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# **Applications of Photon-In, Photon-Out Spectroscopy with Third-Generation, Synchrotron-Radiation Sources**

**Ramada Renaissance Tech World  
Washington, D.C.  
April 25, 1991**

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# Applications of Photon-In, Photon-Out Spectroscopy with Third-Generation, Synchrotron-Radiation Sources

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**MASTER**

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# Applications of Photon-In Photon-Out Spectroscopy With Third-Generation Synchrotron Radiation Sources

Ramada Renaissance Tech World, Washington, D.C.  
Thursday, April 25, 1991

## *Program*

### Session A: Chairman D. Lindle

8:30 A.M.- 8:40 A.M.	Welcome	J. Marx	Lawrence Berkeley Lab.
8:40 A.M.- 9:25 A.M.	Photons: Mother nature's finest test probe	D. Ederer	NIST
9:25 A.M.- 10:10 A.M.	Soft x-ray emission spectroscopy with high-brightness synchrotron radiation sources	J. Nordgren	University of Uppsala, Sweden
10:10 A.M.- 10:30 A.M.	Coffee Break		

### Session B: Chairman T. Callcott

10:30 A.M.- 11:00 A.M.	Anisotropy and polarization of x-ray emission from atoms and molecules	S. Southworth	NIST
11:00 A.M.- 11:30 A.M.	Valence-hole fluorescence from molecular photoions as a probe of shape resonance ionization: Progress and prospects	E. Poliakoff	LSU
11:30 A.M.- 12:00 P.M.	Dynamic screening of core holes	G. D. Mahan	Univ. of Tenn.
12:00 P.M.- 1:30 P.M.	Lunch		

### Session C: Chairman M. Bell

1:30 P.M.- 2:15 P.M.	X-ray resonance magnetic and Raman scattering in heavy Fermion compounds	E. Isaacs	AT&T
2:15 P.M.- 3:00 P.M.	Structural biophysics with third-generation synchrotron radiation sources	G. Bunker	Illinois Institute of Technology
3:00 P.M.- 3:20 P.M.	Break		

### Session D: Chairman H.G. Berry

3:20 P.M.- 3:50 P.M.	Ultra soft x-ray fluorescence yield XAFS: An <i>in situ</i> photon-in photon-out spectroscopy	D. Fisher	Exxon
3:50 P.M.- 4:35 P.M.	X-ray microprobe: Fluorescence as an analytical tool	G. Ice	ORNL
4:35 P.M.- 5:00 P.M.	Conclusion	P. Cowan	NIST

# Mother Nature's Finest Test Probe

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X-rays, as a scientific tool, have been around for a long time. They were discovered almost 100 years ago on November 5, 1895. By February 14, Valentine's Day 1896, Röntgen's paper [1] was translated by A. Stanton for Nature [2]. Among other things the x-ray picture of a living human hand was featured in the article. A few months later in April, M. Pupin presented the results of x-ray experiments to the New York Academy of Sciences. These results were published in Science [3] and the "Woodstock of 1896" was a reality. Pupin, in his article, comments about the emission of x-rays caused by the initial x-ray. He remarks, "Diffuse scattering of the Röntgen radiation by bodies placed in it's path may be also described by saying that every substance once subjected to the action of x-rays becomes a radiator of these rays". So the presence of x-ray fluorescence excited by x-rays was recognized almost the day x-rays themselves were discovered.

The literature since that time has been filled with literally thousands of papers describing x-ray emission and the processes for producing x-ray emission. A few highlights can be listed: Dauvillier [4] used  $K\alpha$  emission spectra to excite fluorescence in iron in 1923. Deslattes observed  $K\alpha$  emission from argon and potassium chloride by fluorescence excitation in 1964 [5]. It was recognized that many of the x-ray satellite structures produced by electron beam bombardment were reduced by using x-radiation for excitation. Sparks [6] observed inelastic resonance emission of x-rays in 1974. Brodmann and co-workers [7] observed VUV fluorescence in gaseous xenon excited by monochromatized VUV synchrotron radiation in 1976. Briand and his co-workers [8] observed x-ray Raman and Compton scattering in manganese using synchrotron radiation in 1981. As synchrotron radiation sources evolved they have become an important tool to probe atomic, molecular and solid state structure. More recently, Deslattes and his co-workers [9] used the wiggler at the Stanford Synchrotron Light Source to study multi-vacancy

