G. D. Goodno, et al., J. Opt. Soc. Am. B 15, 1791 (1998).
3) A. A. Maznez, et al., Opt. Lett. 23, 1319 (1998).

Visible Light pulse (74 fs, 700 nm, 1 µJ, 1 kHz)



**Figure 1.** (a) Constructed apparatus of an OHD-ISRS measurement. (b) Optical heterodyne detected impulsive stimulated Raman scattering signal of liquid carbon tetrachloride measured using a phase mask. Inset: The signal in the early time region is depicted in a magnified scale.

## VI-D Studies of Primary Photochemical/physical Processes Using Femtosecond Electronic Spectroscopy

Ultrafast spectroscopy is playing an essential role in elucidation of photochemical reactions. Thanks to the recent advance in laser technology, we are now able to examine the dynamics of chemical reactions taking place in the femtosecond time region. In this project, we study primary photochemical/physical processes in the condensed phase by time-resolved fluorescence and absorption spectroscopy with a few hundreds femtoseconds time-resolution. Time-resolved fluorescence and absorption spectroscopy are complimentary to each other. The advantage of fluorescence spectroscopy lies in the fact that fluorescence originates from the transition between the "well-known" ground state and the excited state in question. Thus time-resolved fluorescence spectroscopy can afford unique information not only about the dynamics but also other properties of the excited singlet states such as their energies and oscillator strengths. On the other hand, however, time-resolved absorption spectroscopy is considered

to be more versatile because it can detect not only fluorescent excited singlet states but also other "dark" transients. In this year, we investigated the ultrafast dynamics of excited-state proton transfer of anthaquinone derivatives, isomerization of azobenzene, and relaxation of the  $S_2$  state of zinc(II) porphyrins, with use of these time-resolved electronic spectroscopy. In addition, we started construction of a new setup for femtosecond time-resolved infrared spectroscopy.

#### VI-D-1 Ultrafast Excited-State Proton Transfer Dynamics of 1,8-dihydroxyanthraquinone (chrysazin) Studied by Femtosecond Time-Resolved Fluorescence Spectroscopy

#### ARZHANTSEV, Sergei; TAHARA, Tahei

[Chem. Phys. Lett. 330, 83 (2000)]

The steady-state fluorescence spectrum of 1,8dihydroxyanthraquinone (crysazin) shows very large Stokes shift and dual bands emission. This fluorescence feature indicates that a marked geometry change takes places in the excited state. The steady-state fluorescence has been considered as an evidence of the proton transfer reaction across the intramolecular hydrogen bond in the excited state. Femtosecond time-resolved fluorescence intensities of crysazin in hexane have been measured at room temperature for a wide visible wavelength region (470-670 nm) using up-conversion method. Time-resolved fluorescence spectra were reconstructed after deconvolution taking account of the finite instrumental response. The time-resolved fluorescence spectra are presented in Figure 1. The following three points can be noted from these spectra: (1) Both parts in a dual fluorescence (the blue part and the red part) exist even at the time origin. The relative intensity of the blue part is high immediately after photoexcitation, compared with that in the steady-state fluorescence. (2) The fluorescence intensity of the blue part decreases and that of the red part increases in a few picoseconds. (3) After 5 ps, the fluorescence does not show any significant spectral change and it is very similar to the steady-state fluorescence spectrum. The fluorescence intensity decreases monotonously at all the observed wavelengths.

Almost instantaneously appearance of both of the "normal-form type" fluorescence and the "tautomericform type" fluorescence indicates that a barrierless excited-state proton transfer occurs in the time scale of several tens of femtoseconds, reflecting delocalization of the excited-state wavefunction. We assign the fluorescence dynamics in a few picosecond time scale to an additional proton translocation reflecting the intramolecular vibrational relaxation.



**Figure 1.** Reconstructed time-resolved fluorescence spectra of chrysazin. The spectra in the early time region are presented in the top panel. The spectra after 5 ps are presented in the bottom panel.

#### VI-D-2 Femtosecond Dynamics of Photoexcited *trans*-Azobenzene Observed by Time-Resolved Fluorescence Up-Conversion Spectroscopy

## FUJINO, Tatsuya; ARZHANTSEV, Sergei; TAHARA, Tahei

The femtosecond time-resolved fluorescence spectroscopy was applied to study the photochemistry of trans-azobenzene. The excitation wavelength (280 nm, third harmonic pulses of a Ti:saphhire oscillator) in the present experiments corresponds to the blue side of the  $S_2(\pi\pi^*) \leftarrow S_0$  absorption  $(\varepsilon_{280} \approx 10000 \text{ mol}^{-1} \text{ dm}^3)$ cm<sup>-1</sup>), and the molecules were initially photoexcited to the  $S_2(\pi\pi^*)$  state. The femtosecond time-resolved fluorescence signals were measured in the wavelength region from 340 to 680 nm using the up-conversion method. The fluorescence decays obtained from a hexane solution  $(5.0 \times 10^{-3} \text{ mol dm}^{-3})$  at four different wavelengths are shown in Figure 1. These data clearly shows that the temporal behavior of the fluorescence signals varies with the change of fluorescence wavelength. The fluorescence decay at 440 nm looks quite similar to the cross-correlation trace, indicating that the lifetime of the major portion of the fluorescence is shorter than the time resolution. This rapid decay was also dominant in the near-ultraviolet region (340~420

nm). The second fluorescence component becomes noticeable in the fluorescence decay at longer wavelength. In the signals at 560 and 620 nm, the intensity of the second component becomes comparable to that of the first rapid component. A global fitting was performed for the quantitative analysis of the observed decays, and it was clarified that the fluorescence consists of two decay components having lifetimes of ~ 110 and ~ 500 fs. The spectral analysis referring to the steady state fluorescence spectrum clarified that the two fluorescence components exhibit spectra with intensity maxima at ~ 400 and ~ 650 nm. Since these spectra are good mirror images of the  $S_2 \leftarrow S_0$ , and the  $S_1 \leftarrow S_0$ bands in the absorption, they were assignable to the fluorescence from the  $S_2$  and  $S_1$  states, which have planar structure around the central NN bond.



**Figure 1.** Time-resolved fluorescence of trans-azobenzene in hexane solution  $(5.0 \times 10^{-3} \text{ mol dm}^{-3})$  at 440 nm (a), 500 nm (b), 560 nm (c), and 620 nm (d). The dots are experimental data and the solid curves are the results of fitting analysis.

#### VI-D-3 S<sub>2</sub> Emission of a Series of Zinc(II) Porphyrins Studied by Femtosecond Fluorescence Spectroscopy

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Fluorescence from the second electronically excited singlet state ( $S_2$  emission) has been observed for various metalloporphyrins even under the steady-state condition. Zinc(II) porphyrin is one of the typical metalloporphyrins and exhibits S2 emission. However, quantum yields of S2 emission largely depend on the porphyrin peripheral substituents, and in some of zinc(II) porphyrins, no steady-state S2-emission could have been detected. To elucidate what controls the S<sub>2</sub> emission intensity and the radiationless transitions from the S<sub>2</sub> state, we have performed time-resolved fluorescence study for a series of zinc(II) porphyrins, which involves "non-S2-emissive" porphyrins. For all six compounds, S<sub>2</sub> emission was successfully detected by using up-conversion method. The decay rates of the  $S_2$  emission were coincident with the rise rates of the  $S_1$ emission, and the observed S<sub>2</sub> lifetimes vary from 2 ps to 70 fs depending upon the peripheral substituents. There is no clear correlation between the S<sub>2</sub> lifetimes and S<sub>2</sub>-S<sub>1</sub> energy gaps or transition dipole moments of the  $S_2$  state. However, the  $S_2$  lifetime strongly correlates with the intensity ratio of the Q(0,0) and Q(1,0)absorption bands. This leads to a suggestion that a substle difference in the electronic structure of the porphyrin  $\pi$ -system, which is sensitive to the peripheal substituents, remarkably affects the  $S_2 \rightarrow S_1$  internal conversion rate.



Figure 1. Molecular structure and schematic diagram of the relaxation processes of zinc(II) porphyrin.

