

ABSTRACTS

**INTERNATIONAL SYMPOSIUM ON
VUV-SX PHYSICS & CHEMISTRY**

International Symposium on VUV-SX Physics and Chemistry

July 24-26, 1989, Institute for Molecular Science, Okazaki

Sponsored by Institute for Molecular Science
Science and Engineering Research Council (UK)
Nishina Memorial Foundation
Inoue Foundation for Science

July 24

12:30-13:10 Registration
13:10-13:20 Opening Address H. Inokuchi (IMS)

Condensed Matter (I) T. Ishii (Univ. of Tokyo) presiding

13:20-13:50 K. Fukui (IMS), "Core Excitation in GeTe, SnTe and PbTe in Amorphous and Crystalline Phases"
13:50-14:20 M. Taniguchi (Hiroshima Univ.), "Cr 3d Partial Density of States and p-d Hybridization in Ferromagnetic Semiconductor CdCr₂Se₄"
14:20-14:50 M. Onellion (Univ. of Wisconsin), "Testing High Temperature Superconductivity Models using Synchrotron Radiation Photoemission"
14:50-15:20 A. Fujimori (Univ. of Tokyo), "Photoemission Studies of High-T_c Superconductors and Related Compounds"
15:20-15:50 S. Suga (Univ. of Tokyo), "Photoemission and Inverse Photoemission Study of Transition Metal Intercalated and Surface Adsorbed TiS₂"
15:50-16:20 Coffee Break

Condensed Matter (II) T. Okada (Osaka Univ.) presiding

16:20-16:50 E. J. Nordgren (Uppsala Univ.), "Current Status and Future Prospects for Ultra-soft X-ray Spectroscopy"
16:50-17:20 S. Nakai (Utsunomiya Univ.), "Soft X-ray Fluorescent Spectra of Lanthanum Compounds"
17:20-17:50 Y. Nakai (Kyoto Univ.), "Time-Resolved Luminescent Studies of Alkali Halide Crystals Using Single-Bunched Light Pulses from UVSOR"
17:50-18:20 I. Munro (Daresbury Lab.), "Fluorescence Studies of Biosystems"
18:30-20:00 Reception

July 25

Condensed Matter (III) Y. Harada (Univ. of Tokyo) presiding

9:00- 9:30 K. Seki (Hiroshima Univ. & IMS), "Anisotropic XANES Studies of Oriented Molecular Solids and Polymers"
9:30-10:00 H. Fujimoto (IMS), "UPS Studies of Model Systems of Polyethylene and Polythiophene"
10:00-10:30 Coffee Break

Surface S. Sato (Tohoku Univ.) presiding

10:30-11:00 P. Woodruff (Warwick Univ.), "Surface Studies Using SR"
11:00-11:30 Y. Sakisaka (Kyoto Univ.), "Angle-Resolved Photoemission from Thin Crystalline Oxide Films"

- 11:30-12:00 G. Schönhense (Univ. Bielefeld), "Circular Dichroism and Spin Polarization in Photoemission from Adsorbates"
 12:00-12:30 K. Cho, Y. Takeda and Y. Miyamoto (Osaka Univ.), "Theory of Resonant Photoemission from Surface Core Excitons of GaAs (110)"
 12:30-13:30 Lunch

Atom and Molecule (I) T. Sasaki (Photon Factory) presiding

- 13:30-14:00 K. Codling (Reading Univ.), "New Triple Coincidence Techniques Applied to Multiple Ionisation of Molecules"
 14:00-14:30 P. Zimmermann (Tech. Univ. Berlin), "Photoelectron Spectroscopy on Laser-Excited, Aligned Free Atoms"
 14:30-15:00 A. Yagishita (Photon Factory), "Symmetry-Resolved Photoabsorption Spectroscopy of Diatomic and Triatomic Molecules"
 15:00-15:30 M. Ukai (Tokyo Inst. Tech.), "Photoionization Quantum Yields of Simple Molecules"
 15:30-16:00 Coffee Break

Atom and Molecule (II) E. von Nagy-Felsobuki (Newcastle Univ. & IMS) presiding

- 16:00-16:30 O. Dutuit (Univ. Paris-Sud), "Dissociative Ionisation of Molecules by Threshold Electron-Ion Coincidences. Role of Autoionisation"
 16:30-17:00 T. Masuoka (Osaka City Univ.), "Dissociative Double Photoionization of Some Polyatomic Molecules"
 17:00-17:30 J. Eland (Univ. of Oxford & IMS), "Photoelectron-Photoelectron Coincidence Spectroscopy"

Introduction of UVSOR Facility

- 17:30-18:00 K. Kimura (IMS), "Overview of UVSOR Facility"
 18:00-18:30 UVSOR Tour

July 26

Cluster T. Mitani (IMS) presiding

- 9:00-9:30 A. Hiraya (IMS), "Absorption and Fluorescence Spectroscopy of Jet-Cooled Molecules and Clusters"
 9:30-10:00 T. Hirayama, S. Nagaoka and K. Kimura (IMS), "Photoionization Efficiency Curves of Water-Ethylene Clusters"
 10:00-10:30 H. Kroto (Sussex Univ.), "C₆₀ Buckminsterfullerene, The Key to Icosahedral Graphite and Spheroidal Soot particles"
 10:30-11:00 Coffee Break

Topics K. Kimura (IMS) presiding

- 11:00-11:30 J. Bordas (Daresbury Lab.), "Synchrotron Radiation and Muscle Research"
 11:30-12:00 K. Shobatake (IMS), "Synchrotron Radiation-Assisted Etching Reactions and Chemical Vapor Deposition"
 12:00-12:10 Closing Remark I. Munro (Daresbury Lab.)

Core Excitation in GeTe, SnTe and PbTe both in Amorphous and Crystalline Phases

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Group IV Tellurides (GeTe, SnTe and PbTe) are all semiconductor but their electric properties are metallic. They are called degenerate semiconductors. On the other hand, as-deposit films evaporated on the substrates below critical temperature is amorphous and their electric properties are insulator-like. Core absorptions from cation outermost d levels and Te 4d level of group IV tellurides in both two phases and photoemission spectra of GeTe were studied. Figure 1 shows the absorption spectra of GeTe in both amorphous and crystalline phases in the energy region from 27 to 70 eV. The structures around 30 eV and 40 eV correspond to the transition from Ge 3d level and Te 4d level to the conduction bands, respectively. The line shapes are different not only between amorphous and crystalline phase but also between initial Ge 3d level and Te 4d level. A small peak appears at about 40 eV after crystallization. This is also seen in the case of SnTe¹⁾, but not in the case of PbTe. Since Fermi energy is located in the valence band in p-type degenerate semiconductor and the present SnTe and GeTe samples are p-type, the unoccupied states near the top of the valence band probably exist. Therefore, we assign these small peaks at 40 eV to the transition from Te 4d core level to the top of the valence band. Figure 1 also shows the sharp doublet peaks at around 30 eV in the crystalline phase which are due to the transition from Ge 3d levels. The intensity ratio between the first and the second peaks of this sharp doublet is different from the ratio of the statistical weights between M_{IV} and M_{IV} levels (3:2). This tendency is also seen in the transition from Sn 4d and Pb 5d levels in the crystalline phase. We calculated the intensity ratio and the energy splitting of the peaks using atomic model with the intermediate coupling scheme. Calculation results are in agreement with experimental results without the case of PbTe. These sharp doublet peaks are probably due to the excitonic transitions.