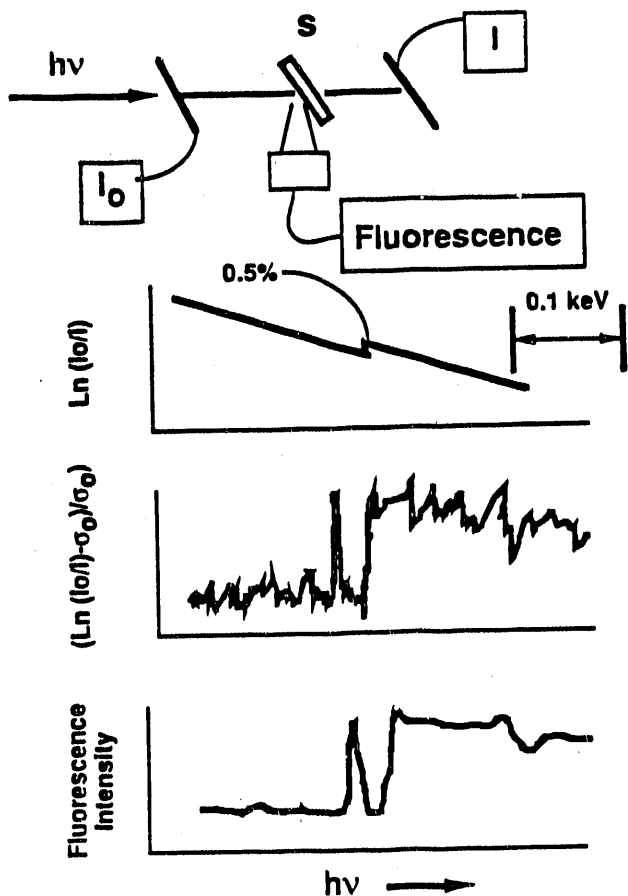
processes in the  $K\alpha$  region of argon. This was perhaps the first use of a wiggler source to do photon-in photon-out experiments.

The purpose of this report and the others presented at this workshop is to give the audience insights into the myriad possibilities that are available through the use of this technology. One can list some of the unique aspects of fluorescence measurements. For example, in many instances x-ray emission yields higher resolution than photo-electron spectroscopy (PES). The threshold excitation dynamics provides spectral sensitivity. Photons are very easy to polarize; electrons are difficult to polarize. Photons are a less damaging probe than other particles. Ultra-high vacuum is not required in many cases. Photons scatter less than electrons and ions. Photons can be used to monitor some processes, such as adsorption of gases on surfaces or molecular dissociation. Fluorescence emission is a very powerful tool to study the x-ray absorption structure in the bulk and from surfaces.

To illustrate the usefulness of the photon-in photon-out technique one can look at the following example. Often it is important to study minute quantities of materials in a solution or a host matrix. In Fig. 1 the logarithm of the intensity is plotted as a function of photon energy. At the absorption threshold for the impurity only a very small change in absorption is observed. Making the subtraction shown in the middle panel and dividing by the total cross section, the tiny change of about 0.5% is emphasized. However, noise associated with the background cross section is present and is amplified by the subtraction of two almost equal large numbers. This noise can be reduced by detecting the fluorescence, because the fluorescence intensity is zero at an energy less than the threshold excitation energy and becomes the only signal detected as the threshold for excitation is exceeded. This point is illustrated schematically in the bottom graph of Fig.1. There are many applications of this technique in the study of molecular bonding, trace analysis and the chemical environment of trace elements.

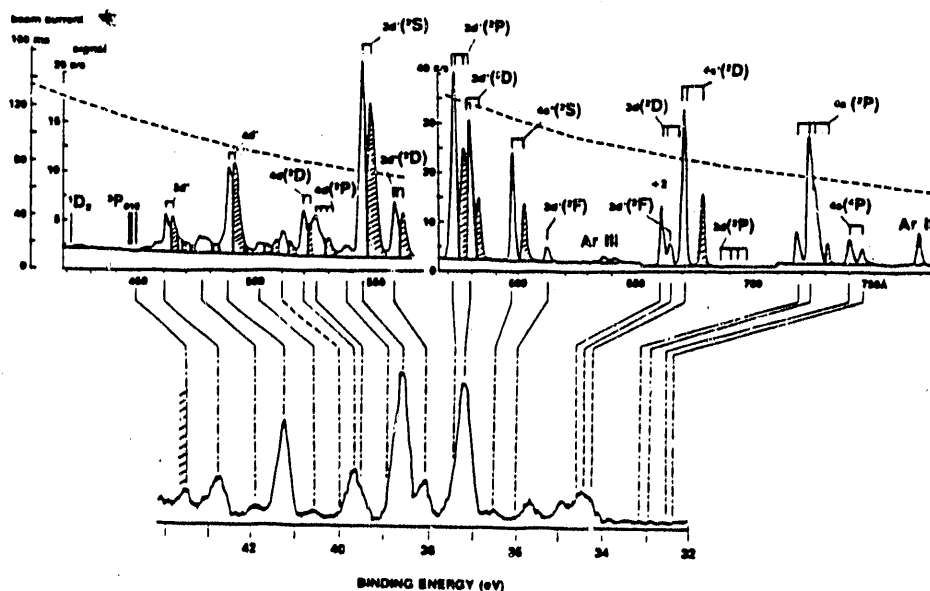
Let's now turn to an example where the high resolution attainable by fluorescence methods produces a spectrum that shows more structure than would be attainable by photoelectron spectroscopy. In this particular work by Samson, Chung and Lee [10], a white light flux of about  $10^{16}$  photons/s from the Tantalus storage ring impinged on low pressure argon gas in a cell. The soft x-rays ionized the argon gas. The excited argon ions radiated in the vuv as they returned to the ground state of the ion.