#### VI-D-4 Construction of Femtosecond IR-IR Pump-Probe Spectrometer

#### FUJINO, Tatsuya; TAHARA, Tahei

An apparatus for femtosecond IR-IR pump-probe measurements was constructed. The setup is based on a regeneratively amplified output of a Ti:sapphire laser that delivers 100 fs pulses of ~ 0.7 mJ at a repetition rate of 1 kHz. These pulses are used to pump a commercial optical parametric generation and amplification (OPG/OPA) system operating with a BBO crystal. The differential frequency between the signal and idler pulses was generated by a AgGaS<sub>2</sub> crystal, and it is used as a frequency-tunable infrared source  $(3 \sim 12 \ \mu m, \sim 3 \ m)$  $\mu$ J). A long-wave pass (> 2500 nm) filter and a Ge filter are used to separate the mid-infrared pulses from the signal and idler. A beam splitter divides the infrared pulse into two parts. The intense pulse was used to excite the fraction of molecules, and the weak one was utilized to probe the induced transmission change. Both pulses are focused on a sample by a CaF<sub>2</sub> lens (focal

length 150 mm), and the sample-transmitted probe (signal) energy as well as the pulse-to-pulse fluctuation (reference) of the probe are measured with the two HgCdTe detectors. The data from the signal and reference detectors are used to determine the IR transmission with (T) and without the pump (T<sub>0</sub>) pulse. The normalized pump-induced transmission change,  $\Delta T/T_0 = T/T_0 - 1$ , is determined as a function of delay time between the pump and probe pulse.



Figure 1. Apparatus for the femtosecond IR-IR pump-probe measurements.

## VI-E Studies of Photochemical Reactions Using Picosecond Time-Resolved Vibrational Spectroscopy

Time-resolved vibrational spectroscopy is a very powerful tool for the study of chemical reactions. It often affords detailed information about the molecular structure of short-lived intermediates, which is not obtainable with time-resolved electronic spectroscopy. However, for molecules in the condensed phase, we need energy resolution as high as  $10 \text{ cm}^{-1}$  in order to obtain well-resolved vibrational spectra. This energy resolution is compatible only with time-resolution lower than one picosecond because of the limitation of the uncertainty principle. In this sense, picosecond measurements are the best compromise between the energy resolution and time resolution for time-resolved frequency-domain vibrational spectroscopy. In this project, we study photochemical processes and short-lived transient species by using picosecond time-resolved Raman spectroscopy. In this year, we studied the picosecond dynamics of the excited state of several fundamental aromatic compounds. In addition, we found that strong hyper-Raman scattering was observed from *all-trans* retinal when amplified picosecond pulses were used for excitation. We obtained information about the low-lying excited singlet states of this molecule from the data of the hyper Raman excitation profile.

#### VI-E-1 Observation of Picosecond Time-Resolved Raman Spectra of *p*-Nitroaniline

#### FUJINO, Tatsuya; TAHARA, Tahei

*P*-nitroaniline is a prototypical molecule that shows intramolecular charge-transfer (CT) with photoexcitation. Because of its simple structure with an electron donor group (-NH<sub>2</sub>) and an acceptor group (-NO<sub>2</sub>), *p*-nitroaniline has a variety of photochemical properties associated with the CT excited state. Timeresolved Raman spectroscopy was performed to study the picosecond dynamics of this CT state in solutions. In this experiment, the excitation pulse (390 nm) was the second harmonics of the regeneratively amplified output of a Ti:sapphire laser. The first Stokes pulse (465 nm, for the water solutions) of H<sub>2</sub> Raman shifter or second Stokes pulse (509 nm, for the toluene solution) of  $D_2$ Raman shifter excited by 390-nm pulse was used as probe. Transient Raman spectra of p-nitroaniline in toluene solution are shown in Figure1. The Raman bands assignable to the  $T_1$  state appeared with the time constant of several tens picosecond after the excitation whereas the  $S_1$  Raman band was not observed. The lifetime of  $T_1$  state was estimated at ~ 5 ns by measuring the decay of the transient Raman bands. In water solution, on the other hand, transient Raman

bands assignable to the  $S_1$  state were observed with its lifetime of ~ 10 ps whereas  $T_1$  Raman band was not observed. These results indicated that the lifetime of  $S_1$  (CT) state and the intersystem crossing rate to the  $T_1$  (CT) state are strongly affected by the change of the solvent polarity.



**Figure 1.** Picosecond time-resolved Raman spectra of *p*-nitroaniline in toluene solution  $(1.5 \times 10^{-2} \text{ mol dm}^{-3})$  at the delay time of 50 ps. Transient spectra (b) was obtained after the subtraction of the solvent (\*) and the ground state signals from (a).

#### VI-E-2 Femtosecond and Picosecond Time-Resolved Spectra of 5-Dibenzosuberenone

#### **UEDA, Atsuhiro<sup>1</sup>; FUJINO, Tatsuya; MIZUNO, Misao; TAHARA, Tahei; TAKAHASHI, Hiroaki<sup>1</sup>** (<sup>1</sup>Waseda Univ.)

Femtosecond time-resolved absorption and picosecond time-resolved resonance Raman spectra of 5-dibenzosuberenone were measured. It was observed in the time-resolved absorption spectra that the  $S_1$  state decayed in a few picoseconds after excitation, while the  $T_1$  state became prominent with time changing in band shape. In the picosecond time-resolved Raman spectra, a Raman band at 1490 cm<sup>-1</sup> was observed immediately after excitation, which was assigned to the  $S_1$  state. Several Raman bands assignable to the  $T_1$  state were also observed to increase in intensity with time. In addition, a T<sub>1</sub> Raman band exhibited a frequency upshift from 1498 to 1517 cm<sup>-1</sup>. The observed frequency shift was considered to be caused by the vibrational cooling process in the T<sub>1</sub> state, and it was detectable thanks to the very rapid intersystem crossing.



Figure 1. Picosecond time-resolved resonance Raman spectra of 5-dibenzosuberenone in acetonitrile.

#### VI-E-3 Resonance Hyper-Raman Scattering of *all-trans* Retinal from a Diluted Solution: Excitation Profile and Energy Levels of the Low-Lying Excited Singlet States

MIZUNO, Misao; HAMAGUCHI, Hiro-o<sup>1</sup>; TAHARA, Tahei (<sup>1</sup>Univ. Tokyo)

Strong hyper-Raman scattering of all-trans retinal was observed from a diluted solution under the resonance condition by using picosecond amplified Ti:sapphire laser pulses for excitation. Figure 1a shows resonance hyper-Raman (RHR) spectra of all-trans retinal in cyclohexane excited at every 10 nm from 770 nm to 840 nm. The concentration of the sample solution is only  $1 \times 10^{-3}$  mol dm<sup>-3</sup>, which is much lower than the concentration in typical RHR measurements (~ 1 mol dm<sup>-3</sup>).<sup>1)</sup> This implies that the intensity of RHR scattering from all-trans retinal is very high. The RHR intensity increases with shortening of the excitation wavelength whereas the spectral pattern does not change significantly. In all-trans retinal, there exist three low-lying excited singlet states, that is, the  ${}^{1}B_{u}$ ,  ${}^{1}A_{g}$  and  ${}^{1}n\pi^{*}$  states. The hyper-Raman resonance enhancement is considered to predominantly arise from two-photon resonance with the  ${}^{1}A_{g}$  state, and hence, RHR intensity is expected to be the maximum when double the excitation photon energy matches the energy of the <sup>1</sup>A<sub>g</sub> state. Figure 2 shows the RHR excitation profile of the intensity of the 1575 cm<sup>-1</sup> band. The slope of the RHR excitation profile is close to that of the onephoton  ${}^{1}B_{u} \leftarrow S_{0}$  absorption band (broken line in Figure 2), which indicates that the energy separation between the  ${}^{1}A_{g}$  state and the  ${}^{1}B_{u}$  state is small. In addition, the spectral pattern of the RHR spectrum is very similar to that of resonance Raman spectrum that is observed with half wavelength of RHR excitation (Figure 1b). It suggests that the resonance mechanism of RHR scattering of all-trans retinal is attributed to the A-term of the vibronic theory<sup>2)</sup> and that Franck-Condon factor between the  $S_0$  state and the  ${}^1A_g$  state resembles that between the  $S_0$  state and the  ${}^1B_u$  state.

#### References

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**Figure 1.** (a) Resonance hyper-Raman (RHR) and (b) resonance Raman (RR) spectra of *all-trans* retinal in cyclohexane  $(1 \times 10^{-3} \text{ mol dm}^{-3})$ .



**Figure 2.** Excitation profile of the  $1575 \text{ cm}^{-1}$  of the RHR band. The black circles indicate RHR band intensities. Broken line shows absorption spectrum of *all-trans* retinal in cyclohexane.

