OKAZAKI
CONFERENCE

The 28th Okazaki Conference[*] on Solid State Chemistry with VUV Synchrotron Radiation

H. Inokuchi, M. Watanabe and K. Seki[#]
UVSOR Facility, Institute for Molecular Science
[#]Department of Material Science, Hiroshima University

During this Conference on "Solid State Chemistry with VUV Synchrotron Radiation" the principal topic for discussion was the interaction of VUV photons with bulk materials as an approach to the production of new materials with VUV photons.

Much of the oscillator strength of materials lies in VUV, resulting in a major interaction between photons and materials in the VUV range. That is, many photochemical, photophysical and even photobiological changes can be produced in that region and there is therefore the possibility to produce quite new materials using VUV photons. For example, this includes the action of VUV photons as a trigger mechanism as exploited during the exposure of film. The programme was arranged to incorporate all these topics and included contributions on fundamental processes in spectroscopy and photoelectron spectroscopy, basic photochemical reactions in solids and molecules, dynamical processes in liquids and proposals for making new materials such as photo-assisted etching, photo-chemical vapor deposition and so on.

Although solid state chemistry is a rather new field in association with synchrotron radiation research, the full and intensive discussions made us feel sure that the Conference has been a milestone in considering the production of new materials with VUV photons. A total number of 25 talks were presented, including 6 invited lectures. The programme, the collected abstracts and the list of participants are presented below.

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[*] Okazaki Conferences are the principal symposia at the Institute for Molecular Science. They are held twice or three times per year, with a total number of participants of about 50, including several invited foreign speakers.

The 28th Okazaki Conference on
Solid State Chemistry with VUV Synchrotron Radiation
5-7, February 1987, Room 101

February 5

12:30-13:30	Registration
13:30-13:40	Opening Address S.Nagakura (IMS)
	Spectroscopy T. Murata (Kyoto Univ. Educa.) Presiding
13:40-14:10	K. Nakamura (Kyoto Univ.), "Core Excitons in Orthorhombic Indium Halides"
14:10-14:40	M. Taniguchi (Univ. of Tokyo), "Electron-Core-Hole Interaction in Layered Semiconductors"
14:40-15:10	N. Kosugi (Univ. of Tokyo), "Near Edge Structure of Coordination Compounds"
15:10-15:40	T. Fujikawa (Yokohama National Univ.), "Theory and Applications of Multiple Scattering in Solids"
15:40-16:10	Group Photograph Coffee Break
	Photoelectron Spectroscopy T. Ishii(Univ. of Tokyo) Presiding
16:10-16:40	T. Takahashi (Tohoku Univ.), "Angle-Resolved Ultraviolet Photoelectron Spectroscopy of Alkali-Metal Graphite Intercalation Compounds"
16:40-17:10	K. Seki (Hiroshima Univ.), "Photoelectron Spectroscopy of Organic Materials"
17:10-18:10	V. Saile (HASYLAB), "Two - Photon Photoemission from Molecular Crystals Combining Synchrotron Radiation with a Laser"
18:30-20:00	Reception, Cafeteria 2F

February 6

	Time Resolved Spectroscopy (I) T. Okada (Osaka Univ.) Presiding
9:00-10:00	I. Munro (Daresbury Lab.), "Time Resolved Flourescence Anisotropy of Biochemical Systems"
10:00-10:30	Y. Hatano (Tokyo Inst. Tech.), "Time Resolved Fluorescence Spectroscopy of Liquid Alkanes"
10:30-11:00	Coffee Break
	Time Resolved Spectroscopy (II) T. Kobayashi (Univ. of Tokyo) Presiding
11:00-12:00	J. Klein (Strasbourg Univ.), "Relaxation of Highly Excited States in Molecular Solids and Liquids
12:00-12:30	T. Mitani (IMS),"Time Resolved Fluorescence and Modulation Spectroscopies of Molecular Crystals"
12:30-13:30	Lunch

Self-Trapped Exciton, Defect Formation
H. Nakagawa (Fukui Univ.) Presiding

13:30-14:00 K. Nasu (IMS), "Dynamics of Tunneling and Relaxation from Free State to Self-Localized State of Exciton"

14:00-15:00 F. C. Brown (Illinois Univ.), "Defect Formation in Solids by Vacuum Ultraviolet Synchrotron Radiation"

15:00-15:30 Coffee Break

Photodesorption S.Ohtani(Nagoya Univ.) Presiding

15:30-16:30 R. Stockbauer (NBS), "Ion Desorption from Surfaces"

16:30-17:00 A. Ichimiya (Nagoya Univ.), "Photon Stimulated Desorption from LiF Surface"

17:00-17:30 H. Kanzaki (Fuji Photo Film Co.), "Photon-Stimulated Desorption of Neutrals from Silver and Alkali Halides"

Introduction to UVSOR Facility I. Koyano (IMS) Presiding

17:30-18:00 M. Watanabe (IMS), "Introduction to UVSOR Facility"

18:00-18:30 UVSOR Tour

February 7

Photofragmentation J.R.Grover (IMS & BNL) Presiding

9:00- 9:20 S. Nagaoka (IMS),"Investigation of Fragmentation Processes Following Core Photoionization of Organometallic Molecules in the Vapor Phase"

9:20- 9:30 H. Shiromaru (IMS),"Measurements of H^+ formation for Hydrocarbons"

9:30-10:30 T.K.Sham (BNL),"Site-Selective Photofragmentation of Molecules and Its Implication to VUV Induced Solid State and Surface Chemical Processes"

10:30-11:00 Coffee Break

Photochemistry in Solids Y.Maruyama (IMS) Presiding

11:00-11:30 H. Masuhara (Kyoto Inst. Tech.), "Photochemistry and Morphological Changes of Polymer and Deposited Organic Films"

11:30-12:00 S.Morita, H.Yamada and S.Hattori (Nagoya Univ.) "Wavelength Dependence of Chemical Process in X-Ray Resist"

12:00-12:30 T. Ito (Univ. of Tokyo), "VUV Photodegradation of Biomolecules --- DNA, ATP and Oligonucleotide"

12:30-13:30 Lunch

Prospective Projects K. Kimura (IMS) Presiding

13:30-14:00 K. Shobatake (IMS), "Photo-Excited Etching Reactions of Silicon Crystals"

14:00-14:30 A. Yoshida (Toyohashi Univ. Tech.), "Thin Film Deposition by VUV Synchrotron Radiation"

14:30-15:00 H. Inokuchi (IMS), "Concluding Remark -Application of VUV Photons to Organic Chemistry-"

Core Excitons in Orthorhombic Indium Halides

Kaizo NAKAMURA, Yasuo SASAKI, Toru KISHIGAMI, Makoto WATANABE*
and Masami FUJITA+

Department of Physics, Kyoto University, Kyoto 606
*Institute for Molecular Science, Okazaki 444
+Maritime Safety Academy, Kure 737

Polarized reflection spectra of orthorhombic InBr and InI (space group D_{2h}^{17}) have been investigated at LHeT by using synchrotron radiation in the energy region 2 - 30 eV. Results on InBr were reported previously.$^{1)}$

Figure 1 shows the spectra of InBr for E//c and for E//a. The first exciton peak at 2.33 eV is due to the transition from the top valence band of bromine 4p, into which considerable amount of In 5s orbital admixes, to In 5p conduction band bottom. This transition is forbidden for E//a. At about 20eV, In 4d core exciton peaks are observed.

Structure between 2 and 7 eV in both materials are compared with the appropriate energy shift. Many peaks coincide in energy suggesting that these transitions occur in In sublattice, that is, In 5s valence band to In 5p conduction band.

Fig. 2 shows the spectra of In 4d core excitons in InI in an expanded energy scale. Spectra of InI are very dichroic. Two main peaks in InBr are separated by 0.8 eV (see Fig. 1). This structure is explained approximately by free ion model. On the other hand, in InI each peak splits into two or more peaks. To understand this dichroism and splitting, analysis including crystal field as well as spin-orbit and exchange interactions is attempted. It is found that the crystal field splitting amounts to 1 eV and is comparable to that of spin-orbit interaction.

1) K. Nakamura, Y. Sasaki, M. Watanabe, and M. Fujita: to be published in Physica Scripta 37 (1987).

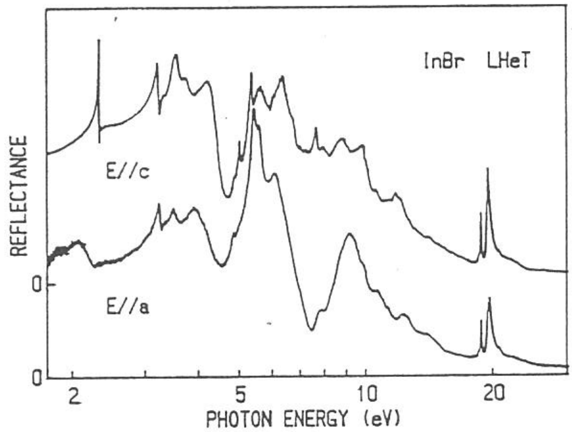

Fig. 1. Reflection spectra of InBr at liquid helium temperature. (a) for E//c and (b) for E//a.

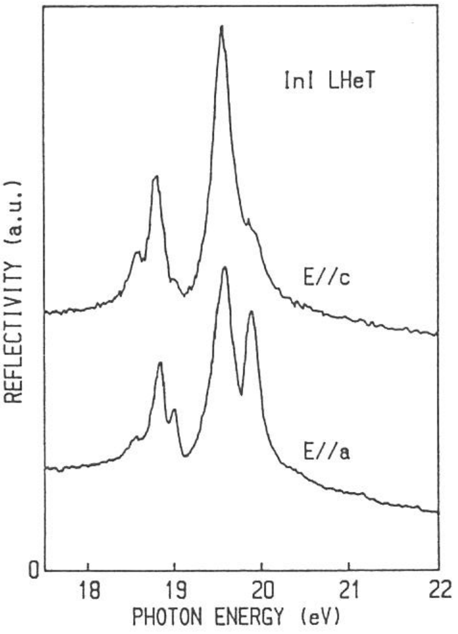

Fig. 2. Reflection spectra of 4d core excitons in InI at LHeT.