A rich spectrum was observed, as shown in Fig. 2, the interpretation of which yields important information about electron correlation in the photoionization process. In the lower panel of the figure there is an accompanying spectrum that was obtained using the best photo-electron spectroscopy techniques. The upper panel shows clearly resolved transitions that appear in the PES spectrum as blended features.



**Fig. 1**

Schematic diagram of experiment to detect fluorescence. As  $h\nu$  is changed the incident intensity,  $I_0$ , the transmitted intensity,  $I$ , passing through sample,  $S$ , and the fluorescence intensity are detected. The logarithm of the ratio  $I_0/I$  is shown in the top graph. A small step indicates an absorption threshold of an impurity in the host sample. The middle graph shows one method of processing the raw data to emphasize the absorption edge of the impurity. The lower graph shows the same results obtained from the fluorescence signal



**Fig. 2**

Argon fluorescence spectrum excited by undispersed synchrotron radiation compared with the photoelectron satellite spectrum produced by 77 eV photons. The dashed curve represents the intensity of the decaying synchrotron radiation. The discontinuity at 570Å is the continuation of the scan after injecting a new beam. The figure is from Ref. 10.



The photoelectron spectrum was obtained with monochromatic excitation rather than white light excitation. One of the goals of studies of this type is to measure the intensity of these multi-electron excitations as a function of the photon energy. To take full advantage of the superior resolution attainable by fluorescence techniques, the high flux of third generation synchrotron sources is required.

Measurement techniques employing photons as a probe are less damaging than those using electrons, and can be used to investigate easily damaged materials like some oxides and some of the high temperature superconductors. To illustrate this point let us look at the electron excited soft x-ray emission of copper metal as shown in Fig. 3a. In Fig. 3b we show a spectrum of the soft x-ray emission of copper oxide, excited by a 3 kilovolts electron beam. The beam current in this case was  $3 \mu\text{A}$ . Comparing the spectrum in the right hand panel with the one on the left, one observes that the copper oxide has been transformed into copper metal. One has to carefully choose materials for study by electron beam excitation.