## VI-F Synchrotron Radiation Stimulated Surface Reaction and **Application to Nanoscience**

Study of synchrotron radiation (SR) stimulated surface reaction is a promising topic both in fundamental and applied science. Dynamical process induced by the photostimulated coreelectron excitations on surfaces is attracting considerable attention in the surface science field. Semiconductor nano-structure fabrication by SR stimulated etching and thin film growth is considered to find an important application in the future devices such as molecular devices and molecular bioelectronics

#### VI-F-1 SR-Stimulated Etching and OMVPE Growth for Semiconductor Nanostructure Fabrication

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#### [Mater. Sci. Eng. B 74, 7 (2000)]

Synchrotron radiation- (SR-) stimulated etching and selective area growth by organometallic vapor phase epitaxy were performed to form ordered array of InP crystals on SiO<sub>2</sub>-patterned InP (001) substrate. The SRstimulated etching was used to pattern the SiO<sub>2</sub> film, because photochemical reaction using SR was expected to provide smooth surfaces, vertical side walls and fine patterning. In the first place, we investigated basic properties of the SR-stimulated etching by using mmsize pattern of SiO<sub>2</sub> mask. The etched depth was observed to increase linearly with the irradiation dose. It was found that the etching depth was controlled very accurately. Next, we used µm-size patterns of SiO<sub>2</sub> masks for fabricating the ordered array of InP crystals. In a atomic force microscope image of the sample after the etching, a steep side wall was observed. However, the etched surface was not smooth, against our expectation. Moreover, some dusts were observed on the surface. By these dusts, it was found that the SRstimulated etching had a resolution of  $\leq 100$  nm at most.



#### Figure 1. AFM observation of SiO<sub>2</sub> mask prepared by SRstimulated etching. In (a) it is shown as a bird view image, and in (b) line profile near circular opening. Steep side wall is observed. However, surface is not smooth, against our expectation.

#### VI-F-2 Aligned Island Formation Using Step-Band Networks on Si(111)

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#### [J. Appl. Phys. 86, 3083 (1999)]

We have achieved control of island formation using a patterned Si(111) surface with a periodic array of atomic-step bands and holes. Liquid metals, Au-Si or Ga, migrate on the patterned surface by annealing and form an island at a particular position in each pattern unit. The islands show highly uniform positions and narrow size distributions. To obtain such good uniformity, the diffusion length of surface atoms should be comparable with the pattern period. High mobility on step bands is also necessary factor. Periodic arrays of Au islands are used as seeds for selective growth using a vapor-liquid-solid reaction (VLS). Figure 1 shows VLS Si pillars grown on a Au-island arranged substrate using disilane gas. All Si pillars grow at the positions where Au islands were located.



2 um

Figure 1. SEM image of Si pillars grown on Au-island arranged Si(111) substrates. The substrate was exposed to disilane gas of  $1 \times 10^{-2}$  Torr for 5 min at 620 °C. The angle of the electron beam incidence was 75°.

#### VI-F-3 Scanning Tunneling Microscopy Study of Surface Morphology of Si(111) after Synchrotron Radiation Stimulated Desorption of SiO<sub>2</sub>

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[J. Vac. Sci. Technol., A 18, 1153 (2000)]

The surface morphology of Si(111) was investigated using scanning tunneling microscopy after desorption of surface SiO<sub>2</sub> by synchrotron radiation (SR) illumination. The surface shows large regions of atomically flat Si(111)-7×7 structure, and is characterized by the formation of single bilayer steps nicely registered to the crystal structure. This is in sharp contrast to Si(111) surfaces after thermal desorption of SiO<sub>2</sub> at temperatures 880 °C and above, where the surface steps are much more irregular. X-ray photoemission spectroscopy is also applied to investigate the process of the synchrotron radiation stimulated desorption.

# VI-F-4 Assignments of Bending and Stretching Vibrational Spectra and Mechanisms of Thermal Decomposition of SiH<sub>2</sub> on Si(100) Surfaces

#### NODA, Hideyuki; URISU, Tsuneo

[Chem. Phys. Lett. 326, 163 (2000)]

Vibrations of hydrogen-chemisorbed Si(100) surfaces with  $3 \times 1$  and  $1 \times 1$  structures were studied by buried metal layer-infrared reflection absorption spectroscopy. The SiH<sub>2</sub> bend scissors mode was found to split into two distinct peaks at 902 and 913 cm<sup>-1</sup>; they were assigned to isolated dihydride (ID) and adjacent dihydride (AD), respectively. The observed differences in the dependence on annealing temperature showed that the small peak near 2090  $\text{cm}^{-1}$  and the 2107  $\text{cm}^{-1}$ peak were assignable to the symmetric stretching mode of ID and less stable AD, respectively. These observations have enabled discussion on the mechanisms of the thermal decomposition of dihydride species. It has been found that AD is slightly less stable than ID and that both AD and ID produce coupled monohydride by thermal decomposition.



**Figure 1.** p-Polarized BML-IRRAS spectra associated with H/Si(100) surfaces with (a)  $1 \times 1$  (b)  $3 \times 1$ . Narrow lines show peak-resolved spectra calculated assuming that the shape of each peak is Lorentzian.

## VI-F-5 Control of Surface Composition on Ge/Si(001) by Atomic Hydrogen Irradiation

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(<sup>1</sup>NTT Basic Res. Lab.)

[Surf. Sci. 436, 9 (1999)]

The surface composition of Ge/Si(001)2×1 surfaces after atomic hydrogen (H) irradiation was investigated using IR reflection spectroscopy in ultrahigh-vacuum. It was confirmed that an extremely high dose of H at room temperature causes an etching reaction of the surface Ge layer. However, when H is irradiated at a temperature higher than 150 °C, the etching reaction dose not occur; instead, Ge segregated at the surface is observed to move into a subsurface and Si tends to exist on the topmost surface as a hydride in mixed Ge-Si and pure Si-Si dimers. This is in remarkable contrast to the Ge/Si(001) surface in the absence of hydrogen, where Ge is segregated at the surface and forms Ge-Ge pure dimers. The phenomenon of 'reverse segregation' by H irradiation may be understood by the thermochemical consideration that Si-H bonds are much more stable than Ge-H bonds. The result of first-principles total energy calculations in which the presence of hydrogen changes the stable composition at the surface from Ge to Si is also consistent with the phenomenon.

#### VI-F-6 Reconstruction of BL4A Beam Line and Infrared Reflection Absorption Spectroscopy System

#### WANG, Zhihong; NODA, Hideyuki; NONOGAKI, Youichi; URISU, Tsuneo

Re-arrangement of the beam line at BL4A has already started this year. Now it is still under construction. The IRRAS (Infrared Reflection Absorption Spectroscopy) system has been moved from BL4B to BL4A2. The reaction gas lines have been reconstructed connecting with new interlock system. The reaction chamber for IRRAS measurement was also reconstructed. The new system only use one chamber instead of formal two for the sample transfer to the measurement chamber to make the transfer more easy and efficient. The interlock system connecting these chambers and turbo molecular pumps also has been changed to the more simple and practical one.



**Figure 1.** Schematic drawing of the BL4A2 beam line with the IRRAS system.

## VI-G Photoionization Dynamics Studied by Electron Spectroscopy Combined with a Continuous Synchrotron Radiation Source

Molecular photoionization is a major phenomenon in vacuum UV excitation and provides a large amount of information on fundamental electron-core interactions in molecules. Especially, neutral resonance states become of main interest, since they often dominate photoabsorption cross sections and lead to various vibronic states which are inaccessible in direct ionization. We have developed a versatile machine for photoelectron spectroscopy in order to elucidate dynamical aspects of superexcited states such as autoionization, resonance Auger decay, predissociation, vibronic couplings, and internal conversion. Introduction of a new methodology, two-dimensional photoelectron spectroscopy, allows us to investigate superexcited states in the valence excitation region of acetylene, nitric oxide, carbonyl sulfide, sulfur dioxide and so on. In this method, the photoelectron yield is measured as a function of both photon energy and electron kinetic energy (binding energy). The spectrum, usually represented as a contour plot, contains rich information on photoionization dynamics.