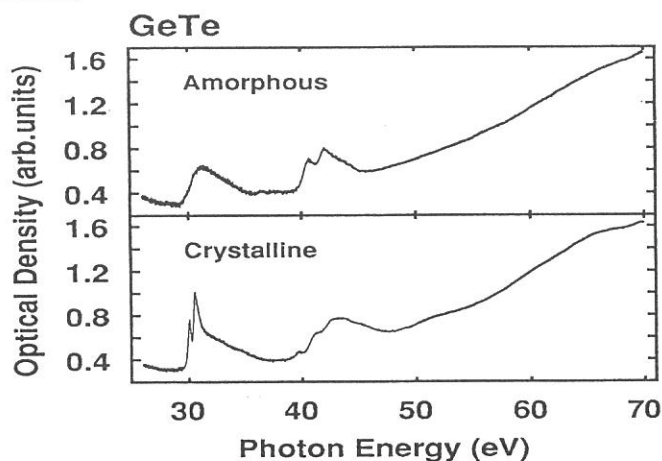


Fig. 1. Absorption spectra of GeTe film at 80 K both in the amorphous and the crystalline phases.

Reference

- 1) K.Fukui, J.Yamazaki, T.Saito, S.Kondo and M.Watanabe : J. Phys. Soc. Jpn. 56 (1987) 4196.

Cr 3d PARTIAL DENSITY OF STATES AND p-d HYBRIDIZATION
IN FERROMAGNETIC SEMICONDUCTOR CdCr₂Se₄

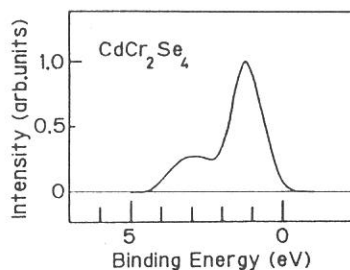
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We have studied the contribution of Cr 3d states to the valence bands of CdCr₂Se₄ by means of the resonant enhancement of the Cr 3d photoemission cross section near the Cr 3p→3d core excitation ($\hbar\omega=47$ eV). The Cr 3d partial density of states (DOS) is evaluated from the spectra taken on and off resonance. A strong peak in the partial DOS located at 1.3 eV below the valence band maximum is assigned to the $t_{2g}\uparrow$ bands without strong dispersion. The second peak located at 2.9 eV is mainly derived from the $e_g\uparrow$ and $e_g\downarrow$ bands, which are spread over in the valence band region between 0 and 5 eV due to the strong p-d hybridization. The results are qualitatively interpreted in terms of a molecular-orbital level scheme and compared with the results of band structure calculation based on the DV-Xa method.



Cr 3d derived partial DOS in CdCr₂Se₄ obtained from the valence band photoemission spectra measured at the antiresonance and on resonance. Contribution from inelastic secondary electrons has been subtracted.

Testing High Temperature Superconductivity Models
Using Synchrotron Radiation Photoemission
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Several tests of proposed models for high temperature superconductors have recently been reported by different research groups.[1-4] These experimental results include the first reported observation of a superconducting gap [1], a more recent report with better electron energy resolution of the gap and electronic states immediately adjacent to the Fermi energy [4], and tests of the resonating valence bond model using the Fermi edge lineshape of the high temperature superconductor materials. [2,3] In addition, a recent angle-resolved photoemission report also provides a detailed test of the band structure calculations [5] and implicitly a test of whether the high temperature superconductor materials studied appear to be Fermi liquids. Finally, results as yet unpublished [6] report a detailed comparison between experimental results and electronic band structure calculations, including a detailed study of the Fermi surface. [6] This talk summarizes the above results. The important conclusions drawn include:

- * There is every indication that the Bi-family high temperature superconductors exhibit Fermi liquid behavior, and do not exhibit electronic structure consistent with a resonating valence bond model for these materials;
- * The superconducting gap studies, if photoemission measures the gap, Δ , yields a ratio between twice the gap and kT of approximately 7, which is inconsistent with the maximum value of this ratio predicted by a weak-coupling BCS theory;
- * The ability to directly observe the superconducting gap by using photoemission, and to directly test the Fermi liquid nature of the high temperature superconductor materials, constitutes the most significant advance in the use of synchrotron-radiation to date in the study of high-temperature superconductor materials.

[1] "Theoretical and Experimental Analysis of the Superconducting Transition Effects on the Fermi Edge Photoemission Spectra," Y. Chang, Ming Tang, R. Zanon, M. Onellion, Robert Joynt, D. L. Huber, G. Margaritondo, P. A. Morris, W. A. Bonner, J. M. Tarascon, and N. G. Stoffel, Phys. Rev. B39, 4740 (1989).

[2] "Possibility of a Resonating Valence Bond State in the High- T_c Superconductor $\text{Bi}_4\text{Ca}_3\text{Sr}_3\text{Cu}_4\text{O}_{16+x}$," Y. Chang, Ming Tang, Y. Hwu, M. Onellion, D. L. Huber, G. Margaritondo, P. A. Morris, W. A. Bonner, J. M. Tarascon, and N. G. Stoffel, Phys. Rev. B39, 7313 (1989).

[3] Comment on "High Resolution Photoemission Study of the Low-Energy Excitations Reflecting the Superconducting State of Bi-Sr-Ca-Cu-O Single Crystals," D. L. Huber, G. Margaritondo, P. A. Morris, W. A. Bonner, J. M. Tarascon, and N. G. Stoffel, Phys. Rev. Lett. 63, 101 (1989).

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[5] T. Takahashi, H. Matsuyama, H. Katayama-Yoshida, Y. Okabe, S. Hosoya, H. Fujimoto, M. Sato, and H. Inokuchi, Phys. Rev. B39, 6636 (1989).

[6] C. G. Olson, private communication.

Photoemission Studies of High T_C -Superconductors and Related Compounds

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It is generally accepted that the Cu-based high- T_C superconductors are doped charge-transfer insulators. Although the insulating states are rather well understood in terms of the impurity Anderson model or the local cluster model, our understanding of the metallic states produced, e.g., by hole doping are far from satisfactory. In order to shed some light on the nature of correlated metals, I will present the results of photoemission studies on some 3d transition-metal compounds showing various types of metal-insulator (MI) transitions.

As for the hole-doped Mott insulator $\text{Li}_x\text{Zn}_{1-x}\text{V}_2\text{O}_4$, the Fermi level (E_F) appears to be pinned at the top of the V 3d lower Hubbard band as the system is doped with holes [1]. The line shapes of the V 3d bands of V_6O_{13} and V_2O_3 are similar to that of $\text{Li}_x\text{Zn}_{1-x}\text{V}_2\text{O}_4$ and do not change appreciably across the temperature-dependent MI transitions [2].

NiS is a charge-transfer compound and its overall photoemission spectra do not change significantly across the temperature-dependent MI transition [3], although the main d band (d^0_L final states) is slightly (by 0.05 eV) shifted to higher binding energy in the insulating phase, consistent with the opening of a charge transfer gap in the insulating phase. The main d band, however, does not seem to show additional shift as one proceeds further into the metallic region as Se is substituted for S [4].