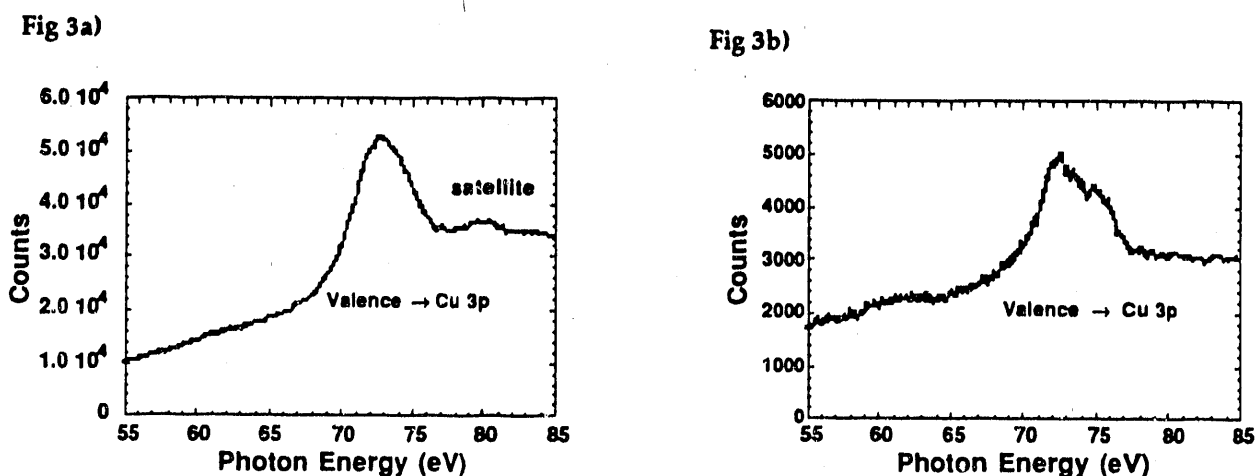


Fig. 3

- a) The  $M_{2,3}$  spectrum of metallic copper excited by a  $3 \mu\text{A}$  beam of 3kV electrons
- b) The  $M_{2,3}$  spectrum of CuO excited by a  $3 \mu\text{A}$  beam of 3kV electrons. Note how the CuO reverts to metallic copper as a consequence of electron beam excitation.

The study of the behavior of atoms at interfaces has important applications for the production of semiconductor integrated circuits and the development of catalysts. It is difficult to study the properties of these atoms in a nondestructive manner. Photons are the perfect probe to study the emission of atoms that are actually buried in a substrate. For example, we have done some experiments with 10% krypton implanted in aluminum. The krypton forms little bubbles that are distributed about  $1000 \text{ \AA}$  below the

surface of the aluminum. In Fig. 4, the aluminum  $L_{2,3}$  spectrum between 68-73 eV is shown. Adjacent to it, at photon energies between 78-83 eV is the krypton emission spectrum. The krypton spectrum would be impossible to observe by photo-electron spectroscopic techniques because the electrons that would be emitted from the krypton would be completely scattered before they reached the surface.

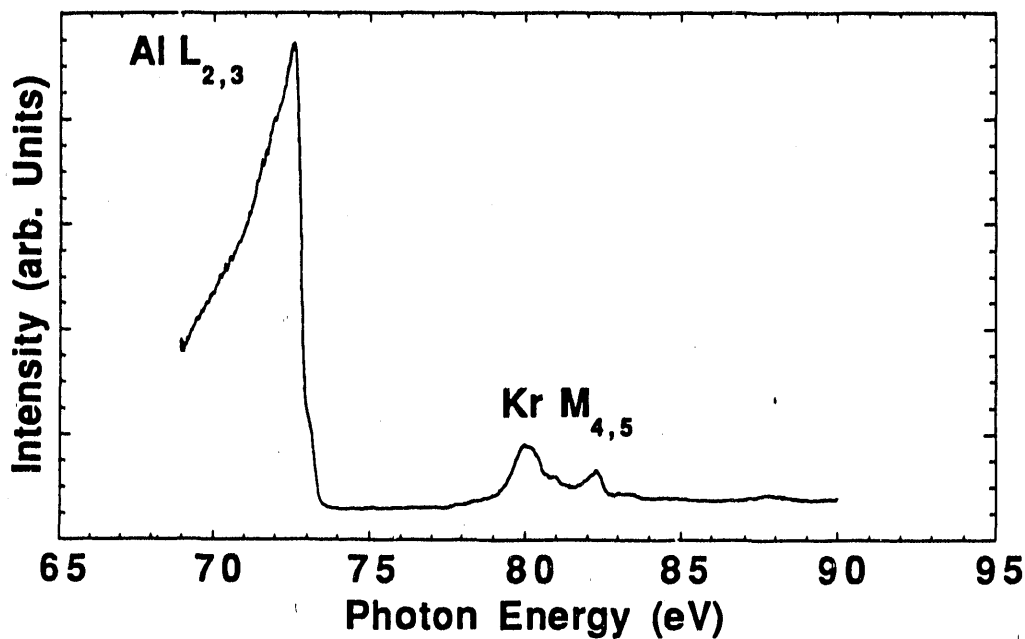


Fig. 4

Spectra of a 10% krypton implanted as bubbles in aluminum. The Aluminum  $L_{2,3}$  emission band appears as the intense feature between 68 eV and 73 eV. The inset shows the krypton  $M_{4,5}$  emission spectrum between 78 eV and about 83 eV.