#### VI-G-1 Superexcitation and Subsequent Decay of Triatomic Molecules Studied by Two-Dimensional Photoelectron Spectroscopy

#### MITSUKE, Koichiro; HATTORI, Hideo<sup>1</sup>; HIKOSAKA, Yasumasa<sup>2</sup>

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[J. Electron Spectrosc. Relat. Phenom. in press]

Photoionization and photodissociation processes of  $SO_2$  and  $CS_2$  in the vacuum UV are studied by using two-dimensional photoelectron spectroscopy with a monochromatized synchrotron radiation source. The principal focus is on the mechanisms of autoionization and neutral dissociation of superexcited states. Photoelectron spectra of SO<sub>2</sub> exhibit characteristic peaks at the electron kinetic energy below 1.8 eV which are assigned as resulting from autoionizing transitions of excited atomic sulfur, S\*, into the ground  $S^+(^4S^{o})$ state. These S\* atoms are in the singlet Rydberg states converging to  $S^+(^2D^0)$ . The precursor molecular states,  $SO_2^*$ , are considered to be multiple-electron excited Rydberg states lying at the photon energy above ~ 22 eV. The onset of the photoelectron yield due to the atomic autoionization accords with that expected from the thermochemical threshold for the formation of S\* through three-body dissociation  $SO_2^* \rightarrow S^* + O + O$ . The two-dimensional photoelectron spectrum of CS<sub>2</sub> provides tangible evidence for the formation of a dipoleforbidden Rydberg state  $(6\sigma_g)^{-1}(3d\sigma_g)^{1-1}\Sigma_g^+$  at the photon energy of 14.88 eV which autoionizes into the  $v_3$ = 1 vibrational state of the antisymmetric stretch  $v_3$ mode of  $CS_2^+$  ( $X^2\Pi_{g,\Omega}$ ,  $\Omega = 1/2$  and 3/2). This Rydberg state is expected to borrow substantial oscillator strength from the  $(6\sigma_g)^{-1}(5p\sigma_u)^{1-1}\Sigma_u^+$  state through vibronic coupling involving the  $v_3$  vibration.

#### VI-G-2 Photoelectron Spectroscopy of Atomic and Molecular Radicals Prepared by RF Atom Source

#### MITSUKE, Koichiro; IWASAKI, Kota

There is very little knowledge on the electronic structures of atomic or molecular radicals, though these transient species often play important roles in the elementary reactions in the stratosphere and various plasmas for industrial purposes. Furthermore, studies of superexcited states of such radicals have not yet evolved mainly owing to their low density, short lifetime with respect to fluorescence emission and collisional quenching, and interference with photoelectron bands of other stable or unstable species. To overcome these serious problems we have employed an intense RF radical source that can operate compatibly with our photoelectron spectrometer installed at the beam line BL3B of the UVSOR facility.

Atomic and molecular radicals are produced by an electrical discharge in the resonant cavity (source) which has been tuned so that its load becomes purely resistive. Radicals escape from the source into a vacuum environment through an aperture of 0.5 mm diameter. Under optimal operating conditions, 90% of the molecular H<sub>2</sub>, O<sub>2</sub>, or N<sub>2</sub> leaves the source in dissociated form. The maximum flux of the radical beam is calculated from a gas flow of 0.5 sccm to be *ca*.  $10^{16}$  radicals cm<sup>-2</sup>s<sup>-1</sup> at the ionization region of an electron energy analyzer which is about 30 cm distant from the aperture of the source. As a result, the maximum density at the analyzer position is estimated to be about  $10^{10}$  radicals cm<sup>-2</sup> by assuming the mean translational energy of the radical beam of < 1 eV.

## VI-H Development of a Laser-Synchrotron Radiation Combination Technique to Study Photoionization of Polarized Atoms

In conventional photoionization experiments, the most standard method has generally been taken to be measurement of energy and angular distributions of photoelectrons from randomly oriented (unpolarized) atoms or molecules. However, information obtained from these experiments is insufficient, since the initial state constituted of atoms and photons is not selected and the internal properties of final photoions and electrons are not analyzed. In this project, we have performed photoelectron spectroscopy of polarized atoms using linearly-polarized laser light, aiming at complete quantum-mechanical photoionization experiments. Initial excitation with a linearly polarized synchrotron radiation permits ensemble of atoms to be aligned along the electric vector of the light. From an angular distribution of photoelectrons from polarized atoms, we are able to gain insight into the magnitude and phase shift difference of transition dipole matrix elements of all final channels which are allowed by selection rules.

#### VI-H-1 Laser Photoionization of Polarized Ar Atoms Produced by Excitation with Synchrotron Radiation

#### MITSUKE, Koichiro; HIKOSAKA, Yasumasa<sup>1</sup>; IWASAKI, Kota

(<sup>1</sup>Inst. Mater. Struct. Sci.)

[J. Phys. B 33, 391 (2000)]

The combination technique is incorporated into an apparatus for two-dimensional photoelectron spectroscopy of atoms and molecules in order to investigate photoionization dynamics of polarized atoms. Ground state Ar atoms are excited with linearly polarized synchrotron radiation to Rydberg states lying below the first ionization potential. Aligned atoms thus formed are ionized by irradiation of laser which is also linearly polarized. Photoelectrons emitted in the direction of the electric vector of synchrotron radiation are sampled and energyanalyzed. Photoelectron angular distribution is measured with respect to the electric vector of the laser (see Figure 1). Derivation is made on the expressions which correlate asymmetric coefficients for the angular distribution with theoretical dynamic parameters involving transition dipole matrix elements. The anisotropy of the present angular distribution can be reasonably explained, assuming that the matrix elements and phase shift differences are essentially independent of the total angular momentum quantum number of the final state and that the spin-orbit interaction in the continuous spectrum is small. In the case of the photoionization of the  $Ar^*(3d[1/2]_1)$  state the ratio of the reduced dipole matrix elements between those for the  $\epsilon p$ and *ɛf* parial waves is evaluated from the observed asymmetry parameter to be 0.60 on the presumption that



the phase shift difference of the two waves is equal to  $\pi/2$ .

**Figure 1.** Geometry of the laser-synchrotron radiation combination experiment for investigating photoionization dynamics of polarized atoms. The electric vector  $\vec{E}_{SR}$  of the monochromatized synchrotron radiation is fixed and parallel to the electron sampling direction  $\vec{p}$ . In contrast, the electric vector  $\vec{E}_{laser}$  of the laser can be rotated around its propagation direction. Photoelectron angular distribution is measured as a function of the angle  $\varphi_e$  between  $\vec{E}_{laser}$  and  $\vec{E}_{SR}$ .

#### VI-H-2 Development of a New Angle-Resolved Energy Analyzer for Photoelectron Spectroscopy of Polarized Atoms

#### IWASAKI, Kota; MITSUKE, Koichiro

A conical electron energy analyzer has been developed to measure the angular distribution of photoelectrons from polarized rare gas atoms excited with synchrotron radiation. Since the photoelectron yield of this type of experiment is quite small, we intend to achieve high angular resolution and wide angular acceptance simultaneously.

Our analyzer consists of a set of an inner and outer conical deflector electrodes, cylindrical lenses, a gas cell and a position sensitive detector (PSD) as shown in Figure 1. Photoelectrons emitted in the gas cell are accelerated between the cell and an extractor electrode, and then focused on an entrance slit by the cylindrical lenses. The electron trajectories between the inner and outer conical electrodes are similar to those expected for a conventional parallel-plate analyzer. However, our conical analyzer has rather larger energy dispersion and larger angular aberration than the parallel-plate analyzer. Energy selected electrons exiting from the conical deflector electrodes are detected with the PSD

$$\frac{\Delta E}{E} = \frac{\Delta R}{1.11R} + k_1 \alpha + k_2 \alpha^2 \approx \frac{1}{30},$$

mounted behind the analyzer. The energy resolution is expressed as

where R denotes the distance between the entrance and exit slits,  $\alpha$  the angular deviation of electrons with respect to the mean trajectory of the incident electrons in the dispersion plane, and  $k_1$  and  $k_2$  angular aberration coefficients. On the other hand, the conical analyzer is incapable of focussing the electron trajectories in the azimuth direction. The azimuth angular resolution is thus estimated to be  $1.5^{\circ}$  from the diameter of the sample volume ( $\phi$  1 mm) and the position sensitivity of the PSD. At a PSD particular position, the angular distribution can be measured in the range of  $0^{\circ}-25^{\circ}$  at the same time. By rotating the PSD about the synchrotron radiation propagation axis, we can obtain the photoelectron angular distribution from  $-5^{\circ}$  to  $95^{\circ}$ with respect to the electric vector of synchrotron radiation.



**Figure 1.** Schematic diagram of the conical analyzer. Principal electrodes of the analyzer are depicted by taking two different views. Left: a cross sectional view on the plane which includes the propagation vectors of the laser and synchrotron radiation. Right: a top view.