As for the doped Cu oxides such as $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$, doping-dependent MI transitions occur via formation of impurity levels at E_F . The resulting metallic states, however, may be essentially due to the formation of a d^9_L band of local 1A_1 symmetry in the vicinity of E_F [5]. In this case also, there is little evidence for a shift in E_F as a function of doping in the metallic region.

Reference

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Photoemission and Inverse Photoemission Study of Transition Metal
Intercalated and Surface Adsorbed TiS_2

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Intercalation of transition metal atoms into the van der Waals gap of layer compounds induces drastic changes of electronic states of host materials. We have studied the electronic states of TiS_2 and transition metal (M:Fe, Co, Ni etc.) intercalated M_xTiS_2 compounds by means of XPS and UPS measurements. An increase of the density of states (DOS) at E_F is observed for M_xTiS_2 in comparison with TiS_2 . The difference of the XPS spectra between M_xTiS_2 and TiS_2 has revealed that the M 3d derived states are spread in a wide energy region from E_F down to $E_B \sim 12$ eV reflecting the presence of d^{n-1} and d^{n-1} states. Corresponding results are confirmed in the constant initial state (CIS) spectra measured in the region of $h\nu = 30 \sim 120$ eV by use of synchrotron radiation.

Empty conduction bands are probed by angle resolved VUV inverse photoemission measurement. A remarkable decrease of the intensity is observed for the first peak just above E_F for Fe and Ni intercalated compounds. A spectrum from ordered Ni adsorbed TiS_2 has shown a result similar to that of Ni intercalated compound.

Thus a strong interaction of the guest atom 3d orbitals with those of S and Ti is experimentally confirmed. These results are compared with recent band calculations.

*These works are done in cooperation with M.Inoue, A.Fujimori and H.Namatame.

CURRENT STATUS AND FUTURE PROSPECTS FOR ULTRA-SOFT X-RAY SPECTROSCOPY.

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Radiative transitions in the ultra-soft x-ray range connect localized core states with outer delocalized valence states by electric dipole interaction. This condition forms a basis for the use of ultra-soft x-ray spectra in the study of the electronic structure of matter. The degree of energy separation between the inner levels in different atoms provides a chemical selectivity, i.e. each atomic species in a molecule or compound gives rise to a separate spectrum. The selective nature of the dipole transitions give rise to an atomic state selectivity that often facilitates the interpretation of spectra and allows detailed studies of the valence electronic structure.

Recently monochromatized synchrotron radiation has been introduced as a means to excite ultra-soft x-ray fluorescence spectra /1/. This advancement, which has been facilitated by employing a high efficiency instrument of novel design /2/ and a powerful wiggler source /3/, has opened up new interesting possibilities for ultra-soft x-ray spectroscopy. One important aspect of this new technique is the feasibility of separating satellite excitations in order to obtain "clean" valence band spectra, which, together with the particular ability of soft x-ray emission to selectively probe the valence band composition provides a useful tool for the study of valence band structure.

Another aspect concerns the ability to tune to resonances and to study the subsequent x-ray decay. In the investigations carried out so far numerous examples of strong resonant behaviour and threshold effects have been observed. Other advantages are found in the bulk probing ability due to the large penetration depth of the exciting photons (as opposed to electrons), and in the relative softness of this means of excitation which allows more fragile compounds to be studied.

In this paper we present results from ultra-soft x-ray fluorescence studies of 3d metals and their oxides with respect to 2p-3d excitations and valence band composition. In particular O K and Cu L emission spectra of the 123 high temperature superconductor will be discussed. Strong threshold effects were observed in the O K spectra and, in particular, large variations in the shapes of these features appear between samples of slightly different oxygen content (and different critical temperature). Threshold effects are also observed in the x-ray emission spectra of solid carbon dioxide and a correlation is made to the corresponding absorption spectra.

An account will be given of recent advances in electron excited ultra-soft x-ray emission spectroscopy applied to free molecules. In this work the study of molecular orbitals and chemical bonding are of particular interest. The work in this field has been going on for quite some years, and recently it has been subject to important experimental improvements. Also, the present paper addresses briefly excitation energy dependence and threshold effects in electron excited spectra in terms of depth profiling and resonant discrete bremsstrahlung.

Finally, we will discuss the future prospects of ultra-soft x-ray spectroscopy, in particular in the light of the new advanced synchrotron radiation sources that will be operative within a few years. Also, the impact of ultra-soft x-ray emission spectroscopy in connection with recent advances in ion source developments and collision physics will be addressed.

References.

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SOFT X-RAY FLUORESCENT SPECTRA OF LANTHANUM COMPOUNDS

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We have measured the $M_{4,5}$ x-ray emission spectra (XES) of Lanthanum compounds, LaF_3 , La_2O_3 and LaBr_3 with x-ray excitation method. X-ray photoelectron spectroscopy (XPS) of the inner core levels in rare-earth (RE) elements has been known to reflect the relaxation process due to the many-body effect including the 4f electrons. XPS give us the information when the core holes are created, while XES provide information on the decay process of the core holes. Therefore, it is very interesting to compare the spectra of XES with those of XPS.

Experiments were performed using an undulator radiation from the 2.5 GeV electron-storage ring at the Photon Factory of National Laboratory for High Energy Physics. An energy spectrum of the undulator radiation used in this study has quasi monochromatic peaks around 475, 950 and 1425 eV. Measurements were performed using a 30 cm bent-crystal spectrometer with RAP crystal.

We have measured the $M_{4,5}$ XES spectra of La compounds to compare them with the 3d XPS spectra of the same compounds. We can get very faint X-ray lines ascribed to the $5p \rightarrow 3d$ transition in Lanthanum compounds. These lines show a drastic chemical effect on the relative intensity of two components of the lines, which are supposed to be due to the $3d^9 4f^0$ state and the $3d^9 4f^1$ state. The results of the present XES study were quite different from those of the XPS. In every compound, the intensity of the $3d^9 4f^0$ state in XES is smaller than in XPS and the intensity of the $3d^9 4f^1$ state in XES is greater than that in XPS. These results give us a remarkable information about the relaxation process of the 3d hole states.

Time-Resolved Luminescence Studies of Alkali Halide Crystals
Using Single-Bunched Light Pulses from UVSOR

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Abstract

Combination of single-bunched light pulses (duration: 0.5 ns, interval: 177.6 ns) from UVSOR (Okazaki, Japan) with a method of time-correlated single-photon counting was applied to study decay behaviors of intrinsic luminescence in nine typical alkali halide crystals (Na,K,Rb) \times (Cl,Br,I). Under excitation into the band-to-band transition, two emission bands, so far called σ emission (fluorescence with a short lifetime) and π emission (phosphorescence with a much longer lifetime), were observed in general at LHeT. The decay behaviors observed were essentially the same as those reported in previous studies where pulsed particles were used as an excitation source.

A novel situation has, however, been recognized in the π emission in NaBr and NaI: A fluorescent component was found clearly to coexist with the long-lived phosphorescent component. By observing decay profiles at several different energies of the π emission band, it was confirmed that both components have almost the same spectral shape. This means that the initial state responsible for these π emission bands involves both levels of a singlet and a triplet associated with the same electronic orbital, which may be slightly split by the exchange interaction.

That is to say, the “ π emission” in NaBr and in NaI involves certainly the characteristics of singlet emission in spite of its appearance as triplet emission. Along with the characteristics of its spectral position, this result suggests that the “ π emission” belongs rather to the family of the σ emission in other crystals.