Electron-Core-Hole Interaction in Layered Semiconductors

M. Taniguchi

Synchrotron Radiation Laboratory, Institute for Solid State Physics,
The University of Tokyo, Tanashi, Tokyo 188, Japan

Core level absorption spectra in semiconductors exhibit quite different behaviour depending on the degree of electron-core-hole (e-c.h.) interaction. For weak e-c.h. interaction, the spectra reflect the density of states (DOS) of empty conduction bands, whereas strong e-c.h. coupling leads to an excitonic enhancement of the absorption near the core absorption thresholds. In an attempt to investigate the conditions that lead to the different behaviour, a comprehensive study of core excitations in GeS, GeSe, SnS and SnSe layered single crystals with black phosphorus (P) have been performed using synchrotron radiation1). The core absorption spectra were measured by partial yield spectroscopy at Flipper II beam line of HASYLAB.

We find consistently that the anion core (S 2p and Se 3d) absorption spectra reflect the DOS of conduction bands, whereas the cation core (Ge 3d and Sn 4d) spectra show intense and sharp spin-orbit doublets at thresholds. The excitonic nature of the latter is exemplified by a strong e-c.h. exchange interaction which leads to a reversal of the intensities of the two components compared to their statistical weight (6:4 for $d_{5/2}$ and $d_{3/2}$ components). The localized nature of the excitations favours their direct recombination decay channel which is observed as a pronounced Fano-type resonance in the valence band photoemission cross section near the core absorption thresholds.

The data are analyzed in terms of band structure, wavefunction and e-c.h. exchange interaction in the compounds. The difference between excitonic and non-excitonic core transition rests on the cationic origin of the states near the bottom of conduction bands as well as the anionic origin of the high DOS features at the top region of valence bands.

By the same line of argument, characteristic features of the 2p core-exciton absorption2) in black P single crystal can be also interpreted.

References
1) M. Taniguchi, J. Ghijsen, R. L. Johnson and L. Ley, in Proceedings of the 17th International Conference on the Physics of Semiconductors, Stockholm (1986).
2) M. Taniguchi, J. Ghijsen, R. L. Johnson, S. Suga, Y. Akahama and S. Endo, Annual Report of HASYLAB (1986).

NEAR EDGE STRUCTURE OF COORDINATE COMPOUNDS

Nobuhiro KOSUGI

Department of Chemistry, Faculty of Science,
The University of Tokyo

The author reviewed metal K-edge XANES (X-ray Absorption Near Edge Structure) spectra of 3d transition metal complexes, which were all measured by him and coworkers at Beam Line 10B of Photon Factory. It is well known that in the compounds containing the first-row elements there are 1s → 2pπ* and 1s → Rydberg transitions below the ionization threshold and 1s → 2pσ* (so-called shape resonance) above or near the threshold; however, it is little appreciated whether we can observe 1s → Rydberg and 4p* transitions in XANES of 3d transition metal compounds. The author found that weak pre-edge structures are 1s → Rydberg transitions in Fe K-edge XANES of $Fe(CO)_5$ by comparing gas phase with liquid phase, and that 1s → 3d transitions show d-d splitting (1s → $3dt_{2g}, e_g$) distinctly in XANES of octahedral $Fe^{III}(CN)_6{}^{3-}$ [$^2T_{2g}$: $(3dt_{2g})^5(3de_g)^0$] but no d-d splitting (1s → $d_{x^2-y^2}$, d_{z^2}) in XANES of square-planar Fe^{II}-phthalocyanine complex [^3E_g : $(d_{x^2-y^2})^0(d_{z^2})^1(d_{xz}d_{yz})^3(d_{xy})^2$], due to anisotropic stabilization of each d level upon core-hole creation. He successfully observed 1s → 4pπ* transitions below the threshold in polarized XANES of square-planar $Ni(CN)_4{}^{2-}$ and Ni-phthalocyanine complexes, and proposed that 1s → 4pπ* and 4pσ* transitions split to two peaks through the orbital interaction with occupied and unoccupied orbitals of the covalent ligands. He also found shake-down and shake-up transitions in polarized XANES of square planar $Cu^{II}Cl_4{}^{2-}$ (completely ionic ligand) and Cu^{II}(trimethylimidazole)$_4{}^{2+}$ (less ionic), respectively, and no satellite structure in Cu^{I} complexes, and interpreted the appearance of satellite structures based on a three-electrons-in-two-orbitals model (configuration mixing between $(d_{x^2-y^2})^1(\text{ligand }\sigma)^2$ and $(d_{x^2-y^2})^2(\text{ligand }\sigma)^1$; the former corresponds to d^9 and the latter to d^{10}).

REFERENCES : Chemical Physics, 91 (1984) pp.249-256 ; 103 (1986) pp.101-109 ; 104 (1986) pp.449-453 ; See also Activity Reports from Photon Factory (Annual).

Theory and Applications of Multiple Scattering in Solids

Takashi Fujikawa
Faculty of Engineering,Yokohama National University
Hodogaya,Yokohama 240, JAPAN

For solid X-ray absorption and X-ray photoelectron spectroscopy, multiple scattering is usually important to describe the dynamics of outgoing photoelectrons especially in the low energy scattering. However,"multiple scattering" is frequently used in the two different meanings. One is used to construct the one electron wave function of an ejected electron to include the potential effect. For example, XANES(X-ray absorption near edge structure) theory has been developed by use of this multiple scattering function[1,2]. As an example, we will talk about the results of XANES analyses based on our short-range order full multiple scattering calculation for halogen doped polyacetylene[3]. Linearly polarized X-ray gives us some useful information;E//c(parallel to chain axis) polarization gives us the information on the X-C correlation(X=Br,I).The nearest X-C distance is longer than the sum of the van der Waals radii of X and C. This result can explain the increase of the anisotropy of electric conductivity with halogen doping. Our XANES analyses also confirm the charge distribution on polyanion I_3^- and I_5^- determined by Mössbauer spectroscopy[4]. In the bromine low doping region it is proved that mono-anions exist. We also obtained the information about the charge distribution on carbon chains around the mono-anions. The maximal amplitude of the charge density is larger than 0.4, which supports the result of Sasai et al.[5].

In another case we use "multiple scattering" to describe the inelastic,resonance and exchange scattering during the travel in the solid sample. As an example of this physical process, the interference effects between intrinsic and extrinsic excitation processes[6,7,8]. Especially, a somewhat detailed discussion will be given for plasmon loss process[7].

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[6]T.Fujikawa:Z.Phys.B54(1984)215.
[7]T.Fujikawa:J.Phys.Soc.Jpn.55(1986)3241.
[8]T.Fujikawa:Z.Phys.B(1987) in press.

Angle-Resolved Ultraviolet Photoelectron Spectroscopy of Alkali-Metal Graphite Intercalation Compounds

Takashi Takahashi
Department of Physics, Tohoku University, Sendai 980, Japan

It is well known that the charge transfer plays an essential role in characterizing the novel properties of graphite intercalation compounds (GICs). Yet at present there is a great theoretical and experimental confusion in the first-stage alkali-metal GICs. The controversial point is the charge balance between the π^* band at the $\tilde{K}$ point and the interlayer band at the Γ point; the electron occupancy of the π^* band in the calculation by Ohno, Nakao, and Kamimura (ONK)[1] is about 0.6 while all the s electron is transferred to the π^* band in the calculation by DiVincenzo and Rabii (DR)[2]. In this report, we present the first angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) on the first-stage alkali-metal GICs single crystals (C_8M, M = K, Rb, Cs).

Figure 1 shows the experimental two-dimensional band structure of C_8K determined in this study [3]. The band calculation by ONK is shown for comparison together with the theoretical π^* band at $\tilde{K}$ point calculated by DR. The agreement in the overall feature between the experiment and the ONK's calculation is very good. The electron occupancy of the experimental π^* band estimated from the dispersive feature is about 0.5 unit electronic charge. This strongly suggests that a K 4s electron in C_8K is shared by the π^* band and the interlayer band with almost equal weight, supporting the ONK band calculation rather than the DR model.

1) T. Ohno, K. Nakao, and H. Kamimura, J. Phys. Soc. Jpn. 47, 1125 (1979).
2) D.P. DiVincenzo and S. Rabii, Phys. Rev. B 25, 4110 (1982).
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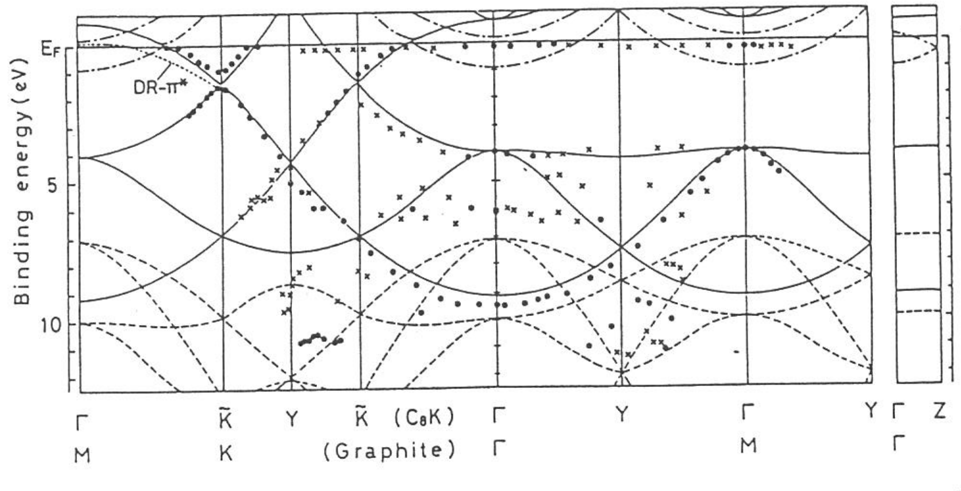

Fig.1 Comparison of experimental and theoretical (ONK) band structure of C_8K

PHOTOELECTRON SPECTROSCOPY OF ORGANIC MATERIALS

Kazuhiko SEKI

Department of Materials Science, Faculty of Science,
Hiroshima University, Hiroshima 730, Japan

Organic materials have several unique points in photoemission experiments such as (i) generally small intermolecular interaction, (ii) rather inactive surface, (iii) insulating electric property, and (iv) feasibility of radiation damages. The first point makes the observed spectra similar to the gas-phase spectrum, and also makes the observation of intermolecular energy-band dispersion difficult. The latter three factors make the experimental conditions different from those of inorganics. After a brief summary of these aspects, we will concentrate on the studies of organic polymers with extended electronic states. (For a more complete survey, see Ref. [1]). The topics included are: (i) extension of pi states at the photopolymerization of diacetylene Langmuir-Blodgett films [2], (ii) formation of intramolecular pi-delocalized states in phenyl-containing polymers [3], and (iii) intramolecular energy-band mapping of polyethylene using model compounds and angle-resolved photoemission with synchrotron radiation [4].