## VI-I Vacuum UV Spectroscopy Making Use of a Combination of Synchrotron Radiation and a Mode-Locked or Pulsed UV Laser

An ultraviolet laser system has been developed which synchronizes precisely with the synchrotron radiation (SR) from the storage ring of the UVSOR facility. A mode-locked Ti:sapphire laser is made to oscillate at the frequency of the ring in a multibunch operation mode. The delay timing between SR and laser pulses can be changed from 0 to 11 ns. We have developed another system, a pulsed dye laser pumped by an excimer laser, for SR-laser combination experiments. The second harmonic of the dye laser is tunable at 265–280 nm with a pulse energy of *ca*. 2 mJ pulse<sup>-1</sup> at a repetition rate of 10–100 Hz. This laser system is mainly devoted to observing neutral species produced by neutral or ionic photofragmentation induced by SR excitation of molecules. The following three combination studies have been performed: (1) two-photon ionization of helium atoms studied as the prototype of the time-resolved experiment, (2) laser induced fluorescence (LIF) excitation spectroscopy of  $N_2^+(X \, {}^2\Sigma_g^+)$  ions produced by synchrotron radiation photoionization of  $N_2$  or  $N_2O$ , and (3) resonance enhanced multiphoton ionization (REMPI) spectroscopy of S( $3s^23p^4 \, {}^3P_{J'}$ , J'' = 0, 2) dissociated from Rydberg states of OCS. Among these topics LIF spectroscopy of ions is making marked progress in improvements of spectral resolution and fluorescence counts. These improvements are brought about by introducing an RF ion trap and by narrowing the laser band-width. As a consequence, we can obtain reliable rotational distribution curves of  $N_2^+(X \, {}^2\Sigma_g^+)$ .

VI-I-1 Rotational State Distribution of  $N_2^+$ Produced from  $N_2$  or  $N_2O$  Observed by a Laser-Synchrotron Radiation Combination Technique

NIIKURA, Hiromichi<sup>1</sup>; MIZUTANI, Masakazu; MITSUKE, Koichiro (<sup>1</sup>GUAS)

#### [Chem. Phys. Lett. 317, 45 (2000)]

Pump-probe spectroscopy making use of a combination of laser and synchrotron radiation has been performed at the beam line BL3A2 in UVSOR to study ionization and dissociation dynamics of  $N_2$  and  $N_2O$  in the vacuum UV energy region. The fundamental light emitted from the planar-type undulator was dispersed by a 2.2 m grazing incidence constant deviation monochromator in the photon energy range 15.5–19 eV. The second harmonic of a mode-locked Ti:sapphire laser was used for laser-induced fluorescence (LIF)

spectroscopy of N<sub>2</sub><sup>+</sup>( $X \, {}^{2}\Sigma_{g}^{+}, v, N$ ) cations produced by synchrotron radiation photoionization. Fluorescence was collected in the perpendicular direction to the two light beams, dispersed by another monochromator, and detected with a photomultiplier tube. To increase the number density of ions, we employed a cylindrical ion trap. The collisional quenching of the rotational distribution of ions can be disregarded in the ion trap. We can clearly resolve the rotational structure of the Rbranch resulting from the transition  $(B^2\Sigma_u^+, v' = 0, N +$ 1)  $\leftarrow (X^2 \Sigma_g^+, v^* = 0, N)$  of  $N_2^+$  produced from  $N_2$ . The yield curves for  $N_2^+$  ( $X^2 \Sigma_g^+, v^* = 0, 1$ ) are also measured as a function of the photon energy of the synchrotron radiation. The rotational temperature of N<sub>2</sub><sup>+</sup> ( $X^{2}\Sigma_{g}^{+}$ , v" = 0) produced from N<sub>2</sub>O<sup>+</sup> ( $B^{2}\Pi$ ) is determined from an LIF spectrum to be in the range of 200–230 K. The analysis based on the impulsive model indicates that the equilibrium bond angle of  $N_2O^+(B^2\Pi)$ in the vibrational ground state is much larger than 130°.

## VI-J Monochromator Newly Developed on the Beam Line BL2B2 in UVSOR

A grazing incidence monochromator has been constructed which supplies photons in the energy region from 20 to 200 eV. This monochromator will bridge the energy gap between the beam lines BL3A2 and BL8B1, thus providing for an accelerating demand for the high-resolution and high-flux photon beam from the research field of photoexcitation of inner-valence electrons or *L*-shell electrons in the third-row atom.

#### VI-J-1 Performance of the Dragon-Type Monochromator at UVSOR

#### ONO, Masaki; YOSHIDA, Hiroaki<sup>1</sup>; HATTORI, Hideo; MITSUKE, Koichiro

(<sup>1</sup>Hiroshima Univ.)

#### [Nucl. Instrum. Methods Phys. Res., Sect. A in press]

A Dragon-type monochromator has been newly constructed at the bending-magnet beamline BL2B2 of the UVSOR facility. The monochromator has been designed to cover the energy range 20–200 eV with three gratings (G1: 80–200 eV, G2: 40–100 eV, G3: 20–50 eV). A resolving power,  $E/\Delta E$ , of 5000 and a photon flux more than  $1 \times 10^{10}$  photons s<sup>-1</sup> at a 100-mA ring current are expected. The optical alignment and performance test have been finished.

The resolving power is evaluated from the ion yield spectra of the rare gas atoms: the  $3d_{5/2}^{-1}5p$  line of Kr (91.2 eV, exploited for G1 and G2), 2snp + 2pns series of He (60–65 eV, for G2) and  $3s^{-1}np$  series of Ar (25–30 eV, for G3). Moreover, the photon flux is estimated by measuring the photocurrent of a gold mesh which is put in the path of the photon beam. Figure 1 summarizes the resolving power and photon flux at a 100-mA ring current when both the entrance and exit slits are set to 100 µm wide. The solid line in Figure 1(b) shows the expected values derived theoretically.<sup>1)</sup> By adjusting the slit widths, we can attain the resolving power of 2000–8000 and the photon flux of 1 × 10<sup>10</sup> photons s<sup>-1</sup> simultaneously at a 100-mA ring current.

The second-order contribution is inspected on the basis of the ion yield spectrum of Kr around 45.6 eV. The peak of the  $3d_{5/2}^{-1}5p$  line at 91.2 eV appears due to the contaminating second-order light. The percentage of the second-order light at 45.6 eV is estimated to be 7% from the ratio between the absorption cross sections at 45.6 and 91.2 eV.

#### Reference

1)H. Yoshida and K. Mitsuke, J. Synchrotron Radiat. 5, 774 (1998).



**Figure 1.** (a) The photon flux at a 100-mA ring current and (b) resolving power when the entrance and exit slit widths are set to  $100 \ \mu$ m. The solid lines in panel (b) indicate the expected values.

#### VI-J-2 Anisotropy of the Fragment lons from Small Molecules Excited with Synchrotron Radiation

## ONO, Masaki; MIZUTANI, Masakazu; MITSUKE, Koichiro

In order to make assignments of core-electron excited states and study their decay dynamics, an apparatus for symmetry-separated absorption spectroscopy has been developed at the end-station of the beam line BL2B2. The spectrometer contains two ion detectors each of which comprises a grid made of copper mesh followed by a ceratron electron multiplier. Two ion detectors are placed in the parallel and perpendicular direction to the electric vector of synchrotron radiation. Retarding voltages were applied to the grids so that only fragment ions with high kinetic energy were allowed to reach the entrance of the ceratron multiplier. The difference in the collection efficiency and sensitivity of the ceratron multiplier between the two ion detectors were corrected by measuring the spectrum of  $SF_6$ . From the  $O_h$  symmetry it is predicted that the fragment ion yield via core excited states of SF<sub>6</sub> should be isotropic.

Figure 1 shows preliminary results of ion yield spectra of the fragment ions from SF<sub>6</sub> and the calculated asymmetry parameter  $\beta$ , when the retarding voltage is set to 5 V. In the ion yield spectra the prominent peaks in the region of > 170 eV are due to the resonance excitation of a sulfur 2*p* electron. The  $\beta$  parameter is almost 2 at low photon energies below 30 eV, which manifests that fragmentation occurs faster than the molecular rotation. There exist several features around 20–60 eV and a broad peak centered at ~ 100 eV in the yield spectra. The interpretation of these features is now in progress. The artificial structures around 110 eV arise from an imperfect photon-flux normalization process involving photocurrent measurements at the gold mesh (see the preceding theme VI-J-1).