Fluorescence Studies of Biosystems

I.H. Munro

Daresbury Laboratory

The most important property of membranes is their selective permeability, which enables selected materials to enter or leave the cell. Obviously methods used to study these transport mechanisms must be fast enough to identify specific molecular motion. The incorporation of fluorescent probes within a membrane permits the technique of Time Resolved Fluorescence Anisotropy (TRFA) to be used to derive detailed information about how the local structure of the cell membrane modifies the rate and range of the motion of the probe. A number of fluorescent probes have been developed and studied using the SRS and the motion of the probe has been correlated with the physical properties of the bilayer such as acyl chain mobility, gel/liquid crystalline phase transitions and disorder due to unsaturation and phase separation.

Recent work at the SRS has included the TRFA behaviour of DPH and t-PnA (trans-partinaric acid) in brain synaptic membranes from rat, trout and *Notothenia neglecta* which show progressively an increasing freedom for probe rotation i.e. reducing correlation times. The rotational correlation time has been measured to be temperature dependent but species independent for DPH, despite the large differences between the fluidity and unsaturation of fatty acids in membranes from different species. In the investigation into homeoviscous response to fluctuations in external environment the regulation of membrane composition and membrane dynamic structure was shown to be an important adaptive response to environmental temperature. The rigidifying influence of external hydrostatic pressure showed that the homeoviscous response also applies to species which live at high pressures.

Other measurements have been carried out using "model" membrane systems, where macroscopic orientation of lipid bilayers is exploited to enable probe molecules lying at different orientations relative to the bilayer normal to be selectively excited by varying the angle of incidence of the excitation beam. At the same time the polarised emission from a particular population of excited probe molecules can be selected by changing the angle between the directions of incidence and observation. Angle and time-resolved fluorescence depolarisation experiments on DPH and TMA-DPH embedded in multibilayers of DMPC (dimyristoyl-) and POPC (palmitoyl-oleoyl-phosphatidylcholine) revealed the absorption moment order parameter (P_2) to be higher than that for the emission moment for each probe and established that a higher fraction of DPH molecules compared with TMA-DPH were lying with their axes parallel to the bilayer surface. Further measurements have studied the effects of hydration and shown that reorientational motion of probe molecules becomes faster with increasing hydration.

Measurements on lipid vesicle and planar multibilayer systems have been used to establish the effect of incorporation of cholesterol within the bilayer. Analysis of the molecular dynamics the probe in terms of the rotational diffusion model reveals that two distinct, though statistically equivalent, solutions exist for vesicles while measurements on planar multibilayers can be interpreted unequivocally. This work has shown that the "wobble-in-cone" model does not provide a satisfactory description of orientational order or reorientational dynamics in these systems.

Kazuhiko SEKI (Hiroshima Univ. and IMS)

XANES (X-ray Absorption Near-Edge Structure) spectroscopy offers information on the vacant states of molecules. By combining the good polarization of synchrotron radiation with well oriented samples, we can get further information for assigning the observed spectral features. We report here such studies for large organic molecules and polymers, measured at Photon Factory beamline 11A using a Grasshopper monochromator.

I. Saturated Polymers.

- (1) Polyethylene $(\text{CH}_2)_n$ and its model compound $\text{H}(\text{CH}_2)_{36}\text{H}$
- (2) Poly(tetrafluoroethylene) $(\text{CF}_2)_n$ and its model $\text{F}(\text{CF}_2)_{20}\text{F}$
- (3) Poly(vinylidene fluoride) $(\text{CH}_2\text{CF}_2)_n$

Oriented samples were prepared as drawn polymer films or as evaporated films of model compounds. The model compounds show clear anisotropy due to almost perfect orientation, and many fine structures were found for $\text{H}(\text{CH}_2)_{36}\text{H}$, which are smeared out in those of polyethylene. For $(\text{CF}_2)_n$, new assignments were proposed which correct the assignments of Ishii et al. for C_6F_{12} .

II. Conjugated π -Electron Systems.

- (1) Poly(p-phenylenes) $(\text{p-C}_6\text{H}_4)_n$
- (2) Polyacenes
- (3) UV Polymerization of a diacetylene $\text{CH}_3(\text{CH}_2)_9\text{C}\equiv\text{C}-\text{C}\equiv(\text{CH}_2)_8\text{COOH}$

The spectra of (1) show only one strong $\text{Cl}s \rightarrow \pi^*$ excitation whose energy is independent of n , not reflecting the change of the π -conjugation length. This was successfully interpreted by CNDO/S MO calculations in equivalent core approximation taking account of the effect of core hole creation. For (2), such effect is smaller, and the change of the spectra of (3) by polymerization could also be interpreted in a similar way considering the effect of the π systems in- and out-of-molecular plane.

UPS Studies of Model Systems of (Polyethylene and) Polythiophene

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Polyheterocycles have recently attracted much attention as conducting polymers with the non-degenerate ground state, in which polarons and bipolarons are expected as non-linear excitations [1]. In a detailed study of these polymers, however, a major problem is caused by the difficulty in controlling their chemical forms. This problem is avoidable by using oligomers as model compounds.

Here we report a combined UPS and theoretical study of the electronic structure of oligothiophenes with 4-8 thiophene rings. The UPS spectra were measured at UVSOR Facility of IMS. In a series of α -linked oligomers (α_n , $n=4-8$), a systematic evolution of the π band is observed: several peaks which correspond to the bonding π band are observed in the region of 0.7-3 eV below the Fermi level (E_F) and become broader with the unit number n of α_n , while the nonbonding π band is observed at 3.5 eV below E_F and its energy is almost independent of n . UPS spectra of α_7 and α_8 are fairly similar with the spectra of polythiophene [2] but with sharper structures. This shows that these oligomers are good model compounds of polythiophene. The effects of irregularity on the π -electron system are studied by using oligomers which contain the β linkage or vinylene at the center of the molecule. It is shown that the β linkages significantly affect the UPS spectrum, but vinylene does not. In order to analyze the UPS spectra, the orbital energies and the optimum geometries of these oligomers were calculated by the semi-empirical MNDO-SCF-MO method [3]. Theoretically simulated spectra derived from the obtained orbital energies agree well with the observed ones, particularly in the π region. It is shown from the optimized geometry that (1) α_n has a planer structure and π electrons can be delocalized, (2)the β linkages prohibit the planarity of the molecules and the delocalization of π electrons, and (3)the oligomers with vinylene are almost planar and the effect of vinylene is small.

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Structural Studies of Surfaces Using Soft X-ray Methods

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Synchrotron radiation in the 2-5keV energy range allows one to perform three complementary surface structural techniques on suitable adsorbate-substrate systems, namely SEXAFS (Surface Extended X-ray Absorption Fine Structure), photoelectron diffraction, and normal incidence standing X-ray wave field absorption. The physical principles, and the nature of the complementary structural information content of these three methods will be demonstrated by their application to a simple model system, chlorine adsorption on Cu(111) to form the ordered Cu(111) ($\sqrt{3} \times \sqrt{3}$) R30°-Cl structure. The first two techniques as both local electron scattering probes of local structure, SEXAFS being primarily sensitive to nearest-neighbour bonding distances, while photoelectron diffraction is a real space directional probe. The standing wave method is particularly helpful in cases in which substrate reconstruction occurs and this is shown clearly in the combined application of the SEXAFS and SXW methods to the structure of the CH₃S-molecular species on Cu(111).