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Two - Photon Photoemission from Molecular Crystals Combining Synchrotron Radiation with a Laser

V. Saile
Hamburger Synchrotronstrahlungslabor HASYLAB at DESY,
Notkestr. 85, D-2000 Hamburg 52, Germany

During the past decade photoelectron spectroscopy has proven to be an excellent experimental technique for the investigation of occupied states in solids and with the advent of inverse photoemission also the conduction bands including their dispersion in k-space became accessible. Bound states, however, like excitons in semiconductors and insulators can usually be studied by neither of these powerful techniques.

In order to apply photoemission also on excited states we have combined VUV-radiation (HeI source or synchrotron radiation) with a laser (1). Until now, two systems, i.e. metal-phthalocyanines and rare gas solids, have been studied successfully.

For the phthalocyanine films (2) it could be demonstrated that the laser prevents or reduces charging of the samples due to holes created in the photoemission process. At low temperatures electrons originating from triplet states and defects populated by the laser have been observed in electron energy distribution curves.

In the case of rare gas solids, excitons or transitions to the bottom of the conduction bands were excited by synchrotron radiation. A dye laser served for ionizing the excitons or for ejecting electrons from the conduction bands into vacuum. The latter process could be exploited for an accurate band gap determination for all rare gas solids (3). From fluorescence and transient absorption spectroscopy (4) it is well accepted that excitons in rare gas solids relax to self-trapped states. By monitoring the number of electrons emitted from excitons upon laser irradiation as a function of the laser-wavelength (5), we have been able to determine the relaxation energies of the excitons. However, a much more precise method for this purpose is to measure directly the kinetic energies of the outgoing electrons. This has been accomplished very recently and a typical result is shown in Fig. 1. While the relaxation energies determined from photoemission are compatible with calculated ones (6), the lifetimes disagree grossly with luminescence data. On the basis of these results we postulate a new type of long living centers created by excitons in rare gas solids.

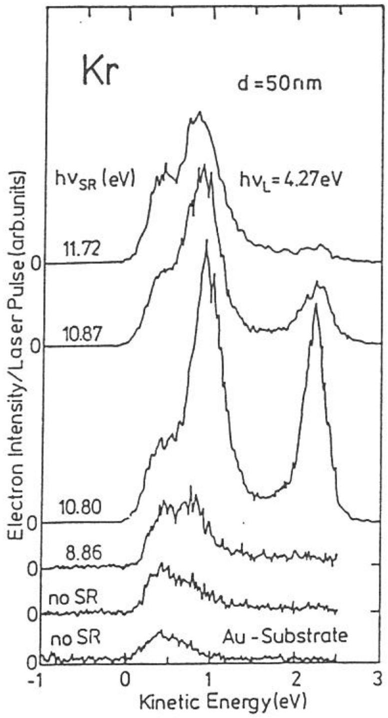

Fig. 1: Photoelectrons from a 50 nm thick Kr film on Au. Only electrons ejected by the laser ($h\nu_L$=4.27 eV) have been detected. The two lowest curves correspond to the signal without synchrotron radiation for the substrate and the Kr/Au sample. At $h\nu$=8.86 eV Kr is still transparent. For $h\nu$=10.80 eV the n'=1 - excitons are excited leading to a pronounced emission at E_{KIN} = 0.9 eV and 2.2 eV. At 10.87 eV there is still exciton absorption and at 11.72 eV interband transitions take place.

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V. Saile, Applied Optics 19, 4115 (1980)

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(3) S. Bernstorff and V. Saile, Opt. Comm. 58, 181 (1986)

(4) For a compilation of data see: N. Schwentner, E.E. Koch and J. Jortner, Electronic Excitations in Condensed Rare Gases (Springer-Verlag, Berlin, 1985)

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Time Resolved Fluorescence Anisotropy of Biochemical Systems

I. H. Munro

Daresbury Laboratory, Warrington WA4 4AD, UK
Institute for Molecular Science, Okazaki 444, Japan

The pulsed properties of storage ring sources have been applied to several research fields for nanosecond and subnanosecond timing studies across an extensive wavelength range from the visible to the x-ray region (1) (2) (3). The source characteristics include a subnanosecond pulse width, a high degree of linear polarisation, identical time registration for all wavelengths and exceptional long term stability in pulse shape and timing. These properties are ideal for studies of time resolved fluorescence anisotropy,in particular, where instrumental pulse shifts (sometimes introduced in the analysis of fluorescence lifetime data) are difficult to justify. So far, fluorescence anisotropy data has been reported from the storage rings at Daresbury, UK, (SRS), Orsay, France, (ACO), Stanford, USA, (SSRL), Hamburg, FRG, (HASYLAB).

At the SRS, the source has a F.W.H.M. of about 200 ps and the pulse repetition frequency is 500 MHz in the multi-bunch mode and 3.125 MHz in the single-bunch made. In single bunch mode, the inter-bunch period is 320 ns and the circulating current is typically between 10 mA and 20 mA at 2 GeV giving up to 10^7 photons per pulse at the sample, depending on the band width selected for excitation. Data is accumulated at rates of about 30 kHz.

At Daresbury, a programme is underway to study the time dependent anisotropy of a variety of intrinsic and extrinsic probes bound in well characterised sites within large molecules such as proteins and within membrane structures (4). Following a rather complex data analysis, it is possible to deduce information about conformational changes and molecular flexibilty, such as segmental rotation, close to the probe site. When the probe is tightly bound then the overall size and shape of the intact protein (including its hydration envelope) can be established (5). Interpretation of the data requires knowledge of the photophysical properties of the probe and of the absence (or otherwise) of competing decay processes such as energy transfer.

An interesting example of the effect of excited state selection on the behaviour of anisotropy decay has been shown for the case of lumazine protein where a negative anisotropy is introduced when high electronic state transitions are selected. Analysis of the time dependent anisotropy both for the amino acid and the prosthetic group yields an estimate of the time dependence of the energy transfer process (6).

A programme has also been established to develope and test effective probes to study membrane fluidity. A range of "quasi-intrinsic" probes have been studied which are usually linear polyenes such as diphenyl hexatriene and its many derivatives (e.g. DPHPC) and also probes containing the triazinylaniline chromophore (7). Using unilamellar lipid vesicles a study has been made of the effect of temperature, pressure, the inclusion of a membrane "stiffener" such as cholesterol and on the fluidising effects of an anaesthetic (e.g. ethanol) on probe mobility within the membrane (4) (8).

An independent study of molecular order and reorientational dynamics of fluorescent probe molecules has been carried out using macroscopically oriented membrane systems such as POPC. Using a range of incident angles for excitation onto the membrane and a range of angles for collection of probe fluorescence, it is possible to describe the order and dynamics of the probe using a Strong Collision model (9). First results reveal that the ordering of the probes (DPH and TMA DPH) included within bilayers of the phospholipid POPC is enhanced and their rates of motion are increased by the addition of cholesterol (10) - a surprising result.

The range of activities in this field, making use both of laser and synchrotron radiation sources and of the techniques of photon counting and phase and modulation spectroscopy (11) is likely to increase and be extended to cover a wide range of materials (e.g. synthetic polymers, nucleic acids etc) in the near future.

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Time-Resolved Fluorescence Spectroscopy of Liquid Alkanes

Yoshihiko HATANO, Department of Chemistry,
Tokyo Institute of Technology, Meguro-ku, Tokyo 152, JAPAN

Fluorescence from liquid alkanes has been one of the important subjects of research in physical chemistry since an early experiment by Hirayama and Lipsky,$^{1)}$ and extensively studied by many groups using different kinds of excitation sources, i.e., α, β, γ and X-rays, accelerated electron beams, UV-photons from discharge lamps, and laser photons. Fluorescence lifetimes as well as excitation spectra have been measured for a variety of liquid alkanes.

Our group$^{2)}$ has measured recently fluorescence lifetimes and excitation spectra of liquid alkanes by means of synchrotron radiation as combined with a delayed coincidence single photon counting technique and compared the obtained results with previous ones. This is an extention of our previous experiment$^{3)}$ in which a superior advantage of the use of SR pulse character in reaction dynamics studies is clearly demonstrated.

Each of excitation spectra of liquid alkanes, i.e., cyclohexane, bicyclohexyl, cis- and trans-decalin, n-decane and n-dodecane, shows a single broad peak at the excitation wavelengths between 163 and 185 nm. The lifetimes show no dependence on the excitation wavelength examined in this experiment and agree well with those obtained using the pulse character of ionizing radiation and laser two photons.

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RELAXATION OF HIGHLY EXCITED STATES IN MOLECULAR SOLIDS AND LIQUIDS

J. Klein
Centre de Recherches Nucléaires & Université Louis Pasteur
STRASBOURG (France)

Frame

- Highly excited states are the states beyond the first excited triplet and singlet (excitation energy in the UV and VUV domain)
- Molecular solids and liquids are characterized by small intermolecular interactions compared to the intramolecular ones.