**Figure 1.** Ion yield spectra and the asymmetry parameter of the fragment ions from  $SF_6$ . A retarding voltage of 5 V is applied to the two copper grids.

## VI-K Thin Film Preparation with Chemical Vapor Deposition Using Vacuum Ultraviolet Radiation

Thin-film deposition at temperatures as low as possible and without damages is one of the key technologies for fabrication of ultra-large scale integrated circuit (ULSI). Photon-assisted chemical vapor deposition is a promising way to prepare particularly dielectric thin-films. Silicon dioxide films have been prepared from tetraethoxyorthosilicate (Si-( $OC_2H_5$ )\_4) with chemical vapor deposition using vacuum ultraviolet radiation. The growth rate increases with decreasing the substrate temperature.

#### VI-K-1 Silica Film Preparation by Chemical Vapor Deposition Using Vacuum Ultraviolet Excimer Lamps

KUROSAWA, Kou; YANAGIDA, Hideaki<sup>1</sup>; TAKEZOE, Noritaka; KAWASAKI, Yasuhiro<sup>1</sup>; FUJITA, Masashi<sup>2</sup>; YOKOTANI, Atsushi<sup>2</sup> (<sup>1</sup>IMS and Univ. Miyazaki; <sup>2</sup>Univ. Miyazaki)

#### [*CLEO-2000* CMX4]

New scheme for silica film fabrication by a photochemical vapor deposition was developed by using excimer lamps in vacuum ultraviolet to ultraviolet spectral region. Smooth and uniform silica films were deposited at room temperature at a deposition rate of 1 nm/min.

#### VI-K-2 Silica Film Preparation by Chemical Vapor Deposition Using Vacuum Ultraviolet Excimer Lamps

KUROSAWA, Kou; YAKEZOE, Noritaka; YANAGIDA, Hideaki<sup>1</sup>; MIYANO, Jyunichi<sup>2</sup>; MOTOYAMA, Yoshikazu<sup>2</sup>; TOSHIKAWA, Kiyohiko<sup>2</sup>; KAWASAKI, Yasuhiro<sup>1</sup>; YOKOTANI, Atsushi<sup>3</sup>

(<sup>1</sup>IMS and Univ. Miyazaki; <sup>2</sup>Miyazaki OKI Electric; <sup>3</sup>Univ. Miyazaki)

[European Materials Research Society Spring Meeting 2000, D-II-4]

We have prepared SiO<sub>2</sub> thin films on silicon wafers from tetraethoxyorthosilicate (TEOS; Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) by photo-chemical vapor deposition with the use of various excimer lamps which emit incoherent light at 302 (XeCl), 222 (KrCl), 172 (Xe<sub>2</sub>), 146 (Kr<sub>2</sub>) and 126 nm (Ar<sub>2</sub>). The film deposition is observed at wavelengths shorter than 172 nm. With 10-mW/cm<sup>2</sup> 172-nm radiation, the growth rate is 8 nm/min on the room temperature substrate. The deposition efficiency depends on the wavelength and shows the maximum value for 146-nm radiation. Addition of O<sub>2</sub> to TEOS induces inhibition of C and H impurity inclusion in the films.

## VI-L Ultraviolet, Visible and Infrared Spectroscopy of Solids

Work of ultraviolet (UV), visible (VIS) and Infrared (IR) spectroscopy of solids have been proceeded. These are mainly performed using synchrotron radiation (beamlines BL7B and BL1B at UVSOR), owing to the wide wavelength continuity of synchrotron radiation with no structure.

#### VI-L-1 Performance of IR-VUV Normal Incidence Monochromator Beamline at UVSOR

FUKUI, Kazutoshi; MIURA, Hiroshi<sup>1</sup>; NAKAGAWA, Hideyuki<sup>1</sup>; SHIMOYAMA, Iwao<sup>2</sup>; NAKAGAWA, Kazumichi<sup>3</sup>; OKAMURA, Hidekazu<sup>3</sup>; NANBA, Takao<sup>3</sup>; HASUMOTO, Masami; KINOSHITA, Toyohiko<sup>4</sup>

(<sup>1</sup>Fukui Univ.; <sup>2</sup>Jpn. Atom. Res. Inst.; <sup>3</sup>Kobe Univ.; <sup>4</sup>Univ. Tokyo)

The beamline BL7B at the UVSOR facility for solid-state spectroscopy has been reconstructed and opening for users. This beamline consists of a 3 m normal incidence monochromator and covers from vacuum ultraviolet to infrared region. The optical configuration and the performance, such as photon number, purity and resolving power, have been investigated. The resolving power is over 8000 at around 180 nm and enough for solid-state spectroscopy over whole wavelength range. High purity and low stray of the monochromated light is almost fulfilled over whole range. The wavelength accuracy is less than 0.1 nm.

# VI-L-2 Pseudogap Formation in the Intermetallic Compounds $(Fe_{1-x}V_x)_3AI$

OKAMURA, Hidekazu<sup>1</sup>; KAWAHARA, Jun<sup>1</sup>; NANBA, Takao<sup>1</sup>; KIMURA, Shin-ich<sup>1</sup>; SODA, Kazuo<sup>2</sup>; MIZUTANI, Uichiro<sup>2</sup>; NISHINO, Yoichi<sup>3</sup>; KATO, Masaaki<sup>3</sup>; SHIMOYAMA, Iwao<sup>1</sup>; MIURA, Hiroshi<sup>4</sup>; FUKUI, Kazutoshi; NAKAGAWA, Kazumichi<sup>1</sup>; NAKAGAWA, Hideyuki<sup>4</sup>; KINOSHITA, Tovohiko<sup>5</sup>

(<sup>1</sup>Kobe Univ.; <sup>2</sup>Nagoya Univ.; <sup>3</sup>Nagoya Inst. Tech.; <sup>4</sup>Fukui Univ.; <sup>5</sup>Univ. Tokyo)

[Phys. Rev. Lett. 84, 3674 (2000)]

Optical conductivity data of the intermetallic compounds (Fe<sub>1-x</sub>V<sub>x</sub>)<sub>3</sub>Al ( $0 \le x \le 0.33$ ) reveal that their density of states around the Fermi energy ( $E_F$ ) is strongly reduced as x is increased. In particular, Fe<sub>2</sub>VAl (x = 0.33) has a deep, well-developed pseudogap of 0.1–0.2 eV at  $E_F$  and a small density ( $-5 \times 10^{20}$  cm<sup>-3</sup>) of carriers, which is highly unusual for intermetallic compounds. It is shown that the pseudogap results from the band structures of Fe<sub>2</sub>VAl, rather than from temperature-dependent correlation effects. Based on the present results, we propose a simple model that consistently explains both the semiconductorlike transport and the metallic photoemission results previously observed from Fe<sub>2</sub>VAl.

### VI-M Dynamics and Relaxation of Atoms and Molecules Following Core-Level Excitation

Monochromatized X-ray from synchrotron radiation excites a core electron of an atom or molecule, and the core hole thereby created is usually filled by an outer-orbital electron through an Auger process. In molecules, the core electrons are localized near the atom of origin, in contrast to valence electrons, which are often delocalized over the entire molecule. Although core electrons do not participate in chemical bonding, the energy of an atomic core-level in the molecule depends on the chemical environment of the atom. Site-specific excitation and fragmentation are thus of considerable interest. To elucidate the dynamics and relaxation of atoms and molecules following core-level excitation, we have used photoelectron spectroscopy and the energy-selected-photoemission photoion coincidence method.