Angle-Resolved Photoemission from Thin Crystalline Oxide Films

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■ We have made angle-resolved ultraviolet photoemission spectroscopy (ARUPS) studies of epitaxial NiO(100)¹ and FeO(111) films² formed in the final stage of oxidation of Ni(110) and Fe(110) surfaces and of epitaxially grown YBa₂Cu₃O_{7-x}(001) [YBCO(001)] single-crystal thin films³ at Photon Factory, National Laboratory for High Energy Physics. Particular emphasis is on revealing the dispersive nature of the valence states of the oxides, not on the electron correlation effects. Dispersion is difficult to handle in the localized cluster approach. Previous UPS measurements on cleaved NiO samples suffered charging problem. Charging distorts a spectrum and prevents a determination of the Fermi level, and therefore the spectra have often been aligned at the top of the valence band. This is a reason why an experimental energy dispersion relation $E(\mathbf{k})$ is still missing for transition-metal oxides. However, charging problems did not occur for our samples of thin films.

■ Well-ordered NiO(100) [FeO(111)] (~5 Å thick) was prepared by a clean Ni(110) [Fe(110)] surface to 100 L oxygen at 300K and subsequent annealing at 700K [600 K], and the single-crystal YBCO(001) films (~1000 Å) were prepared epitaxially on SrTiO₃(001). The ARUPS measurements were done using a 150° spherical-sector-type analyzer with an acceptance angle of ± 1°. Total experimental resolution was 0.1–0.2 eV. The cleanness of the surfaces was confirmed by Auger electron spectroscopy and their crystalline order by LEED. The base pressure in the system was 1×10^{-10} Torr.

■ We measured off-normal emission spectra of each sample in some symmetry directions. Our findings are summarized as follows: ① all the features in NiO(100) show small but distinct dispersion of ~0.5 eV, ② the so-called Fe 3d states in FeO(111) show little dispersion, while the O 2p states exhibit a considerable dispersion of 2~3 eV, and ③ the dispersive nature of the valence bands including the states near E_F is found in YBCO(001), and a clear Fermi edge is seen.

■ We are pleased to thank the staff of the Photon Factory for their excellent support (Proposal Nos. 84-080, 88-U-002).

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CIRCULAR DICHOISM AND SPIN POLARIZATION
IN PHOTOEMISSION FROM ADSORBATES

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Spin-resolving techniques are presently attracting wide interest because they can provide a detailed insight into specific aspects of, e.g., photoemission. Recent experimental work in this field is discussed with emphasis on the complementary nature of the information gained by exploiting the photon- and/or electron-spin.

A recent but very promising achievement is the experimental verification of Circular Dichroism in the Angular Distribution of Photoelectrons (CDAD). This phenomenon has been theoretically predicted for spatially oriented molecules /1-3/. Employing circularly polarized Synchrotron radiation at BESSY we have performed case studies for adsorbed CO, NO, C₆H₆, and CH₃I as well as for clean graphite(0001) and Pd(111). In all cases huge photoelectron-intensity differences occurred upon reversal of photon helicity. The effect arises (without spin-orbit interaction) through an interference of final-state partial waves differing in their m quantum numbers by 1. Its angular and energy dependence allows extracting information on photoemission dynamics at a surface (matrix elements and their relative phases) and on adsorbate structure (e.g. molecular orientation). For CO a first numerical model calculation /3/ shows reasonable agreement.

Spin Polarization (SP) of photoelectrons induced by circularly polarized light is a direct consequence of spin-orbit interaction. SP-spectroscopy thus provides a unique method to experimentally determine the symmetries of electronic bands of high-Z materials exploiting the "relativistic" selection rules $\Delta m_j = \pm 1$ (for circ. pol. light). This method has been applied to a number of transition-metal surfaces and to adsorbed rare-gas atoms, and is illustrated by typical examples. For rare-gas monolayers sharp excitonic resonances ($\Delta E = 80\text{meV}$) could be identified via a "spin-labelling" technique.

Finally, a different aspect of SP-spectroscopy with ferromagnetic surfaces is mentioned. Since this method allows a direct distinction between majority and minority bands, it is suitable to investigate possible exchange splittings of adsorbate-induced bands. For chalcogen np-derived bands on 3d-ferromagnets we have observed substantial spin-splittings giving evidence of strong exchange coupling between overlayer and substrate (p-d hybridization).

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Resonant photoemission due to surface core excitons at Ga-site, arising from the surface relaxation of GaAs(110), has been calculated with the full consideration of the dependences on the energy and polarization of incident light, and of the energy, emission angle, and spin-state of photoelectron. Surface band structure of final-state valence-hole and the electron-hole exchange and anisotropic Coulomb interactions in the core exciton states have been taken into account. The decay of the core exciton is assumed to occur, as experimentally suggested by Lapeyre and Anderson /1/, only through direct recombination. This leads to an interference effect between the resonant and direct emission processes. A puzzling polarization dependence in the measurement can be understood as due to the combined effects of the polarization dependent angular distribution and surface refraction of photoelectrons. Angle resolved CIS and EDC have been calculated and compared with the available experimental data /2/. The agreement is rather good, but, in some cases, the phase relation of the two emission processes, direct and resonant, has not been well reproduced. The possibility of measurable spin polarization has been demonstrated for angle resolved spectra.

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New Triple Coincidence techniques Applied to Multiple Ionisation of Molecules

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Over the last 3 years we have developed two triple coincidence techniques in order to study the detailed dynamics of molecular dissociative photoionisation. The first is a photoelectron-photoion-photoion coincidence (PEPIPICO) experiment used to study the double photoionisation process.^[1] In this technique, two identical time-of-flight (TOF) drift tubes are employed. The first detects of photoelectron (the START pulse), the second detects two correlated photoions (giving two STOP pulses). The data are accumulated, at a single wavelength, as a 3-dimensional histogram of TOF coincidences. The y axis is the TOF of the first ion, the x axis the TOF of the second ion and the z axis the coincidence count rate. The various fragment pairs (eg. C^+O^+ , $C^{2+}O^+$ etc.) appear as cigar-shaped features lying side-by-side with length related to their dissociation energies. We have studied the various fragmentation channels of CO in the region of the C(1s) excitation and find dissociation energies to be given by a simple Coulomb repulsion model.

The second triple coincidence experiment involves the use of an intense subpicosecond laser (wavelength 600nm, pulse length 0.6ps, focussed intensity $\sim 10^{16}W/cm^2$) to multiply-ionise the CO molecule. In order to analyse the fragmentation spectrum, a new "covariance mapping" technique was devised. This allows unambiguous correlation of atomic ions with molecular parent ions.^[2]

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PHOTOELECTRON SPECTROSCOPY OF LASER-EXCITED ALIGNED FREE
ATOMS

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The combination of laser and synchrotron radiation offers the possibility to study innershell excitation processes of optically excited atoms. One very interesting aspect of this technique is the use of the well-defined polarization of both radiation sources: By the absorption of polarized laser radiation an atomic alignment or orientation is produced; the subsequent excitation with synchrotron radiation therefore probes a target of aligned or oriented atoms [1].

Important parameters for the description of the resonant two-photon process and of the influence on the angular distribution of the photoelectrons are the geometry of the experimental set-up (especially the relative orientation of the polarization vectors) and the symmetry character of the intermediate and final states.