While hard x-rays have been used over ninety years in many techniques, the soft x-ray portion of the spectrum was neglected until the 1930's when diffraction gratings were used to diffract the x-rays. Pioneering soft x-ray measurements were made during this period in the laboratories of Siegbahn [11] and Skinner [12] to obtain information about the band structure of solids. Soft x-ray emission spectroscopy is especially powerful because the shallow core levels have a natural width that is about a factor of ten less than deeply bound levels. Thus the valence band spectrum is not unduly broadened by the width of the core level, and the soft x-rays can be utilized for experiments that map out the electronic structure, through transitions between the valence band and a core level. This map is modified by the dipole selection rule and one obtains an angular momentum resolved localized density of states of one of the elements in the compound under investigation. Soft x-rays as a probe have drawbacks, namely, low efficiency spectrometers have to be used to study fluorescence processes that have a

yield of typically about  $10^{-4}$  for low Z elements. The yield hasn't changed in the intervening years since the seminal work of Siegbahn and Skinner, but technology has advanced. High sensitivity multi-wavelength detectors and better diffraction gratings are available. These in combination with high brightness synchrotron sources make photon-in photon-out spectroscopy a viable and exciting scientific technique.

At present we employ a spectrometer mounted on a beam line at the National Synchrotron Light Source (NSLS) [13]. The spectrometer incorporates toroidal gratings which have a gain of 10 in efficiency over spherical gratings, and a position sensitive detector which further enhances the sensitivity of the instrument by another factor of 100. At NSLS an electron beam, white light, or monochromatic radiation from the storage ring can be used to excite the sample. With a monochromatized beam, about  $10^{13}$  photons per second fall on the sample in a 4 eV bandwidth with an electron current of 500 mA in the ring.

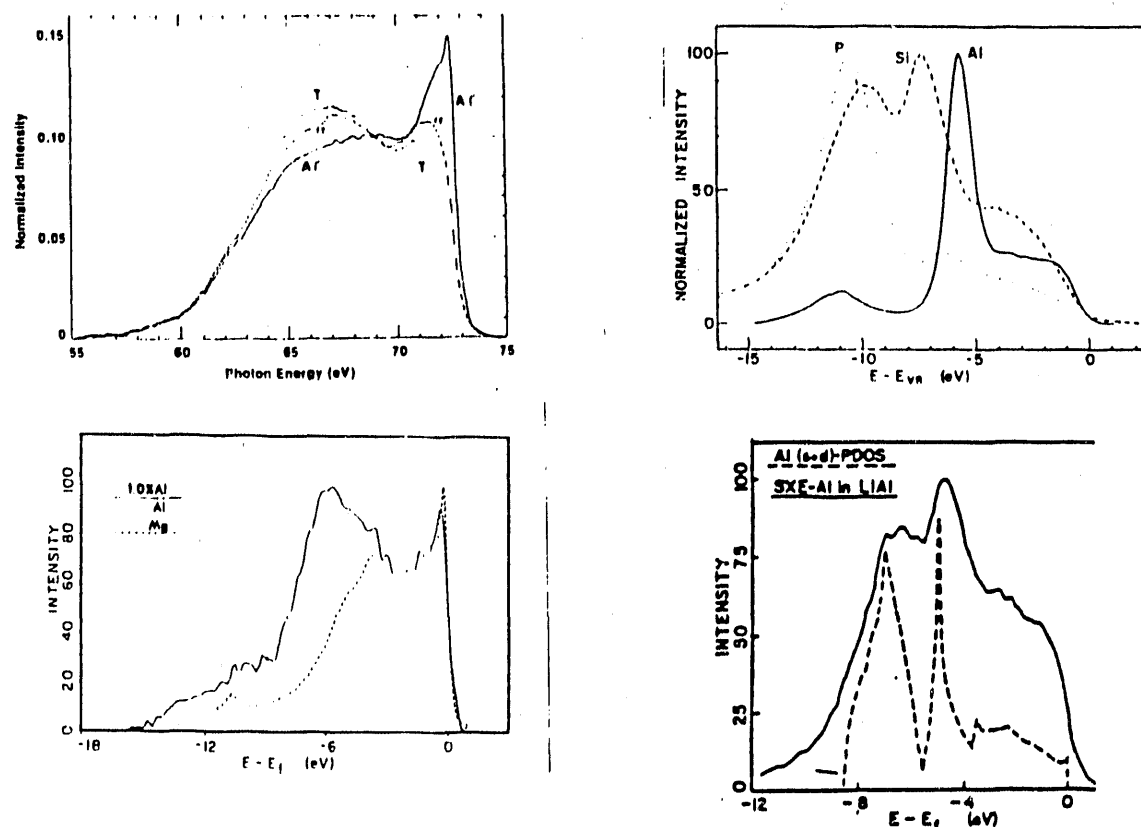


Fig. 5

a) Soft x-ray emission (SXE) spectra of quasicrystalline Al-Mn alloy ( T phase) and the alpha phase of Al-Mn-Si compared with the spectrum of aluminum. b) SXE spectra of Al in  $Al_{0.80}Ga_{0.20}As$  (——), P in  $GaAs_{0.45}P_{0.55}$  (.....) and Si(- - - -). c) SXE spectrum of 1% Al in Mg alloy compared with the spectrum of Mg and Al. d) SXE of Al in a 50-50 Alloy of aluminum and lithium(——),density of states calculation from ref. 16 (- - - ). The figure is taken from Ref. 13.