# VI-M-1 Site-Specific Phenomena in Si:2p Core-Level Photoionization of $X_3Si(CH_2)_nSi(CH_3)_3$ (X = F or Cl, n = 0-2) Condensed on a Si(111) Surface

NAGAOKA, Shin-ichi; MASE, Kazuhiko<sup>1</sup>; NAGASONO, Mitsuru<sup>2</sup>; TANAKA, Shin-ichiro<sup>3</sup>; URISU, Tsuneo; OHSHITA, Joji<sup>4</sup>; NAGASHIMA, Umpei<sup>5</sup>

(<sup>1</sup>KEK-PF; <sup>2</sup>MAX-lab; <sup>3</sup>Nagoya Univ.; <sup>4</sup>Hiroshima Univ.; <sup>5</sup>Natl. Inst. Adv. Interdisciplinary)

[Chem. Phys. 249, 15 (1999)]

We used photoelectron spectroscopy and the energyselected-photoelectron photoion coincidence (ESPEPICO) method to study site-specific phenomena in the Si:2p photoionization of X<sub>3</sub>Si(CH<sub>2</sub>)<sub>n</sub>Si(CH<sub>3</sub>)<sub>3</sub> (X = F or Cl, n = 0-2) condensed on a Si(111) surface. The site-specific excitation and the occurrence of different chemical shifts at two Si sites were revealed in the total electron-yield spectra and the photoelectron spectra of  $F_3Si(CH_2)_nSi(CH_3)_3$  (n = 1, 2), although they were not clearly revealed in those of Cl<sub>3</sub>SiSi(CH<sub>3</sub>)<sub>3</sub>. We conclude that these site-specific phenomena are easily observed in molecules in which the two Si sites are located far apart and in which electron migration between the two Sicontaining groups does not occur. This was supported by our ab initio calculation. Site-specific fragmentation was revealed in the ESPEPICO spectrum of F<sub>3</sub>SiCH<sub>2</sub>-CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>, although it was negligible for Cl<sub>3</sub>SiSi-(CH<sub>3</sub>)<sub>3</sub> and was less remarkable in F<sub>3</sub>SiCH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub> than in F<sub>3</sub>SiCH<sub>2</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>. Site-specific fragmentation also occurred when the two Si sites were located far apart.

#### VI-M-2 Site-Specific Fragmentation Following C:1s Core-Level Photoionization of 1,1,1-Trifluoroethane Condensed on a Au Surface and of a 2,2,2-Trifluoroethanol Monolayer Chemisorbed on a Si(100) Surface

#### NAGAOKA, Shin-ichi; TANAKA, Shin-ichiro<sup>1</sup>; MASE, Kazuhiko<sup>2</sup>

(<sup>1</sup>Nagoya Univ.; <sup>2</sup>KEK-PF)

We used photoelectron spectroscopy, the energyselected-photoelectron photoion coincidence (ESPEPICO) method, the Auger-electron photoion coincidence (AEPICO) method, and the ab initio method to study site-specific phenomena in the C:1s

photoionization of 1,1,1-trifluoroethane (CF<sub>3</sub>CH<sub>3</sub>, TFEt) condensed on a Au surface. Site-specific excitation and occurrence of different chemical shifts at two carbon sites were evident in the total electron-yield spectrum and the photoelectron spectrum, and site-specific fragmentation was evident in the ESPEPICO spectrum. The fragmentation processes inferred from the ESPEPICO and AEPICO results were very different from those occurring in the vapor phase. We also studied the effect of the surface on the site-specific phenomena observed in a 2,2,2-trifluoroethanol (TFEtOH) monolayer chemisorbed on a Si(100) surface  $(CF_3CH_2OSi\{substrate\})$ . The molecular structure of TFEtOH is the same as that of TFEt except that it has a hydroxyl group substituted for one of the hydrogen atoms. Although site-specific phenomena were also observed in TFEtOH, the fragmentation process was very different from that of TFEt because of the chemisorption structure of TFEtOH on Si(100).

#### VI-M-3 Ion Desorption Induced by Core-Electron Transitions Studied with Electron-Ion Coincidence Spectroscopy

MASE, Kazuhiko<sup>1</sup>; TANAKA, Shin-ichiro<sup>2</sup>; NAGAOKA, Shin-ichi; URISU, Tsuneo (<sup>1</sup>KEK-PF; <sup>2</sup>Nagoya Univ.)

#### [Surf. Sci. 451, 143 (2000)]

The recent investigations of ion desorption induced by core-electron transitions using electron-ion coincidence (EICO) spectroscopy are described. In a study of CF<sub>3</sub>CH(OH)CH<sub>3</sub> chemisorbed on a Si(100) surface using photoelectron photoion coincidence (PEPICO) spectroscopy, site-specific ion desorption is directly verified, that is, F<sup>+</sup> desorption is predominant for C 1s photoionization at the -CF<sub>3</sub> site, while H<sup>+</sup> desorption is predominantly induced by C 1s photoionization at the -CH3 site. A study of condensed H<sub>2</sub>O using Auger electron photoion coincidence (AEPICO) spectroscopy showed that H<sup>+</sup> desorption is stimulated by O KVV Auger processes leaving two-hole states. The H<sup>+</sup> desorption probability is found to depend on the bonding character of the orbitals where holes are created and on the effective hole-hole Coulomb repulsion. AEPICO investigations of H<sup>+</sup> desorption induced by resonant core-electron excitations of condensed H<sub>2</sub>O clearly showed that one-electron-onecore hole or one-electron-two-valence hole states are responsible for the H<sup>+</sup> desorption mechanism. These

investigations demonstrate that EICO spectroscopy combined with synchrotron radiation is a novel and powerful tool for the study of ion desorption induced by core-electron excitations. Furthermore, a comparison of PEPICO and photoelectron spectra showed that the surface core-level shift of condensed H<sub>2</sub>O is 0.7 eV. This study shows that PEPICO spectroscopy is also promising as a method to investigate the electronic structure of the specific sites responsible for ion desorption.

## VI-M-4 Electron–Ion Coincidence Study for the TiO<sub>2</sub>(110) Surface

#### TANAKA, Shin-ichiro<sup>1</sup>; MASE, Kazuhiko<sup>2</sup>; NAGASONO, Mitsuru<sup>3</sup>; NAGAOKA, Shin-ichi; KAMADA, Masao

(<sup>1</sup>Nagoya Univ.; <sup>2</sup>KEK-PF; <sup>3</sup>MAX-lab)

[Surf. Sci. 451, 182 (2000)]

Photo-stimulated desorption from the TiO<sub>2</sub>(110) surface was investigated by using electron-ion coincidence spectroscopy and synchrotron radiation. The desorption of O<sup>+</sup> ions was observed to be coincident with the emission of photoelectrons from the O1s, Ti2s, Ti2p, Ti3s and Ti3p levels, and their satellite peaks due to the shake-up excitation. However, no ion desorption was observed in coincidence with the O2s or valence photoelectrons. The O<sup>+</sup> peak intensities in the coincidence spectra are analyzed, and the result is unexpected from a simple expansion of the Knotek-Feibelman model. The shake-up excitation of O1s levels yields O<sup>+</sup> desorption more efficiently than does the O1s single-electron excitation.

#### VI-M-5 Development of Electron-Ion Coincidence Spectroscopy for Study of Vapor-Phase Dynamics

# MASE, Kazuhiko<sup>1</sup>; NAGAOKA, Shin-ichi (<sup>1</sup>KEK-PF)

An electron-ion coincidence spectrometer for vaporphase dynamics study is being built now. The equipment consists of an electron gun, a cylindrical mirror analyzer (CMA) and a reflectron-type time-offlight ion mass analyzer. Sample gas is excited with the electron beam and the CMA analyzes energy of emitted or scattered electrons. Mass spectra of produced ions are measured with a multichannel scalar taking the energyanalyzed electron signal as the starting trigger.

#### VI-M-6 High-Resolution Angle-Resolved lon-Yield Measurements of $H_2O$ and $D_2O$ in the Region of O 1s to Rydberg Transitions

OKADA, Kazumasa<sup>1</sup>; UEDA, Kiyoshi<sup>2</sup>; TOKUSHIMA, Takashi<sup>1</sup>; SENBA, Yasunori<sup>1</sup>; YOSHIDA, Hiroaki<sup>1</sup>; SHIMIZU, Yuuichiro<sup>2</sup>; SIMON, Mare<sup>3</sup>; CHIBA, Hisashi<sup>2</sup>; OKUMURA, Hiroki<sup>4</sup>; TAMENORI, Yuusuke<sup>5</sup>; OHASHI, Haruhiko<sup>5</sup>; SAITO, Norio<sup>6</sup>; NAGAOKA, Shin-ichi; SUZUKI, Isao H.<sup>6</sup>; ISHIGURO, Eiji<sup>7</sup>; KOYANO,

#### Inosuke<sup>4</sup>; IBUKI, Toshio<sup>8</sup>; HIRAYA, Atsunari<sup>1</sup>

(<sup>1</sup>Hiroshima Univ.; <sup>2</sup>Tohoku Univ.; <sup>3</sup>LURE; <sup>4</sup>Himeji Inst. Tech.; <sup>5</sup>JASRI; <sup>6</sup>Electrotech. Lab.; <sup>7</sup>Univ. Ryukyus; <sup>8</sup>Kyoto Univ. Edu.)