Experimental examples are given for core-excited Li I $1s^n n'l$ -states starting from laser-excited aligned Li I $1s^2 2p^2 P_{3/2}$ atoms. The production of laser-excited aligned free atoms is discussed in some detail with respect to hyperfine coupling, power broadening and radiation trapping effects.

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Symmetry-Resolved Photoabsorption Spectroscopy of Diatomic and Triatomic Molecules

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We have reported the first measurements of fragment-ejection asymmetries as a direct probe of the anisotropy of molecular photoabsorption in the vicinity of K-shell ionization threshold of N_2 , using an angle-resolved photoion spectroscopic technique[1]. In this talk we present more detailed results on the photoabsorption anisotropy of N_2 , O_2 and N_2O molecules. Figure 1 shows molecular orientation parameters of N_2 with a total-ion curve.

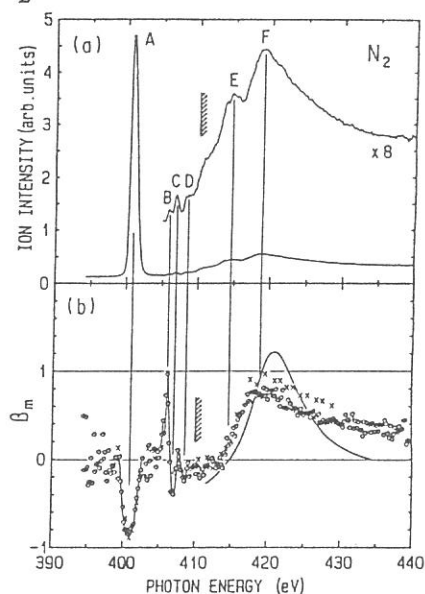


Fig. 1. (a) Total-ion yield spectrum and (b) molecular orientation parameters of N_2 in the vicinity of K-shell ionization threshold.

(o) present,
(x) Yagishita et al.[1]
and (—) Dill et al.[2].

From these orientation parameters depending on photon energies, we can experimentally determine symmetries of photoexcited states. We also display, for the first time, symmetry-resolved photoabsorption spectra of N_2 , O_2 and N_2O .

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PHOTOIONIZATION QUANTUM YIELDS OF SIMPLE MOLECULES

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Measurements of the photoionization quantum yields (η), i.e., the absolute probabilities of photoionization on a single photoabsorption event, of polyatomic molecules in the energy range from VUV up to soft X-ray are of great importance in order to elucidate the role of the superexcited states in the photoionization process competing with dissociation. Although several efforts have been devoted to the measurements of the photoionization quantum yields, very few reports are available even for the simplest molecules. Furthermore, serious conflicts exist in some cases.

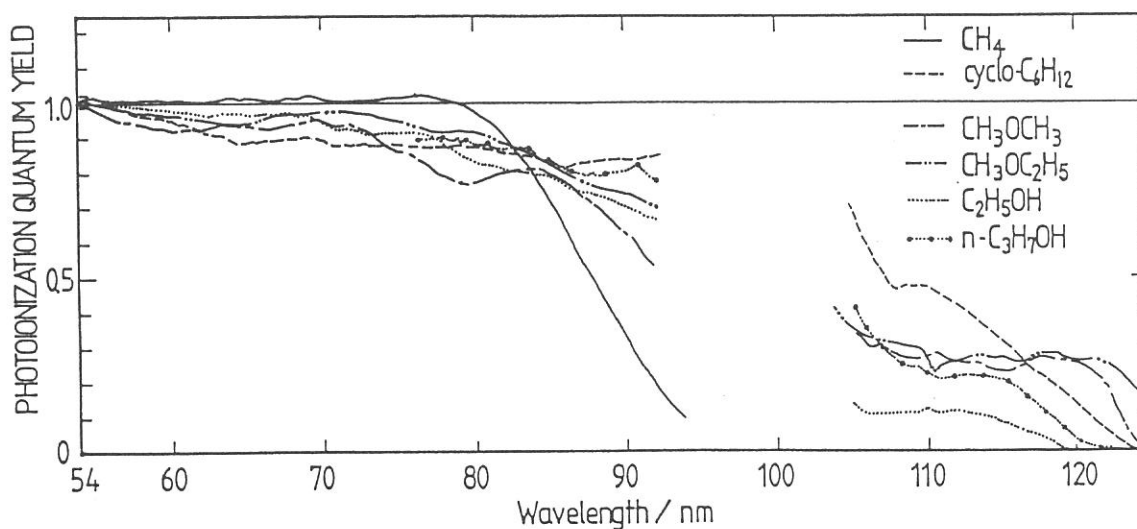
In the present paper, we present the photoionization quantum yields of some simple, but chemically important, organic molecules obtained in the extreme-UV region.

Photoionization quantum yields are obtained using a multiple-staged photoionization chamber [ref.1]. In the present work, metal foil filters are employed as the window materials for incoming SR beam. In 52-80nm and 74-94nm regions, Sn and In foils of about 1000Å thickness with about 1% transmittance are respectively, used. Absolute photon flux is obtained by photo-currents of rare gas atoms ($\eta=1$).

Figure.1 shows the obtained ionization quantum yields. A large discrepancy from unity in the η values is observed, which diminishes with the increase in the photon energy. A considerable portion of the superexcited states existing in this region is shown to undergo dissociation and other non-ionizing channels. Enhancement of the fluorescence intensity is observed in the excitation spectra of the VUV and visible emission, which confirms the above non-ionizing decay channels of the superexcited states.

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Fig.1 η for CH₄, c-C₆H₁₂, C₂H₆O, and C₃H₈O.



DISSOCIATIVE PHOTOIONISATION OF MOLECULES BY THRESHOLD ELECTRON-ION COINCIDENCES. ROLE OF AUTOIONISATION

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Dissociative photoionisation of small molecules has been extensively studied over the past years. The measurement of fragmentation branching ratios, dissociation lifetimes, isotope effects and fragment ion angular distribution as a function of parent ion internal energy gave a lot of informations about the dissociation mechanisms. Diatomic and triatomic ion dissociation can be rather well understood when the potential surfaces are reasonably known. For polyatomic ions, the statistical RRKM theory can explain most of the results concerning the breakdown diagram and the dissociation rates of ions made up of at least five or six atoms, when the internal energy is not too high (1). For intermediate size molecular ions, the situation is more complex and both theoretical approaches must be combined(2).

We will present the case of intermediate size molecular ions, prepared by photoionisation with VUV photons (30-100 nm), choosing some examples, in particular CH_4^+ selected in a very wide range of internal energy. The ground state of CH_4^+ is already known to dissociate according to the statistical theory (3). However we will show that it is not the case for internal energies larger than 8eV. Isotope effects observed for CD_4^+ and CD_3H^+ give some more insight into the dissociation mechanisms. Internal conversion and direct dissociation mechanisms are investigated. A special attention will be given to the dissociation of ions formed in the especially large Franck-Condon gap between the X and A states (16-22 eV photon energy). In this energy region, the ions can only be formed by resonant autoionisation. In previous studies, this process has been shown to occur in a general way for molecules which are at least triatomic (4).

The role of resonant autoionisation in ion dissociation will be discussed in the light of several other examples (CO_2^+ , H_2O^+ , HBr^+ , H_2CO^+ ...) taken from the work of different groups. In particular it will be shown that in some cases, the dissociation of Rydberg states can precede the resonant autoionisation process, which then occurs in a fragment.