It is possible to study an element in very different environments [14]. Fig. 5 is an illustration of the  $L_{2,3}$  emission band of aluminum obtained from different materials containing aluminum. The upper left hand panel of this figure shows several forms of aluminum as a constituent of an alloy containing manganese. The manganese-aluminum alloy used to obtain the spectrum labeled T has decagonal symmetry, a phase that is not possible for ordinary crystalline materials. Both the T phase and the alpha cubic phase, shown as the dotted and dashed curve respectively in the figure, have a spectrum that differ from that of pure aluminum shown as the solid line. These spectra provided evidence which disprove the prediction [15] that the band would be shifted to lower energy and, that the Fermi edge,  $E_F$ , would be strongly enhanced [16] as the phase changed from octahedral to icosahedral symmetry.

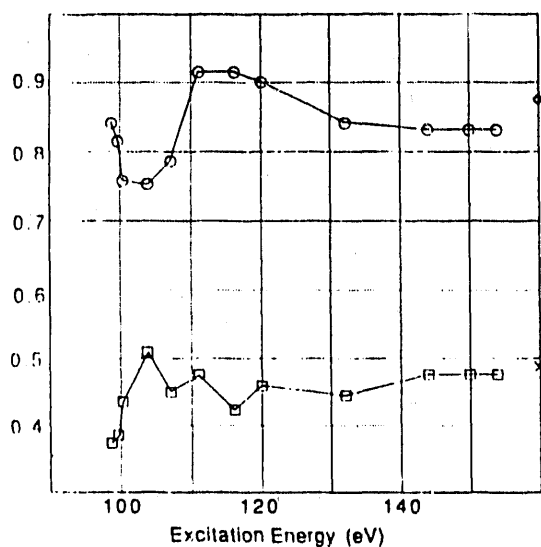
Aluminum can also take on ionic character. In the upper right frame the  $L_{2,3}$  emission spectrum of aluminum in aluminum phosphide is shown as the solid line. The  $L_{2,3}$  emission of phosphorus and silicon are shown as the dashed and dotted lines. Aluminum phosphide is a tetragonally bonded compound and the spectrum should resemble that of silicon, also tetragonally bonded. In this case the aluminum has donated s-type electrons to the phosphorus, which is indicated by the enhancement of the electrons located deeply in the band. The more deeply bound s electrons have vanished from the aluminum spectrum and appear in the phosphorus spectrum. The portion of the band at about -12 volts overlaps very strongly with the prominent s bonding band in the phosphorus, indicating there is strong hybridization between the electrons in the aluminum and those in the phosphorus.

In the lower left hand corner panel we see aluminum as an impurity in magnesium. The solid line represents the  $L_{2,3}$  spectrum of aluminum at one atom percent concentration in the magnesium host. Aluminum has one extra electron compared to the magnesium. That electron has essentially been "buried" at the bottom of the band and appears as an enhancement about 6 eV below the Fermi level. Pure aluminum is shown as a dotted curve and pure magnesium as a dashed curve for comparison. The band itself mimics that of magnesium in that it is narrower than that of pure aluminum.

Finally in the lower right hand panel, we have aluminum appearing tetragonally bonded in a 50-50 alloy of lithium aluminate. This tetragonally bonded system has a spectrum that looks very much like silicon which is shown in the panel above it. The comparison between the calculated local density of states for the lithium aluminate at the aluminum site is shown as a dashed curve. The qualitative agreement between the calculations and the measurements shows up quite nicely.

Another example of the physics that can be learned via photon-in photon-out techniques is illustrated by a study in which the fluorescence was observed as a function of the excitation energy of the photons [17]. In this experiment the  $L_{2,3}$  emission spectrum of crystalline silicon is excited by monochromatized synchrotron radiation. In Fig. 6 intensity ratios for different features in the emission band are plotted as a function of the excitation energy between 100 eV and 150 eV. As we increase the photon energy, the excitation becomes very similar to that provided by the electron gun where 2 kV electrons were used to excite the valence band fluorescence

Between 100-120 eV the ratio of peak a to peak b, and peak c to peak b changes in a rather pronounced way. The peaks a, b, and c have been identified in the panel at the bottom of Fig. 6. The structure between 100 eV. and 120 eV excitation energy has been attributed [17] to an interband shake-up process excited by the outgoing electron.