Main Features

- Due to the weak coupling the isolated molecular characteristics prevail in the dense phase
- However, the intermolecular interactions promote :

(i) perturbative changes

+ the energy levels are broadened (in small excitonic bands)

+ the level diagram undergoes typical "red shift"

+ internal conversion, intersystem crossing, autoionization which are the main decay processes of an excited isolated molecule are conserved

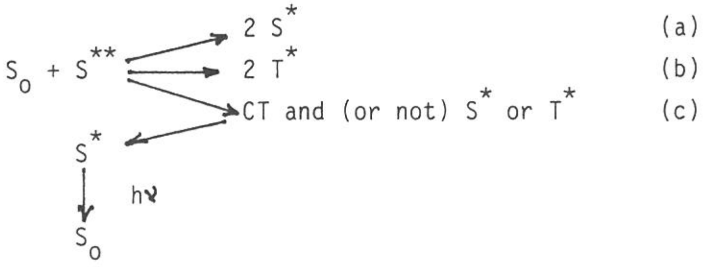
(ii) new specific relaxation modes (see decay scheme)

+ vibrational relaxation leading to an energy dissipation via the bulk

+ transitions to charge transfer (CT) states where the hole (positive ion) and the electron occupy different molecular sites (c)

+ transitions to biexcitonic configurations of two excited triplet (T^*) (b) or two singlet (S^*) (a)

- In the dense phase the slowing down of a "hot" electron produced in an autoionization or a direct ionizing process may promote the concomittant creation of a S^* (or T^*) exciton **and** a CT or free charge state(c).



Experimental Evidence

- single photon excited (S^{**}) photon-photon coincidence revealing the desexcitation of the two correlated S^* in channel (a) (1)

- magnetic field modulated fluorescence decay (1,3) due to
  - fine structure interactions decoupling in channel (b)
  - hyperfine interaction decoupling in the CT or charge carrier recombination process (channel (c))

- electrical field modulated fluorescence decay (4) due to perturbed CT or charge carrier recombination (channel (c))

- single photon excited (S^{**}) fluorescence photon-emitted photoelectron coincidence (channel c) (2).

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Time Resolved Fluorescence and Modulation Spectroscopies of Molecular Crystals.

Tadaoki Mitani

Institute for Molecular Science, Myodaiji, Okazaki 444

The highly excited states in anthracene crystals have been investigated by time-resolved fluorescence spectroscopy based on single-photon counting technique and by electric and magnetic field-modulation spectroscopies in the energy range of 4-20 ev using a synchrotron radiation source. By the former technique, the dynamical behaviors of the highly excited states in a short time period less than several nanoseconds have been elucidated in details: The time-resolved fluorescence spectrum from the lowest exciton is significantly dependent on time and exciting photon energy in an initial stage of decay of about 100 ps after the pulse excitation. Its excitation spectrum show a remarkable dependence on the exciting photon energy and exhibit a high quantum efficiency at the exciton bands. To the contrary, for the delayed fluorescence component by about 1 nsec obeying a purely single-exponential decay, the excitation spectra are almost independent of the exciting photon energy. The close correlation between exciting and emitted photon energies in the initial stage of the decay curves indicates that the fast component of fluorescence emitted immediately after pulsed excitation is predominantly due to the annihilation of excitonic polaritons at the crystal surface before the radiative recombination of excitons takes place within the bulk crystal.

The time-decay contains a long tail being continued to sub-nanosecond, which may be concerned with geminate recombination between the excitons and electron-hole pairs. From the modulated excitation spectra by applying alternative electric- and magnetic-field, it was found that such a relaxation process is quite sensitive to the magnitudes of both modulation fields; the fluorescence is quenched in a low field regime but strongly enhanced by applying the high fields. Their efficiensies have characteristic thresolds for the excitation energy, T_1+T_1 and E_g+T_1 for magnetic field and E_g+S_1, E_g+2S_1 and E_g+3S_1 for electric fields, where E_g, S_1 and T_1 present a band gap energy, the lowest singlet and triplet exciton energy, respectively. These characteristic features provide a qualitative understanding of complicated relaxation processes in anthracene crystals.

Dynamics of Tunneling and Relaxation from Free State to Self-Localized State of Exciton

– Theory for Intermediate Coupling Case –

Keiichiro Nasu
Institute for Molecular Science

The rates of tunneling and relaxation of an exciton from its free (F) state to its self-localized (S) state are worked out, so as to clarify the non-adiabatic effects of the exciton-phonon coupling on these rates, as well as the adiabatic ones. The Frenkel exciton coupling with the longitudinal acoustic phonon is taken as a typical example. The localization is assumed to occur successively through a series of exciton states with different localization raduii, and also through a one-dimensional configuration coordinate space of phonon, called "tunnel-mode". The manifold of vibronic states in the exciton tunnel-mode coupled system is numerically calculated, and the vibronic relaxation within this system is brought about through the coupling between the tunnel-mode and other phonon modes, which acts as a resovior. The rates are calculated within the generalized master equation method, and the results1) are compared with the recent experiment in pyrene2), in a quite good agreement.

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Abstract of talk at 28th Okazaki Conference on Solid State Chemistry with VUV Synchrotron Radiation. Institute of Molecular Science, Okazaki, Japan, February 6, 1987.

Defect Formation In Ionic Solids By Vacuum Ultraviolet Synchrotron Radiation*

Frederick C. Brown

Department Of Physics, University Of Illinois
1110 West Green Street
Urbana, IL 61801, USA

In this talk recent results will be presented on the efficiency of production of F-centers in the alkali halides by both strongly absorbed vacuum ultraviolet radiation (photon energies 5 to 1500 eV) as well as by monochromatic x-ray radiation near the bromine K-edge (13.4 keV). The main part of the work was carried out at the low emittance 1 GeV electron storage ring at the Synchrotron Radiation Center, Stoughton, Wisconsin. This facility is now fully operational with circulating beam currents at either 800 MeV or 1 GeV in excess of 100 ma. One of the unique features of the machine is low energy electron injection from a 100 MeV microtron. The storage ring contains four long straight sections one of which is now occupied by a variable gap 64 pole undulator. Part of the work on the defect production in ionic crystals was carried out using an intense monochromatic photon beam (50 to 1500 eV) from the extended range grasshopper monochromator[1] on the University of Illinois beam line. Other parts of the spectrum were covered by laboratory sources including a rotating anode x-ray tube with a bent silicon crystal monochromator.

In order to observe F-centers over a wide dynamic range, a sensitive laser-induced luminescence technique was developed[2,3] which could detect a very small number of point defects (10^{10} cm^{-3}) during the early stages of growth as well as high concentrations (10^{18} cm^{-3}) as the coloration approached saturation. This technique makes use of the large separation between F-center absorption and emission (Stokes shift), and it requires that the alkali halide crystal be cooled to 77K. F-center production efficiences of the order of one

KeV/F-center were obtained during early stages of growth for KBr and KCl throughout the spectral range studied. The efficiency was observed to drop sharply in regions of very strong absorption such as in the exciton bands (6-8eV)and in the near vacuum ultraviolet below 60eV. These effects are probably due to proximity of the surface resulting in secondary electron emission and photo desorption which, in regions of very small x-ray absorption depth, can compete with F-center formation by electron-hole recombination. The results overall are consistent with a model in which the absorbed vacuum untraviolet photon initiates a sequence of electron scattering events resulting in approximately $h\nu/2E_g$ electron-hole pairs (E_g is the band gap). F-centers and H-centers are then generated by the well known self trapped exciton recombination mechanism.[4] At 6.7 eV, just below the exciton peak in KBr, a self trapped exciton is found to recombine with an efficiency of about 0.007 to form an F-center. At low temperature in KBr the maximum efficiency of luminescence[5] is found to be only about 0.03, therefore other inelastic phonon processes and back reactions compete favorably with F-center generation and luminescence. A definite increase in early stage F-center formation efficiency was observed at the K-edge of Br in KBr(13.4 keV). This is probably because the energy distribution of secondary photoelectrons changes appreciably above the edge, as pointed out many years ago by Itoh, Sharma and Smoluchowski.[6]

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Ion Desorption from Surfaces

Roger Stockbauer
Surface Science Division
National Bureau of Standards
Gaithersburg, MD 20899

Electron and photon stimulated desorption (ESD and PSD) are the surface analogues of radiation induced gas phase ionization and radiation damage in solids[1]. In stimulated desorption, beams of incident electrons or photons incident on a surface containing bulk atoms or adsorbed monolayers of atoms or molecules will cause electronic excitation in the surface species. These excitations can lead to desorption of ions, neutrals or metastable species from the surface. A major difference between surface and gas phase dissociative ionization processes is that the surface provides pathways for electronic deexcitation which are not available in the gas phase.

Ion desorption has unique properties which make it a useful surface probe. Ions are desorbed only from the outermost surface layer making ion desorption highly surface sensitive. Mass analysis of the desorbing ion can be used to identify the surface species. Since ion desorption is, in general, a fast process ($\sim 10^{-14}$s) the surface species moves little between the time of excitement and desorption. Hence, by measuring the angular distribution of the ions information is gained about the bonding configuration of the neutral species. Lastly, the photon energy dependence of the ion emission can be used, in some cases, to identify the species or site to which the ion was attached on the surface.

Since there is much theoretical and experimental interest in the physics and application of ion desorption, it is necessary to know something about the desorption mechanism. A picture of the mechanism has evolved which views ion desorption as a three step process. The first step is the formation of a core hole by photon, electron or even ion impact, the second is the decay of the core hole leaving 2 holes localized on a single bond resulting in a long-lined repulsive state, the third is the expulsion of the ion from the surface.