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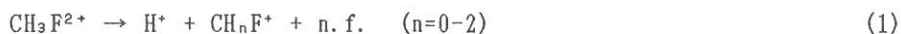
Dissociative Double Photoionization of Some Polyatomic Molecules

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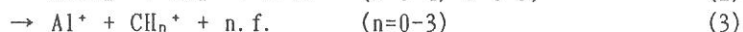
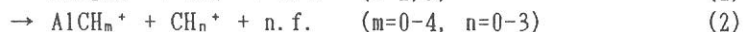
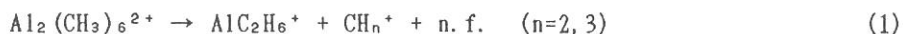
In order to study photoionization processes of gas molecules, a new apparatus has been constructed, whose capability includes measurements of angle resolved photoelectrons as well as time-of-flight measurements of photoions in coincidence with total, energy selected, or threshold electrons.¹ A constant-deviation grazing incidence monochromator² installed at the UVSOR synchrotron radiation facility in Okazaki and a set of optical filters provided monochromatic radiation. The molecules such as C₂H₂, CH₃F, C₂H₄O, and Al(CH₃)₃ have been studied by the photoion-photoion coincidence (PIPICO) method and TOF mass spectrometry in the photon energy range 35-125 eV.

CH₃F: Stable CH₃F²⁺ was not observed in all the energy range studied. A PIPICO spectrum measured at 100 eV shows at least four dissociation processes,



At low energies below about 40 eV, only the four pathways are open, i.e., the C-H bond breakage (1) and rearrangement reaction (2). These two processes are due to two-electron ejection from the outermost 2e orbital. The fragmentation H⁺+CH_n⁺ (the C-F as well as C-H bond breakage) starts to occur at about 40.5 eV because of two electron ejection such as (5a₁,2e)⁻¹ and (1e2e)⁻¹. The observed dissociation pathways are correlated with the electronic states of CH₃F²⁺ calculated by the Green's function method.³

Al(CH₃)₃: This organometallic compound is suitable to examine how the dissociation pathways are different in two cases; the valence double ionization and Al:2p core-level ionization, because the threshold for the latter is expected to be about 80 eV. PIPICO studies show the following 5 dissociation processes in the case of the valence double ionization,



The first three processes are mainly related to the C-Al bond breakage. As the internal energy of molecules increases, the C-H bond(s) dissociates sequentially. On the other hand, the latter two are related to the C-H and C-Al bond breakage and start at higher energies than the first three processes. In the case of Al:2p core ionization, the latter two processes are enhanced. This means that the LVV Auger decay results in at least one electron removal from the inner valence orbital(s) related with the C-H bond. The molecular orbitals participating in the Auger decay would be those having large charge densities closer to the Al atomic nucleus.

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PHOTOELECTRON-PHOTOELECTRON COINCIDENCE SPECTROSCOPY

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We have developed a new photoelectron-photoelectron coincidence spectrometer which consists of two large hemispherical analysers both viewing the same ionization volume through multielement accelerating lenses which gather electrons from a large solid angle. Ionization is by filtered HeII light and the sample is an effusive jet. Double ionization is distinguished by detection of coincidences between electrons from the two analysers, with due allowance for time-of-flight changes during scanning. Since both electron kinetic energies are measured the energy balance in double photoionization is completely determined and the technique yields spectra of doubly-charged ions just as conventional photoelectron spectroscopy gives spectra of singly-charged ions. State selectivity observed in the spectra reflects details of electron correlation and if the ionization is direct it provides a test of Wannier theory.

In addition to doubly-charged ion spectra we measure the distribution of electron energies for a given final state. These distributions further test the theory, and directly show the existence of indirect double ionization pathways analogous to autoionization. Latest results will be reported.

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Absorption and Fluorescence Spectroscopy of Jet-Cooled Molecules and Clusters

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Molecular and atomic clusters have been extensively studied in this decade. However, information of the energy levels and dynamic behavior of their highly excited states is quite limited. This is partly because that direct absorption spectra of clusters have not been available until recently. Direct absorption and fluorescence spectroscopy on molecules and clusters in jets using synchrotron radiation has been developed recently by us.

In Xe jets, a broad absorption band at the red side of the 3P_1 atomic line and continuum absorption below 134nm with maxima at 130 and 120nm were observed and assigned to the Xe clusters. Except for the absorptions to the repulsive states, fluorescence excitation spectrum monitored at UV ($\lambda > 180\text{nm}$) follows well the absorption spectrum above 125 nm, then decrease abruptly. This decrease in emission intensity at about 125 nm is due to the opening of the ionization process. Optically prepared states being responsible for the UV fluorescence are assigned to those of Xe clusters. Fluorescence from Xe_2Cl^* ($\lambda_{\text{fluo}} > 450\text{ nm}$) is found for the excitation at around Xe cluster band in HCl/Xe jets and assigned as the Xe_2Cl^* formation in Xe_nHCl hetero-cluster.

The direct absorption spectrum was also obtained for jet cooled benzene and benzene clusters. Remarkable vibrational cooling ($T_{\text{vib}} < 185\text{ K}$) was observed in the S_1 and Rydberg regions. The ϵ_{max} value of the S_1 in the jet is found to be 1400 which is two times larger than that measured in room temperature vapor. In the S_2 region, a shoulder at 205 nm which has not been noticed previously is clearly observed, and assigned to the S_2 origin induced by pseudo-Jahn-Teller distortion. The vibrational structure of the S_2 state is found to be explained reasonably as a v_1 progression built on the S_2 electronic origin and on the two, 8_0^1 and 6_0^1 , false origins.

Two broad absorption maxima observed at 186 and 207nm in the absorption spectrum of benzene seeded in rare-gas under low nozzle temperature, are assigned to the Bz clusters corresponding to the S_3 and S_2 system of benzene monomer, respectively.

Photoionization Efficiency Curves of Water-Ethylene Clusters

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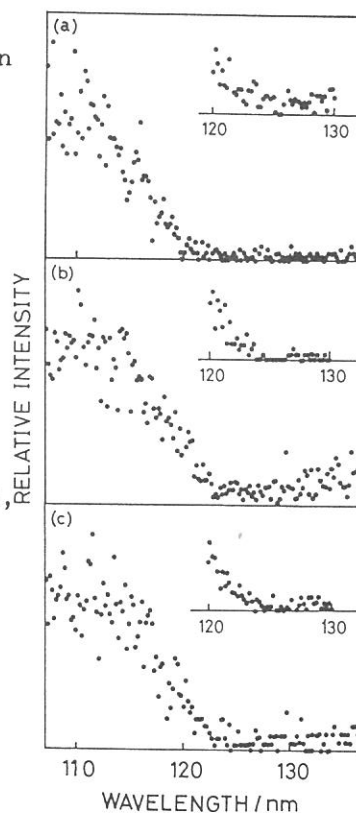
Oil and water will not blend. It is interesting to study the properties of the interface between oil and water. The cluster can be regarded as a model of the interface. Hence, it seems worthwhile to make a detailed investigation of oil-water binary clusters in order to elucidate the properties of the interface between oil and water.

Photoionization measurements for ethylene-water binary clusters were performed by use of synchrotron radiation from the beam line BL2B2.