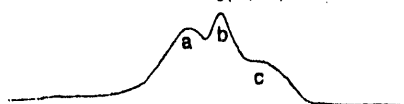


**Fig. 6**

Peak height ratios as a function of excitation energy. The peaks are denoted according to the scheme below the caption. The cross and diamond symbols placed at 160-eV excitation energy refer to the spectrum excited by 2-keV electrons. The plotting symbols are :

- a/b
- c/b
- e-gun (a/b)
- ×- e-gun (c/b)

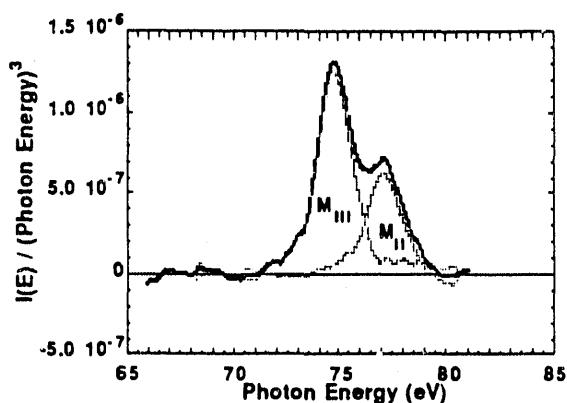
The figure is taken from Ref. 17



In 1987, we witnessed another "Woodstock" at the March meeting of American Physical Society. The discovery of high temperature superconductors provided a shock to the scientific community that was similar to the one in 1896, when the discovery of x-rays was announced. Our group has used x-ray fluorescence to investigate the electronic structure of these new superconductors and related materials to learn more about the density of states and the validity of band structure calculations for several of these compounds [18]. Copper is a fundamentally important constituent in

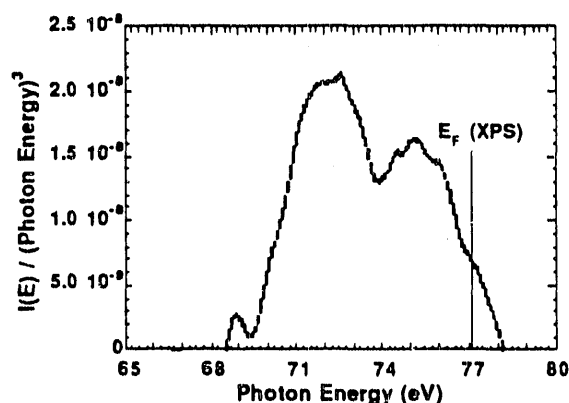
many of the superconducting compounds, the interposition of the copper 3d and the oxygen 2p orbitals producing the difference between a garden variety mineral, and an exciting superconductor. We have devoted a fair amount of energy, in the last several years, to the study of the copper  $M_{2,3}$  emission spectrum for a number of oxides containing copper. Because of the fragility of the compound (recall Fig. 3), photon excitation was used to obtain the spectrum of copper oxide which is shown as the solid line in the upper panel of Fig. 7. The deconvolved  $M_3$  and  $M_2$  bands are shown as the dotted curves. The ratio of the  $M_3$  to the  $M_2$  band is 2 to 1 as one would expect from a statistical ratio of the density of 3p core levels. The band, according to a calculation by Evarestov and Veryazov [19] should be about 2 volts in breadth with a low value for the density of states at  $E_F$ . The width of the calculated valence band agrees quite well with our measurements. One notes that this band is much narrower than that of metallic copper, which is about 5 volts in breadth.

For comparison our measurements for copper  $M_3$  emission in the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  is shown in Fig. 8. The measurements were obtained by deconvolving the  $M_{2,3}$  spectrum assuming the spin-orbit splitting and branching ratio obtained for  $\text{CuO}$ . The Fermi energy, determined from x-ray photoemission spectroscopy is shown as the thin vertical line overlaid on the measurements. These measurements are in good qualitative agreement with the calculation of Marksteiner, *et al* [20]. For the high  $T_c$  superconductors we have found that, in almost all cases, a one electron model without correlations yields a copper valence partial density of states in good qualitative agreement with the SXE measurements. The differences between the SXE measurements and the calculations might be due to the absence of correlations in the calculations.