In general, the most common type of core hole decay which leads to two localized holes is Auger decay. Hence, the term Auger Stimulated Desorption (ASO) has been used to describe the ion desorption mechanism. A specific case of ASD was developed by Knotek and Feibelman[2] for maximal valency compounds in which the valence electrons are depleted from the metal cation and reside on the anion. TiO_2 in which the titanium is configured as Ti^{4+} and oxygen as O^{2-} was used as a model maximum valency compound. As in the general ASD process they viewed the initial step of ion desorption as the formation of the core hole in the metal cation Ti^{4+}. However, the decay of this core hole cannot proceed by the normal Auger decay mechanism since the valence electrons on the Ti are depleted. Instead, they postulated an interatomic Auger decay where an electron from the O anion fills the core hole with the subsequent emission of 1 or 2 electrons. If 2 electrons are emitted, the oxygen has lost 3 electrons and is configured as an O^+ surrounded by Ti^{4+} ions and the resulting coulomb repulsion expels the O^+ from the surface.

The Knotek - Feibelman as well as the more general ASD models predict that the ion desorption cross section should have the same energy dependence as the core hole production. This, in fact, has been demonstrated in a large number of both maximal valency as well as covalent systems. The original Knotek - Feibelman (K-F) model, however, predicted that ion desorption should be strong for maximal valency but greatly reduced for non-maximal valency compounds. While this appears to be true for a number of systems studied, an exception is MgO.

In recent experiments[3] on MgO(100) and (111) done at HASYLAB, we detected little or no ion desorption at any of the Mg core levels. Since MgO is a highly ionic compound, according to the model it should be a very strong ion emitter. The fact that it is not, is probably due to reneutralization, to bonding geometry, or to lattice-dynamics.

We did observed, however, O^+ and H^+ desorption from the O1s level in MgO(100) and (111). The desorption cross section above the O 1s edge follows the absorption cross section of the core hole as given by high energy electron energy loss spectra. Two additional features are observed below the O1s onset which we ascribed to O1s surface core excitons. The decay mode of the exciton in which the excitonic electron remains a spectator results in the loss of 3 electrons from the O^{2-} which then desorbes as an O^+.

The requirement of maximal valency has been investigated further by observing the effects of electronic and lattice defects on desorption from two crystal faces of TiO_2, the (100) and (110).[4] Since these surfaces are identical electronically as can be seen from their photoelectron spectra, any difference in their relative ion yield must be due to their different geometry. The valency of the surfaces can be reduced by ion sputtering and then restored by annealing. As the surfaces are annealed, the ion yield from both decreases and then increases as one would expect from the K-F model. Above 600K, however, the ion yield from the (110) surface decreases drastically while that from the (100) saturates at a level ~6 times that of (110). The difference is due to the fact that the (100) surface facets, that is, it forms pyramidal structures with {011} planes. Measurement of the angular distribution of the ions from this surface shows that they are emitted from the edges of the facets rather than from the planar faces. This study as well as the MgO study shows that while the formation of a core hole is a necessary condition for ion desorption, it is not always sufficient. Geometry of the surface plays a significant role in the ion desorption.

Lastly, one must consider the effect of secondary electrons in the ion desorption process. If the secondary electrons produced by the primary photon or electron beam have sufficient energy as they pass through the surface layer into the vacuum, they can produce excitations which lead to ion desorption. To evaluate this effect, an overlayer experiment was performed at HASYLAB in which ion desorption was measured from a YbO_x overlayer on Sm bulk.[5] The Sm and Yb excitations are clearly distinguishable in the Constant Final State (CFS) spectra. The Sm spectrum has a broad structure with many peaks between 125 and 165eV while the YbO_x has only 1 narrow peak at 181eV. The ion yield from the overlayer shows both structures. The Sm structure in the ion yield can arise only if the secondary electrons from the Sm bulk excite the Yb core level which then Auger decays to initiate the desorption. An evaluation of these data and those of other groups proposing to show secondary electron stimulated desorption (SESD) shows this to be one of the few clear cases of SESD.[6] The effect is dominant here due to the fact that the direct ASD process is weak since the dominant decay made of the Yb core hole is a direct recombination which does not lead to desorption. In general the SESD is always present as a background and should become more dominate at higher X-ray energies. SESD affects only the ability to detect the bonding partner of the desorbed ion; it has no effect on the mass or angular distribution determination.

In summary, the basic mechanism of ion desorption has been well establish over the past few years. The future holds many challenges and much excitement.

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Photon Stimulated Desorption from LiF Surface

Ayahiko Ichimiya, Yoshitaka Yamada and Tsuneo Yasue
Department of Applied Physics, Nagoya University, Nagoya 464, Japan
Tetsuji Gotoh, Yoichi Kawaguchi, Masahiro Kotani, Shunsuke Ohtani,
Yukichi Shigeta, Shoji Takagi and Yuji Tazawa
Institute of Plasma Physics, Nagoya University, Nagoya 464, Japan

Photon stimulated desorption (PSD) from LiF (100) surface is observed in the photon energy region between 30 and 70 eV. The experiments were carried out using the UVSOR. The relative yields, which were normalized with the relative photon intensity, were measured as a function of the incident photon energy (the desorption yield spectrum).

In both yield spectra of Li^+ and F^+ ions there are a rapid rise of ion yields at about 56 eV, and a structure at about 58 eV. However the considerable difference in the yield spectra of Li^+ and F^+ ions is observed above 60 eV. The Li^+ yields are almost constant between 61 and 67 eV, while there are a sharp peak at 60.2 eV and a deep valley at 63.5 eV in the F^+ yield spectrum. A threshold of PSD of Li^+ ions was not observed down to 27 eV. That of F^+ ions was observed to be about 30 eV.

Desorption of neutral Li and HF species was observed, while that of F species could not observed because of rather abundant atomospheric F gas. In the Li yield spectrum there is a sharp peak at about 61 eV reproduciblly. Relative intense background yields were observed over all the photon energies. The HF yield spectrum, however, does not show the strong energy dependence.

In order to consider the mechanism of PSD of positive ions, we compare the ion yield spectra with the photoabsorption spectrum. The structures at 56 and 58 eV are also seen in the photoabsorption spectrum. The structures in the photoabsorption spectrum are ascribed due to the creation of the Li^+ core exciton in the crystal. Therefore the initial step of PSD of positive ions is the core excitation of the Li^+ 1s state. The valence band should well localize on F^- ions in the complete ionic crystal of LiF. Then following two different decays of the core exciton are considered;

$$Li^{+*}+F^- \rightarrow Li^*+F^++e^- \qquad (1)$$

and

$$Li^{+*}+F^- \rightarrow Li^++F+e^-, \qquad (2)$$

where asterisks indicate the core-excited state. Since the sharp peak in the Li yield spectrum locates at nearly the same energy as that in the F^+ yield spectrum, it is considered that the desorption of Li^* and F^+ takes place simultaneously. Therefore the process of eq. (1) is dominant in the desorption processes. The background yields are due to the thermal process which is attributed by the photoinduced defects as already observed.

Photon-stimulated desorption of neutrals from silver and alkali halides

H. Kanzaki, Ashigara Research Laboratories, Fuji Photo Film

PSD studies are reviewed for silver and alkali halides under valence excitation. In addition to those on bulk crystals[1,2], recent results on microcrystals of silver halide will be included.

For PSD from bulk surface, there is a distinct difference of desorption species between silver and alkali halides; halogen molecules and alkali and halogen atoms, respectively. In AgBr, photo-holes diffuse as a neutral hole-vacancy complex, which is transformed to bromine molecule at the surface. On the other hand, the self-trapped hole (STH) is stable in alkali halide. Halogen atom desorption due to STH is followed by the alkali desorption due to F-center near the surface. Thus, the origin of molecule vs. atom difference can be understood as due to the different nature of stable photo-excited states.

On the other hand, however, there are evidences suggesting the importance of surface-residence time of desorption precursors. In bulk AgBrI mixed crystals, for example, iodine desorption which corresponds to stable species turned out far less efficient than bromine. The situation changes completely for microcrystals, in which idodine desorption is the strongest. Apparently, the desorption efficiency has changed by the existence of thin gelatin layer in contact with microcrystals.

The gelatin layer covering silver halide surface is also responsible for the strong PSD of CO_2, through either of the following two mechanisms. One is the reaction of gelatin with bromine from excited silver halide. The other is due to the excitation of interface-state at the surface of silver halide, the nature of which becomes evident from the desorption yield spectra at the lower energy side of silver halide absorption threshold.

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INVESTIGATION OF FRAGMENTATION PROCESSES FOLLOWING CORE PHOTOIONIZATION OF ORGANOMETALIC MOLECULES IN THE VAPOR PHASE

Shin-ichi NAGAOKA

Institute for Molecular Science, Myodaiji, Okazaki 444

We have studied the fragmentation following Pb 5d core photoionization of tetramethyllead (TML). In the threshold electron spectrum of TML, several sharp bands are seen in the region 44 – 75 nm, and are assigned to the photoionization from the Pb 5d core levels. The photoionization efficiency curve for the Pb^+ ion has an appearance quite different from those for other fragments. Moreover, almost all peaks of the Pb^+ curve in the region 44 – 75 nm are found to coincide in position with the peaks in the threshold electron spectrum. Branching ratio of each fragment in various states of the TML parent ion were determined by use of the threshold electron – photoion coincidence method, and are given in Figure 1. From these results, it is concluded that the Pb^+ ion is predominantly produced following Pb 5d core photoionization.

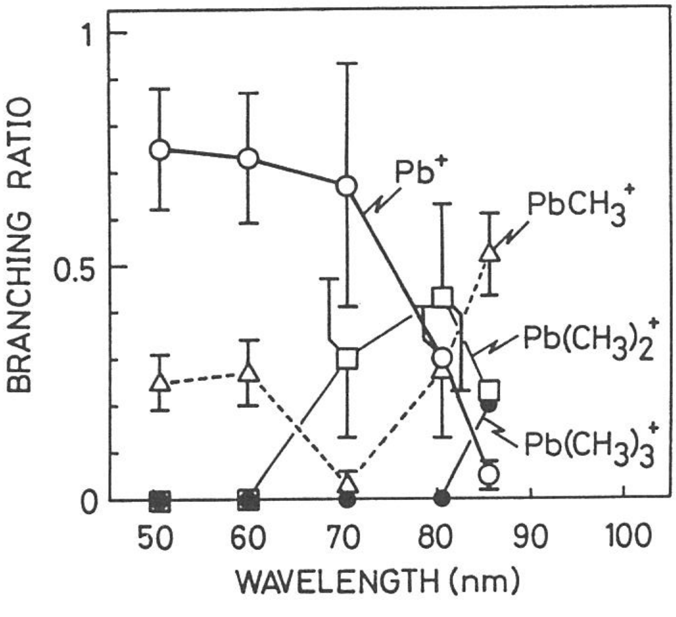

Figure 1. Braiching ratio.