Figure 1 shows the photoionization efficiency curves for $(C_2H_4)(H_2O)_n^+$ ($n=1-3$) near the threshold.

At the interface between oil and water, H_2O molecules form strong hydrogen-bonds among themselves. It seems that oil is more likely to link to water than to gather in a block. However, since water is closely united, oil cannot get into water phase. Oil can form the pseud-hydrogen-bond with water only at the interface.

Fig. 1. Photoionization efficiency curves for $(C_2H_4)(H_2O)$ (a), $(C_2H_4)(H_2O)_2$ (b) and $(C_2H_4)(H_2O)_3$ (c) near the threshold.



C_{60} BUCKMINSTERFULLERENE, THE KEY TO ICOSAHEDRAL GRAPHITE
AND SPHEROIDAL SOOT PARTICLES

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ABSTRACT

Recent work has aimed at understanding the formation of chains in space and has focused attention on the possibility that they are produced at the same time as carbonaceous dust in red giant stars. These experiments confirmed that very long chains are produced in a plasma when carbon particles form. During these experiments a most exciting discovery was made; that a particular cluster, C_{60} , was spectacularly resistant to further growth. The properties of C_{60} have been rationalised on the basis of a closed carbon cage with truncated icosahedral symmetry similar to that of a football. Geodesic and aromatic factors account perfectly for the stability of such a molecule.



Perhaps the most exciting advance made has been the development of a simple refined nucleation mechanism which not only accounts for C_{60} but also, for the first time, explains the detailed structure of carbon microparticles. The "Icospiral Nucleation Scheme" involves the proposal that when carbon nucleates curved and closing graphitic shells form rather than flat sheets as has traditionally been supposed and these wrap up under epitaxial control.

The proposed gas phase nucleation mechanism is strongly supported by the electron microscope data on carbon microparticles which Iijima obtained in 1980. A most recent study of the nucleation mechanism has produced detailed atomic coordinates which have enabled us to simulate the electron microscope observations.

Overall the results are a striking example of the insight that cluster research can give into the structure of solid materials in bulk. The mechanism also appears to have all the basic ingredients necessary for the solution the old problem of soot formation. The proposal has recently gained significant support from the discovery by Gerhardt, Loffler and Homann that C_{60}^+ is the major ion in a sooting flame as predicted by the nucleation scheme.

The proposal has a wide range of implications; in particular for:

- i) The composition of carbon vapour
- ii) The mechanism of carbon nucleation
- iii) The structure of graphitisable carbons
- iv) Fluid carbon phases and carbon fibres
- v) Soot formation and combustion efficiency
- vi) The structure of interstellar and circumstellar grains
- vii) Structure and synthesis of new polyaromatic hydrocarbons
- ix) New metal-carbon complexes and intercalation compounds

SYNCHROTRON RADIATION AND MUSCLE RESEARCH

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The sarcomere of striated muscle constitutes its physiological and, in many respects, its crystallographic unit cell. Frog sartorius and semitendinosus muscles at rest have a sarcomere length of 2300.0 nm. Clearly, useful X-ray diffraction measurements on such an unusually large paracrystalline structure require an X-ray source of extremely high brilliance.

Following the installation of the high brilliance lattice at the Daresbury SRS, it is possible to measure routinely the very crowded diffraction diagram yielded by striated muscle. The crystallographic unit cell of muscle can be changed at will simply by mechanically stretching the tissue. This permits to phase the very low angle meridional reflections and the determination of electron density maps corresponding to the mass projection of the protein components onto the muscle axis. These experiments have revealed some novel features in the structure which appear to have a direct relationship with the capacity of some muscles to develop passive tension. At higher angles, the diffraction diagram of striated muscle is dominated by the internal structure of the contractile apparatus (i. e. the thick and the thin filaments). Here, the very high spectral brilliance of the SRS, combined with the development of an improved X-ray camera, detector and data acquisition system, has allowed the collection of two dimensional diffraction diagrams from "live" muscle tissues, with time resolution in the millisecond range, and, consequently, to follow the structural changes accompanying the process of muscle contraction. The new data reveals at least two intermediate structural states associated with muscle contraction during isometric tetani. The time course of each myosin based reflection shows a general disordering of the paracrystalline arrangement followed by a modification of the cross bridge configuration. At the plateau of tension, a residual rigor like pattern can be detected. The actin based reflections are all strengthened at the plateau of tension, however, the time courses for these changes differ from layer line to layer line, indicating once again that several different structural processes are in action.

A description of these results and their implication for our understanding of the mechanism of muscle contraction will be given.

This work has been carried out in collaboration with G. P. Diakun, J. E. Harries, R. Lewis, G. R. Mant, M. Martin Fernandez and E. Towns-Andrews.

Synchrotron Radiation-Assisted Etching Reactions and Chemical Vapor Deposition

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Research activities of the title subjects at the UVSOR facility along with the results obtained from other facilities will be reviewed. An apparatus used for synchrotron radiation (SR)-assisted etching reactions and CVD is essentially a gas-filled vacuum chamber connected to four differentially pumped vacuum chambers and to 750 MeV storage ring. The light used for these experiments was either unfocused SR from a bending magnet (BL8a) or undulator light (BL3A1).

In the SR-assisted etching reactions of various poly-Si samples and SiO_2 the depths and profiles of the surfaces were measured against Cl_2 or SF_6 pressure ranging from 0.016 to 1 Torr for varied spectrum of SR irradiated. Fig. 1 illustrates a plot of the SiO_2 etch rate against SF_6 pressure when the undulator light at 251 or 143 Å is irradiated. The fitted curves are calculated transparent light intensity through 4.9 cm long gas layer, impinging upon the surface. The result suggests that irradiation of surface species by SR promotes the rate determining process of etching reaction. In contrast SR-assisted etching of poly-Si surfaces with Cl_2 gas shows different pressure-dependent behaviors from SiO_2 etching (see Fig. 2), suggesting that different mechanisms are applied for these reactions.

Results obtained for the SR-excited CVD will be also described.

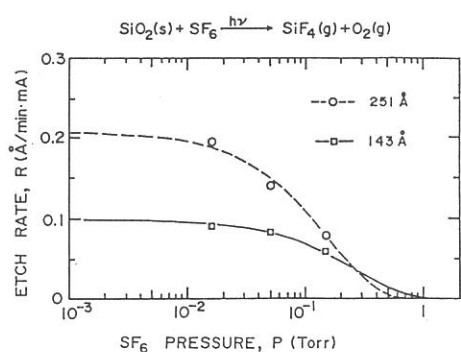


Fig. 1. Etch rates vs. SF_6 pressure for undulator radiation upon SiO_2 surface at 143 and 251 Å.

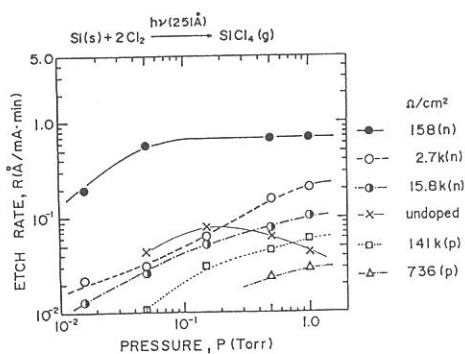


Fig. 2. Etch rates of various poly-Si samples vs. Cl_2 pressure for unfiltered undulator radiation whose first order light is peaked at 251 Å.