[Chem. Phys. Lett. 326, 314 (2000)]

Angle-resolved energetic-ion yield spectra have been observed in the O 1s excitation region of  $H_2O$  and  $D_2O$  with the incident photon-energy resolution better than 14000. Vibrational structures appear in most of the Rydberg members and are ascribed to the bending vibrations. The assignments of the electronic states are established on the basis of the angular distribution data for the energetic ions.

#### VI-M-7 Molecular Deformation in the O $1s^{-1}2\pi_u$ Excited States of CO<sub>2</sub> Probed by the Triple-Differential Measurement of Fragment lons

SAITO, Norio<sup>1</sup>; UEDA, Kiyoshi<sup>2</sup>; SIMON, Mare<sup>3</sup>; OKADA, Kazumasa<sup>4</sup>; SHIMIZU, Yuuichiro<sup>2</sup>; CHIBA, Hisashi<sup>2</sup>; SENBA, Yasunori<sup>4</sup>; OKUMURA, Hiroki<sup>5</sup>; OHASHI, Haruhiko<sup>6</sup>; TAMENORI, Yuusuke<sup>6</sup>; NAGAOKA, Shin-ichi; HIRAYA, Atsunari<sup>4</sup>; YOSHIDA, Hiroaki<sup>4</sup>; ISHIGURO, Eiji<sup>7</sup>; IBUKI, Toshio<sup>8</sup>; SUZUKI, Isao H.<sup>1</sup>; KOYANO, Inosuke<sup>5</sup>

(<sup>1</sup>Electrotech. Lab.; <sup>2</sup>Tohoku Univ.; <sup>3</sup>LURE; <sup>4</sup>Hiroshima Univ.; <sup>5</sup>Himeji Inst. Tech.; <sup>6</sup>JASRI; <sup>7</sup>Univ. Ryukyus; <sup>8</sup>Kyoto Univ. Edu.)

[Phys. Rev. A in press]

Measurement of mass-, energy-, and angle-resolved fragment ions revealed that the  $\beta$  value for C<sup>+</sup> with kinetic energy  $\geq$  3 eV is ~ 0.9 in the region of the O 1s  $\rightarrow 2\pi_u$  excitation and that  $\beta$  value for O<sup>+</sup> with kinetic energy  $\geq$  4 eV varies from -0.23 to -0.57 across the O 1s  $\rightarrow 2\pi_u$  resonance. These findings postulate that the CO<sub>2</sub> molecule excited to the lower branch of the vibronically split O 1s<sup>-1</sup>2 $\pi_u$  excited states deforms into a bent geometry while the molecule excited to the higher branch remains in a linear geometry.

# VI-M-8 Resonant Auger Spectrum Following Kr:2p $\rightarrow$ 5s Photoexcitation

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(<sup>1</sup>Kyoto Univ. Edu.; <sup>2</sup>Electrotech. Lab.; <sup>3</sup>JASRI; <sup>4</sup>Hiroshima Univ.)

[J. Phys. B in press]

Resonant Auger electron spectra following Kr:2p  $\rightarrow$  5s photoexcitation have been measured for the first time using monochromatized undulator radiation and a cylindrical-mirror electron-energy analyzer. It is found that the kinetic energy of the resonant Auger electron is higher than that of the corresponding normal Auger electron. The angular distribution of the resonant Auger

electrons is nearly isotropic relative to the polarization direction of the incident light.

#### VI-M-9 Angle-Resolved Electron and Ion Spectroscopy Apparatus on the Soft X-Ray Photochemistry Beamline BL27SU at SPring-8

UEDA, Kiyoshi; YOSHIDA, Hiroaki<sup>2</sup>; SENBA, Yasunori<sup>2</sup>; OKADA, Kazumasa<sup>2</sup>; SHIMIZU, Yuuichiro<sup>3</sup>; CHIBA, Hisashi<sup>1</sup>; OHASHI, Haruhiko<sup>3</sup>; TAMENORI, Yuusuke<sup>3</sup>; OKUMURA, Hiroki<sup>4</sup>; SAITO, Norio<sup>5</sup>; NAGAOKA, Shin-ichi; HIRAYA, Atsunari<sup>2</sup>; ISHIGURO, Eiji<sup>6</sup>; IBUKI, Toshio<sup>7</sup>; SUZUKI, Isao H.<sup>5</sup>; KOYANO, Inosuke<sup>4</sup>

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We have designed and constructed the apparatus for the angular distribution measurements of photoejected electrons and ions from free molecules, as a part of the endstation of a c-branch of the beamline 27SU, a soft Xray photochemistry beamline at SPring-8. The experimental procedures are described in combination with the use of a capability to switch the horizontal and vertical directions of the linear polarization of the light produced by the figure-8 undulator. As typical examples of the experimental results, we present angle-resolved energetic ion yield spectra of the O 1s excitation region of CO<sub>2</sub> and the angle-resolved resonant Auger emission of Ne following the 1s  $\rightarrow$  3p excitation.

#### VI-M-10 Monochromator for a Soft X-Ray Photochemistry Beamline BL27SU of SPring-8

OHASHI, Haruhiko<sup>1</sup>; ISHIGURO, Eiji<sup>2</sup>; TAMENORI, Yuusuke<sup>1</sup>; OKUMURA, Hiroki<sup>3</sup>; HIRAYA, Atsunari<sup>4</sup>; YOSHIDA, Hiroaki<sup>4</sup>; SENBA, Yasunori<sup>4</sup>; OKADA, Kazumasa<sup>4</sup>; SAITO, Norio<sup>5</sup>; SUZUKI, Isao H.<sup>5</sup>; UEDA, Kiyoshi<sup>6</sup>; IBUKI, Toshio<sup>7</sup>; NAGAOKA, Shin-ichi; KOYANO, Inosuke<sup>3</sup>

(<sup>1</sup>JASRI; <sup>2</sup>Univ. Ryukyus; <sup>3</sup>Himeji Inst. Tech.; <sup>4</sup>Hiroshima Univ.; <sup>5</sup>Electrotech. Lab.; <sup>6</sup>Tohoku Univ.; <sup>7</sup>Kyoto Univ. Edu.)

A high-resolution monochromator using varied line space plane gratings (VLSG) and spherical focusing mirrors was installed in one of three branches of BL27SU. The performance of the monochromator was evaluated from the photoabsorption spectrum of nitrogen molecule. The resolving power over  $10^4$  was confirmed.

## VI-N Study on RF-Photocathode for Compact X-Ray Sources

Electron storage rings are useful and practical devices as x-ray sources because which produce a number of photons owing to high electron current and various insertion devices. However, these synchrotron radiation facilities usually occupy large area and cost much. So that there have been many works to investigate more compact x-ray sources such as x-ray lasers and free electron lasers. It is also useful to use laser undulator radiation or backward Compton scattering caused by the interactions of electron beams with laser photons, if we provide enough electrons to produce practical intensity of x-rays. RF-photocathode would produce dense electron beam so that it is a useful candidate of a electron source. It is necessary to search good materials as the photocathode for construction of a practical compact x-ray source. Cesium telluride has reported to have a good quantum efficiency, so that we have been studied about it.

#### VI-N-1 Preliminary Study on Photoemission from Cesium Telluride Irradiated by Polarized Photon

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Cesium telluride is a good candidate for a material to be used as a photocathode for RF-gun because of its high quantum efficiency and long life. The quantum efficiency of the photocathode for polarized photon measured with changing the incident angle of the light gives us important information about the optical constants of the materials of the photocathode.

We preliminary measured the quantum efficiency of cesium telluride by using linear polarized photon. Figure 1 shows a sketch of our experimental set up. A Xe lamp was used as a light source. The light from the Xe lamp passed through a monochrometer and a polarizer then enter a vacuum chamber in which cesium telluride was evaporated on molybdenum block as a photocathode. The incident angle of the light was  $60^{\circ}$ . We rotated the polarizer in order to change the direction of polarization. Figure 2 shows the quantum efficiency for the incident light of 250nm wavelength with changing the direction of polarization. The quantum efficiency has peaks at  $90^{\circ}$  and  $270^{\circ}$ . The direction of polarization was parallel to the reflection plane at these angles.

For the further study, we should change the incident angle of the light and measure the quantum efficiency in order to obtain the information of optical constant of cesium telluride.



Figure 1. Sketch of experimental set up.



**Figure 2.** Quantum efficiency of cesium telluride with rotation angle of polarizer for incident light of 250 nm.