Measurements of H^+ Formation from Hydrocarbons

Haruo Shiromaru, Institute for Molecular Science

The C-H bond dissociation energies of ethylene and acetylene, D_0(R-H), where R = C_2H_3, C_2H, are important quantities to be accurately determined. The D_0 values have often been obtained with the relationship $D_0 = E_{th}(R^+) - I(R)$, where $E_{th}(R^+)$ is the threshold energy for $RH + h\nu = R^+ + H + e^-$, and I(R) is the adiabatic ionization energy of the R radical. The disadvantage of this method is that there are some uncertainties in the I(R) value affecting the result of D_0. A new method recently proposed for determining the D_0 values from the H^+ threshold energy is briefly explained here.[1]

The H^+ threshold energies for ethylene and acetylene have been measured with a Q-pole mass filter by scanning in the wavelength region 58 - 70 nm on the beam port BL2-B2 in the UVSOR facility of this Institute.[1] Then the D_0(R-H) values have been deduced from the relationship $D_0(R\text{-}H) = E_{th}(H^+) - I(H)$, where $E_{th}(H^+)$ is the threshold energy for $RH + h\nu = R + H^+ + e^-$, and I(H) is the ionization energy of H atom (13.598 eV).

From the onsets of the efficiency curves, the following values have been obtained[1]

$E_{th}(H^+)$ = 18.66 eV, D_0 = 5.06 eV for ethylene

$E_{th}(H^+)$ = 19.35 eV, D_0 = 5.75 eV for acetylene

The D_0 values deduced here are in good agreement with those obtained from the analysis of the photofragment translational spectra but considerably higher than those derived from $E_{th}(R^+)$.

Synchrotron radiation is suitable for determining the C-H bond dissociation energies from the H^+ formation because of its high intensity and stability in the wavelength region used.

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Site-Selective Photofragmentation of Molecules and Its Implication to VUV Induced Solid State and Surface Chemical Processes

T. K. Sham, Chemistry Department
Brookhaven National Laboratory, Upton, NY 11973 USA

Photofragmentation of molecules following the excitation and ionization of core electrons was for sometime a relatively unknown phenomenon in comparison with similar processes involving valence electrons. In recent years, the availability of intense and tunable VUV and soft X-rays from electron storage rings has greatly facilitated the experimental investigation of the photofragmentation of molecules following the creation of a core hole.[1,2]

This presentation will deal with some general considerations of the phenomenon, the experimental situations, the interpretation of the results and its implications. Major developments in the last five years in this area will also be reviewed.

One unique feature of the core electron excitation and ionization process is that the core hole created in the process decays predominantly via the Auger channel for low z (atomic number) elements such as carbon, nitrogen and oxygen. These processes are Franck-Condon like and often resulted in various two-hole state in the molecular orbitals.[3] These two-hole states (or the Coulomb repulasion U between the core holes) play a determined rule in the fragmentation pattern of the molecules.[4] For site selectivity, it is important to consider the core levels that are closest to the valence levels. The K hole in carbon for example interacts directly with the chemically sensitive electrons in the molecular orbitals. Fig. 1 illustrates the site selectivity when the photon is tuned to the 1s → π* absorption of the carbonyl carbon of acetone. It can be seen from Fig. 1 that C^+ and O^+ are produced with large abundance at the resonance involving the carbonyl carbon.

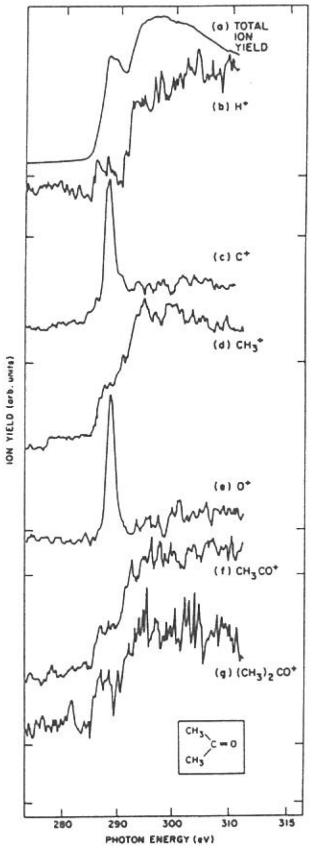

Fig. 1. C K edge absorption spectra of acetone recorded in the ion yield mode.

The partial ion yield absorption spectra shown in Fig. 1 were recorded with a set-up in which the synchrotron light passed through a glass capillary array (50% transmission) into the ionization area of a UTI 100 C mass spectrometer. With differential pumping, a pressure differential of 10^{-5} was achieved across the channel plane and the partial pressure of the gas in the ionization region was ~ 10^{-4} torr.

Photofragmentation patterns of CH_3COOH, C_6H_6, C_6H_5Cl and $C_2H_3Cl_3$ are also discussed. These molecules all exhibit an intense C 1s → π* transition which correlates with the breaking of all the bonds at the absorbing carbon site.

Recently developed techniques such as threshold photoelectron-photoion coincidence,[5] photoion-photoion coincidence[6] and Augerelectron-photoion coincidence[7,8] have enabled more detailed studies of the process. Some of these results will be discussed.

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PHOTOCHEMISTRY AND MORPHOLOGICAL CHANGES OF POLYMER AND DEPOSITED FILMS

Hiroshi MASUHARA

Department of Polymer Science and Engineering
Kyoto Institute of Technology, Matsugasaki, Kyoto 606

Since photophysical and photochemical processes of π-electronic molecules have been studied in detail, photo-induced morphological changes such as annealing and ablation of organic solid containing these molecules can be correlated with their photoprocesses. Major spectroscopic and photochemical data, however, are limited to UV and visible wavelength regions, so that studies on laser photochemistry of organic solid are fruitful at present. Here, annealing and ablation phenomena of organic films containing representative π-electronic chromophores are described.

Vacuum-deposited films of ω-(1-pyrenyl)alkanoic acids gave two kinds of new fluorescence which were ascribed to some minor aggregates of pyrenyl chromophores. Most of these chromophores were in another aggregate which is nonfluorescent or transfers excitation energy rapidly to a neighbouring isolated pyrene. Upon irradiation with a 308 nm excimer laser and a Xe-lamp, these films showed characteristic fluorescence spectral change, indicating interconversions between these aggregates. Since annealing phenomena were observed with an optical microscope, the present structural change of aggregates is considered to give a molecular viewpoint for laser annealing.(1)

Increasing laser irradiation intensity lead to ablation of organic films. This process of poly(methyl methacrylate) films doped with pyrene and benzophenone and poly(N-vinylcarbazole) films was investigated, using the 308 nm and 248 nm excimer lasers, respectively. The presence of absorbing chromophores resulted in efficient etching. Scanning electron micrographs revealed that the surface condition of etched areas depends on spectroscopic as well as chemical characters of the chromophore, its concentration, laser irradiation intensity.(2,3)

In both studies we examined effects of irradiation intensity and repetition rate of excimer lasers and came to the conclusion that some nonlinear laser processes such as interactions between excited states and successive two-photon absorption are involved. This means an important role of the higher excited state in photo-induced morphological changes.

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WAVELENGTH DEPENDENCE OF CHEMICAL PROCESS IN X-RAY RESIST

S. Morita, H. Yamada and S. Hattori
Nagoya University, Department of Electro Mechanical Engineering
Furo-cyo, Chikusa-ku, Nagoya 464, JAPAN

Introduction

Conventional poly-methyl-methacrylate(PMMA) film spin coated revealed positive pattern without any additional developing treatments, when it was exposed to syncrotron radiation(SR) through an X-ray mask[1]. The phenomenon is known as a self development. However, the self developed pattern depth was saturated at the high X-ray dose. In this study, phenomena of self development were investigated experimentally and it was observed that the self development was enhanced significantly by using a short wave length region of SR and elevating a substrate temperature of resist in a vacuum up to 160 ℃[2-4]. Effects of X-ray wavelength on chemical process in organic resists were discussed with using IR, ESCA and mass spectra.

Experimentals

Ultra violet syncrotron orbital radiation(UVSOR) from the electron storage ring at Institute for Molecular Science, Okazaki was used as an X-ray source, which were operated usually at 600MeV and 30mA with an orbital radius of 2.2m. Two types of resists used were fromed by a wet and a dry process which are conventional poly-methyl-methacrylate(PMMA) and plasma polymerized methyl-methacrylate(PPMMA). In order to limit the wavelength range of SR exposure, polyimide, berillium and aluminum film were selected as a filter.

Results and Discussions

When the resist films were exposed to an X-ray through any filters, the self development did not show any tendency to saturate in this experimental conditions and was enhanced significantly by heating the substrate at higher temperature than the melting point. IR spectra showed that polyer was decomposed by scissoring the chain. However the decomposition of polymer was accompanied by side chain dissociation significantly on the surface for the direct exposure without the filter.

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4) Preparing submission to appropriate journal.

VUV Photodegradation of Biomolecule--DNA, ATP and Oligonucleotide

Takashi Ito

Institute of Physics, College of Arts and Sciences, University of Tokyo,
Meguroku, Komaba 3-8-1, Tokyo 153

Our recent concerns on the effects of VUV radiation have been focused on such important biomolecules as DNA and related compounds. The work using SR shows that a long thread-like DNA molecule is fragmented effectively in VUV region by induced nicks on the backbone.1) But to analyse detailed processes occurring in this complex molecules is facing some difficulties. On the other hand, with ATP molecule, a building block of such a polynucleotide, the release of adenine is observed upon VUV radiation above 7 eV.2) Detailed processes are not understood either, but pentose sugar is a likely candidate first destructed. A oligonucleotide dApdA, two deoxyadenosine(dA) linked by phosphodiester bond (p), is thought to be a good model substance to investigate further; complete photoproducts analysis maybe possible. Densitometric analysis of thin-layer chromatogram of VUV-irradiated dApdA in the range from 7.3 to 22.5 eV showed that adenine and 5'-dAMP are the two major photoproducts independent of photon energy employed, indicating a specific site is selectively destructed in this molecule regardless of the primary excited states. The site-selective degradation from the highly excited state seems a remarkable characteristic of the VUV radiation action.

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Synchrotron Radiation-Assisted Etching of Silicon Surface

Nobuo HAYASAKA, Atsunari HIRAYA, and Kosuke SHOBATAKE

Institute for Molecular Science, Myodaiji, Okazaki 444 Japan
* Sponsorial Research Fellow from VLSI Research Center,
Toshiba Corporation, Komukai Toshiba-cho, Saiwai-ku, Kawasaki
210 Japan

The photo-assisted etching of heavily phosphorous-doped polycrystalline silicon (n^+ poly-silicon) by chlorine was studied using synchrotron radiation from UVSOR as a vacuum UV light source. The apparatus used for the present study is described in 1986 UVSOR Activity Report. Formation of electronically excited Cl^+ ions upon VUV irradiation was confirmed from the emission spectra observed from a glow in the light path. The quantum yield for the removal of the Si atoms at a chlorine pressure of 0.3 Torr was found to be about 0.5 % photon^{-1} using the Ti-filtered light, which is mostly in the soft x-ray region, 1-20 nm.

Negative bias applied to the Si crystal was found to increase the etch rate. A micrograph of the silicon surface photo-etched for 230 mA hr irradiation at a 75 volt bias voltage and 0.3 Torr Cl_2 gas pressure is illustrated in Figure 1, the etch depth of which was measured to be 900 ± 100 Å, corresponding to the quantum yield =1.0%.

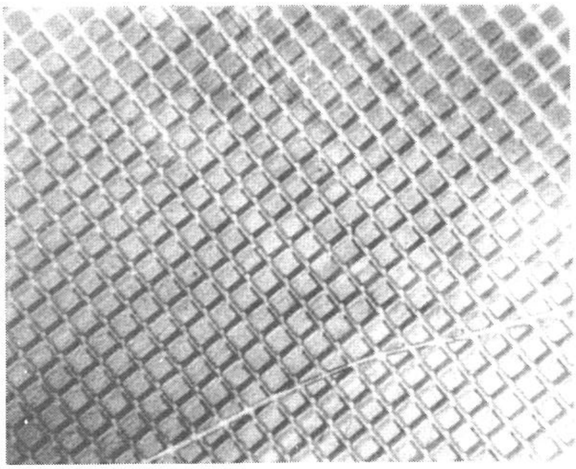

Fig. 1. Micrograph of a Si surface obtained by photo-assisted etching by Cl_2 gas at 0.3 Torr using SR with a Ti filter 500 Å thick. The rectangular lines are due to nickel mesh of 20μm used for an application of negative bias (at 75 V) to the Si sample. The etch depth was measured to be 900 ± 100 Å.

THIN FILM·DEPOSITION BY VUV SYNCHROTRON RADIATION

Akira YOSHIDA

Toyohashi University of Technology, Tempaku, Toyohashi, 440

Thin films play a dominant role in solid state electronics. Various CVD (Chemical Vapor Deposition) techniques have been accepted to deposit thin films. The most common deposition methods are "thermal" CVD and plasma-enhanced CVD (PCVD). In recent years, photochemical vapor deposition (Photo CVD) is expected to be one of new low temperature fabricating processes. In most cases, lasers and/or discharge tubes are used as a light source. Many kinds of materials have been deposited by this method. Also, doping, alloying, and fabricating some devices are tried. Recently, SOR excited chemical vapor deposition (SOR CVD) has been proposed. Synchrotron radiation is suitable as a light source in photo CVD process, because of a continuous spectrum from soft X ray to visible light range, large dissociation and ionization cross sections of many reactant gases in the VUV region, and no contamination from the chamber wall in order to obtain a high quality film. Kyuragi and Urisu1) deposited amorphous hydrogenated silicon and silicon nitride films from the gas source (SiH_4 or $SiH_4 + N_2$). Their experimental results are shown in Fig.1. We have a plan to fabricate thin films from various source gases by using the photo CVD system (Fig.2), characterize the film properties and investigate the film deposition mechanism by photochemical reaction.

1) H.Kyuragi and T.Urisu: Final Program and Late News Abstracts of 17th Conf. on Solid State Devices and Materials, p.16 , Aug. (1985)

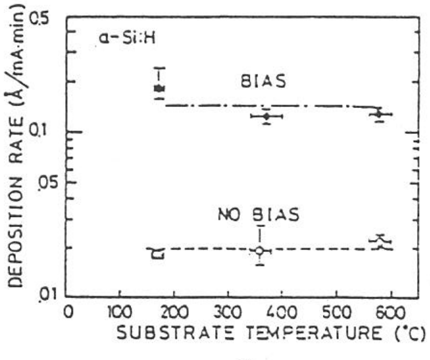

Fig.1 1)

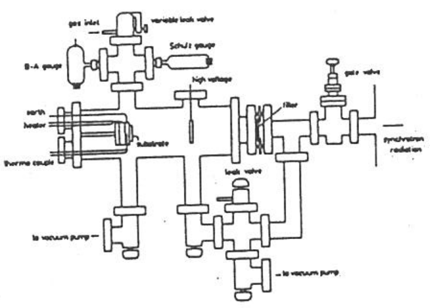

Fig.2

Concluding Remark-"Application of VUV Photons to Organic Chemistry"

Hiroo Inokuchi, Institute for Molecular Science

Since we started the first 'Okazaki Conference' in 1975, a total of 28 Conferences has been held. However, the present one, entitled "Solid State Chemistry with VUV Synchrotron Radiation" is the first Conference on synchrotron radiation research since the UVSOR Facility was constructed. The 5th Conference, entitled "Higher Excited States of Molecules and Molecular Crystals" was held on December 4-7th, 1977 on subjects related to synchrotron radiation research, but at that time our machine was only being planned.

As mentioned by Dr. Saile, UVSOR, a 'chemical machine', is located in the garden of IMS, and therefore it is quite easy for visiting scientists to work on it co-operatively with the in-house staff of our Institute. We would like to extend the co-operative research to new fields, for instance, synthetic chemistry.

Several years ago, during the observations of polarized absorption spectra of an elongated st-1,2-polybutadiene film in the vacuum ultraviolet region using ISSP-SRL, we found a peak at 284.9 ± 0.2 eV, due the to $\pi^* \longrightarrow C_{1s}$ absorption of oriented vinyl radicals as shown in Figure 1 (Chem. Phys. Lett. 70, 220 (1980)). A similar band was found in the spectrum of polyethylene film, the peak intensity of which increased appreciably with the illumination time of SRL. These findings suggest that the SRL illumination produces double bonds in hydrocarbon chains of single bonds; that is to say, we can rearrange chemical bonds by means of synchrotron radiation. Therefore, we will use the UVSOR as a 'light knife.'

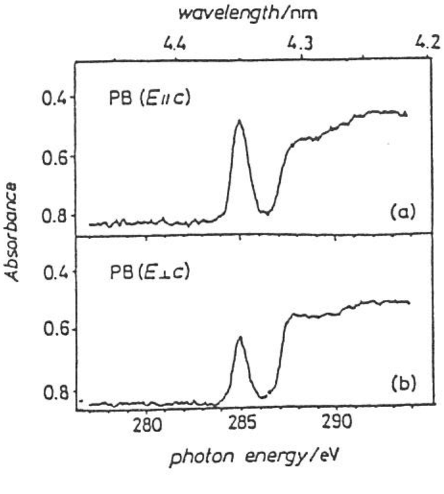

Figure 1. Polarized C_{1s} absorption spectrum of elongated st-1,2-polybutadiene film. a)E // c, b)E ⊥ c. E: Electric vector of incident light, c: direction of elongation.

LIST OF PARTICIPANTS

F. C. Brown	Department of Physics	University of Illinois	Urbana, IL 61801, USA
S. M. B. Costa	Institute Superior Technico	Lisbon, Portugal	
T. Fujikawa	Faculty of Engineering	Yokohama National University	Hodogaya, Yokohama 240
H. Fujimoto	Inst. for Molecular Science	Myodaiji, Okazaki 444	
K. Fukui	Inst. for Molecular Science	Myodaiji, Okazaki 444	
J. R. Grover	Chemistry Department	Brookhaven National Lab.	Upton, NY 11973, USA
Y. Hatano	Department of Chemistry	Tokyo Institute of Technology	Meguro, Tokyo 152
N. Hayasaka	VLSI Research Center	Toshiba Corporation	Saiwai, Kawasaki 210
H. Hayashi	Inst. for Molecular Science	Myodaiji, Okazaki 444	
A. Hiraya	Inst. for Molecular Science	Myodaiji, Okazaki 444	
N. Hoshino	Inst. for Molecular Science	Myodaiji, Okazaki 444	
A. Ichimiya	Department of Applied Physics	Nagoya University	Chikusa, Nagoya 464
T. Imamura	Inst. for Molecular Science	Myodaiji, Okazaki 444	
T. Inagaki	Osaka Kyoiku University	Tennoji, Osaka 543	
H. Inokuchi	Inst. for Molecular Science	Myodaiji, Okazaki 444	
T. Ishii	Synchrotron Radiation Lab.	ISSP, University of Tokyo	Tanashi, Tokyo 188
T. Ito	College of Arts and Sciences	University of Tokyo	Meguro, Tokyo 153
N. Itoh	Department of Physics	Nagoya University	Chikusa, Nagoya 464
Y. Iwasa	Faculty of Engineering	University of Tokyo	Bunkyo, Tokyo 113
N. Kakuta	Inst. for Molecular Science	Myodaiji, Okazaki 444	
H. Kanamori	Inst. for Molecular Science	Myodaiji, Okazaki 444	
H. Kanzaki	Ashigara Research Laboratories	Fuji Photo Film Co., Ltd.	Minamiashigara, Kanagawa 250-01
K. Kimura	Inst. for Molecular Science	Myodaiji, Okazaki 444	
J. Klein	Centre de Recherches Nucleares	& Universite Louis Pasteur	Strasbourg, France
K. Kobayashi	College of Liberal Arts	Toyama University	Toyama 930
T. Kobayashi	Department of Physics	University of Tokyo	Bunkyo, Tokyo 113
N. Kosugi	Department of Chemistry	University of Tokyo	Bunkyo, Tokyo 113
Masahiro Kotani	Department of Chemistry	Gakushuin University	Toshima, Tokyo 171
Masao Kotani	Inst. for Molecular Science	Myodaiji, Okazaki 444	
I. Koyano	Inst. for Molecular Science	Myodaiji, Okazaki 444	
Y. Maruyama	Inst. for Molecular Science	Myodaiji, Okazaki 444	
H. Masuhara	Kyoto Institute of Technology	Sakyo, Kyoto 606	
T. Matsukawa	College of General Education	Osaka University	Toyonaka, Osaka 560
T. Mitani	Inst. for Molecular Science	Myodaiji, Okazaki 444	
S. Morita	Department of Electronics	Nagoya University	Chikusa, Nagoya 464
I. H. Munro	Synchrotron Radiatio Source	Daresbury Laboratory, SERC	Warrigton WA4 4AD, UK
T. Murata	Kyoto University of Education	Fushimi, Kyoto 612	
S. Nagaoka	Inst. for Molecular Science	Myodaiji, Okazaki 444	
H. Nakagawa	Department of Electronics	Fukui University	Fukui 910

Y. Nakai	Department of Physics	Kyoto University	Sakyo, Kyoto 606
K. Nakamura	Department of Physics	Kyoto University	Sakyo, Kyoto 606
M. Nakamura	Inst. for Molecular Science	Myodaiji, Okazaki 444	
N. Nakashima	Inst. for Molecular Science	Myodaiji, Okazaki 444	
T. Nanba	Department of Physics	Tohoku University	Sendai 980
K. Nasu	Inst. for Molecular Science	Myodaiji, Okazaki 444	
S. Ohtani	Institute of Plasma Physics	Nagoya University	Chikusa, Nagoya 464
T. Okada	Faculty of Engineering Science	Osaka University	Toyonaka Osaka, 560
K. Okuyama	Inst. for Molecular Science	Myodaiji, Okazaki 444	
I. Plazibat	University of Split	Split, Yougoslavia	
V. Saile	HASYLAB, DESY	Notkest. 85, D-2000 Hamburg 52	West Germany
N. Sato	Department of Chemistry	Kumamoto University	Kumamoto 860
S. Sato	Photon Factory	Nat. Lab. for High Energy Phys.	Oho, Ibaraki 305
M. Satoko	Inst. for Molecular Science	Myodaiji, Okazaki 444	
K. Seki	Dept. of Materials Science	Hiroshima University	Naka, Hiroshima 730
T. K. Sham	Chemistry Department	Brookhaven National Lab.	Upton, NY 11973, USA
H. Shiromaru	Inst. for Molecular Science	Myodaiji, Okazaki 444	
K. Shobatake	Inst. for Molecular Science	Myodaiji, Okazaki 444	
P.-S. Song	Department of Chemistry	University of Nebrasaka	Lincoln, NE 68588-0304, USA
R. Stockbauer	National Bureau of Standards	Gaithersburg, Maryland 20899	USA
I. Suzuki	Electrotechnical Laboratory	Sakura, Ibaraki 305	
M. Suzuki	Inst. for Molecular Science	Myodaiji, Okazaki 444	
S. Suzuki	Inst. for Molecular Science	Myodaiji, Okazaki 444	
K. Tabayashi	Inst. for Molecular Science	Myodaiji, Okazaki 444	
Y. Takagi	Inst. for Molecular Science	Myodaiji, Okazaki 444	
T. Takahashi	Department of Physics	Tohoku University	Sendai 980
N. Tamai	Inst. for Molecular Science	Myodaiji, Okazaki 444	
K. Tanaka	Photon Factory	Nat. Lab. for High Energy Phys.	Oho, Ibaraki 305
K. Tohji	Inst. for Molecular Science	Myodaiji, Okazaki 444	
J. Tanaka	Department of Chemistry	Nagoya University	Chikusa, Nagoya 464
M. Taniguchi	Synchrotron Radiation Lab.	ISSP, University of Tokyo	Tanashi, Tokyo 188
K. Tanimura	Department of Physics	Nagoya University	Chikusa, Nagoya 464
Y. Udagawa	Inst. for Molecular Science	Myodaiji, Okazaki 444	
N. Ueno	Faculty of Engineering,	Chiba University	Chiba 260
Y. Wada	Inst. for Molecular Science	Myodaiji, Okazaki 444	
M. Watanabe	Inst. for Molecular Science	Myodaiji, Okazaki 444	
K. Yamamoto	Inst. for Molecular Science	Myodaiji, Okazaki 444	
I. Yamazaki	Inst. for Molecular Science	Myodaiji, Okazaki 444	
T. Yasue	Department of Applied Physics	Nagoya University	Chikusa, Nagoya 464
A. Yoshida	Toyohashi Univ. of Technology	Tempaku, Toyohashi 440	
K. Yoshihara	Inst. for Molecular Science	Myodaiji, Okazaki 444	

APPENDIX

ORGANIZATION

Staff

Director	Hiroo INOKUCHI	Professor
Light Source Group		
	Toshio KASUGA	Associate Professor
	Hiroto YONEHARA	Research Associate
	Toshio KINOSHITA	Engineer
	Masami HASUMOTO	Engineer
Measurement Systems Group		
	Makoto WATANABE	Associate Professor
	Kazutoshi FUKUI	Research Associate
	Kusuo SAKAI	Section Chief Engineer
	Osamu MATSUDO	Unit Chief Engineer
	Jun-ichiro YAMAZAKI	Engineer
	Eiken NAKAMURA	Engineer
Secretary	Takayo OHTE	
Guest Scientists		
	Hisashi KOBAYAKAWA	Adjunct Associate Professor from Nat. Lab. High Enegy Phys. (April 1986 - March 1987)
	Teruo HOSOKAWA	Visiting Research Fellow from NTT (April 1985 - March 1987)

Representative of Beam Lines

BL2A	Kosuke SHOBATAKE	Dept. Molecular Assemblies
BL2B2	Katsumi KIMURA	Dept. Molecular Assemblies
BL3B	Inosuke KOYANO	Dept. Molecular Assemblies
BL8B2	Hiroo INOKUCHI	UVSOR and Dept. Molecular Assemblies
Others	Makoto WATANABE	UVSOR

Steering Committee (June 1986 - March 1988)

Hiroo INOKUCHI	IMS	Chairman
Toshio KASUGA	IMS	
Katsumi KIMURA	IMS	
Inosuke KOYANO	IMS	
Tadayoshi SAKATA	IMS	
Yasuo UDAGAWA	IMS	
Makoto WATANABE	IMS	
Hisashi KOBAYAKAWA	IMS and Nat. Lab. High Energy Phys.	
Yoshihiko HATANO	Tokyo Inst. Tech.	
Takehiko ISHII	Univ. of Tokyo	
Yoshio NAKAI	Kyoto Univ.	
Takeshi NAMIOKA	Tohoku Univ.	
Shunsuke OHTANI	Nagoya Univ.	
Tadashi OKADA	Osaka Univ.	
Taizo SASAKI	Osaka Univ.	

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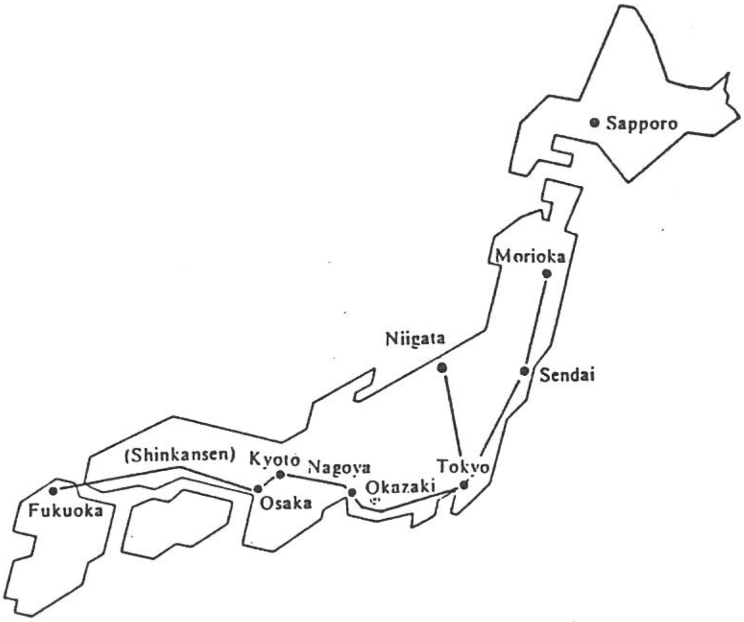
J. Chem. Phys. 85 (1986) 5717.

LOCATION

Ultraviolet Synchrotron Orbital Radiation (UVSOR) Facility, Institute for Molecular Science (IMS) is located at Okazaki. Okazaki (population 280,000) is 260 km southwest of Tokyo, and can be reached by train in about 3 hours from Tokyo via New Tokaido Line (Shinkansen) and Meitetsu Line.



Address is as follows.
UVSOR Facility
Institute for Molecular Science
Myodaiji, Okazaki 444, JAPAN

Telephone : 0564-54-1111 (IMS), ex. 400-409 (UVSOR)
Fax : 0564-54-2254 (IMS)
Telex : 4537475 KOKKEN J (IMS)