**Fig.7**

The  $M_{2,3}$  SXE spectrum of copper in  $\text{CuO}$  excited by monochromatic x-rays. The  $M_3$  and the  $M_2$  spectra are shown split by the spin-orbit energy of the 3p core.  $I(E)$  is the photon count/eV.



**Fig.8**

The  $M_3$  SXE spectrum of copper after deconvolution in  $\text{Bi}_2\text{Sr}_2\text{CaCuO}_{8-\delta}$ . The Fermi edge obtained by XPS is shown as the vertical line.  $I(E)$  is the photon count/eV.

In summary, photon-in photon-out experiments employing the latest technology can provide site specific information about the nature of the chemical bond in compounds; the technique can nondestructively access atoms buried many atomic layers beneath the surface, and it provides information about the dynamics and the symmetry of these excited states through the observation of the the x-ray emission as a function of the excitation energy. High vacuum isn't required. Fragile samples are less likely to be damaged, and the technique has inherent high resolution.

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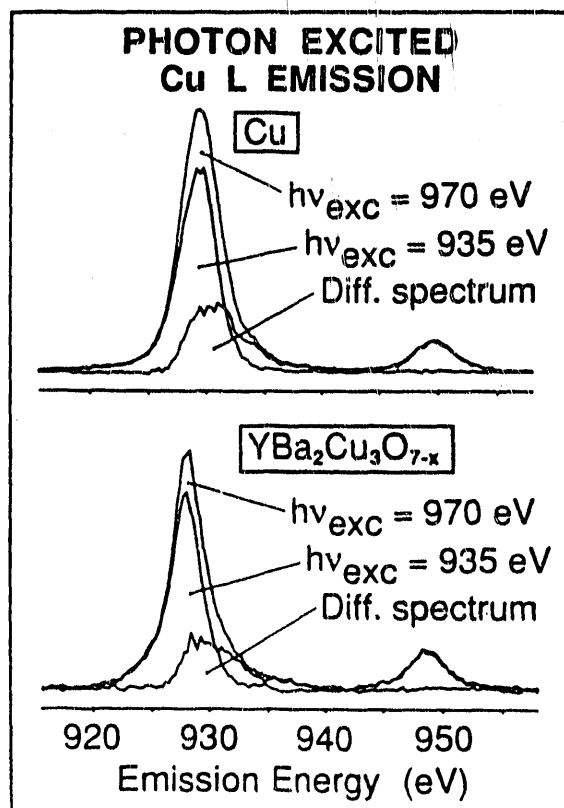
## SOFT X-RAY EMISSION SPECTROSCOPY WITH HIGH-BRIGHTNESS SYNCHROTRON RADIATION SOURCES.

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Sweden

The development of high brilliance synchrotron radiation sources has provided a new basis for soft x-ray emission spectroscopy (SXES) in the study of the electronic structure of matter. SXES, which was an established method already a couple of decades ago, has been subject to a renaissance due to the properties of this means of excitation. These properties are i) electromagnetic radiation rather than particle beams, ii) high brilliance, i.e. high intensity and spatial confinement, which permits sharp monochromatization, and iii) well defined polarization. One should bear in mind in this context that SXES requires quite powerful excitation due to the low fluorescence yield (typically 0.1%) and the limited acceptance angles of high resolution analyzing instruments for these wavelengths.

Photon excitation, as opposed to electron excitation of soft x-ray emission has some advantages in that it can penetrate deep into the sample and provide true bulk information. The selectivity of monochromatized photon excitation offers the ability to separate satellite structure from diagram lines, which is necessary in order to fully use the inherent state selective properties of x-ray transitions. This is particularly important for more or less metallic systems where core hole screening leads to large energy overlap between the two kinds of transitions. Obviously, this selectivity also allows more detailed studies of the very satellite processes since the excitation energy dependence can be established. Although a monoenergetic electron beam can provide an element of selectivity in this respect this means of excitation suffers from the low energy tail of electrons contributing to the excitation, since in most cases the sample density is high enough to cause considerable inelastic scattering.

Separation of satellite structure by selective excitation is demonstrated in Fig.1 where the Cu L emission spectra of metallic copper and a superconducting oxide are shown. Reducing the excitation energy to 935 eV (just above the  $L_3$  threshold) from 970 eV leads to a different form of the  $L_3$  spectrum. This difference comes about by the removal of satellites caused either by shake processes in the  $L_3$  excitation or by Coster-Kronig decay of  $L_2$  vacancies, both processes being energetically forbidden at the lower excitation energy. In the local one electron approximation the threshold excited  $L_3$  spectrum then reflects the "clean" 3d partial



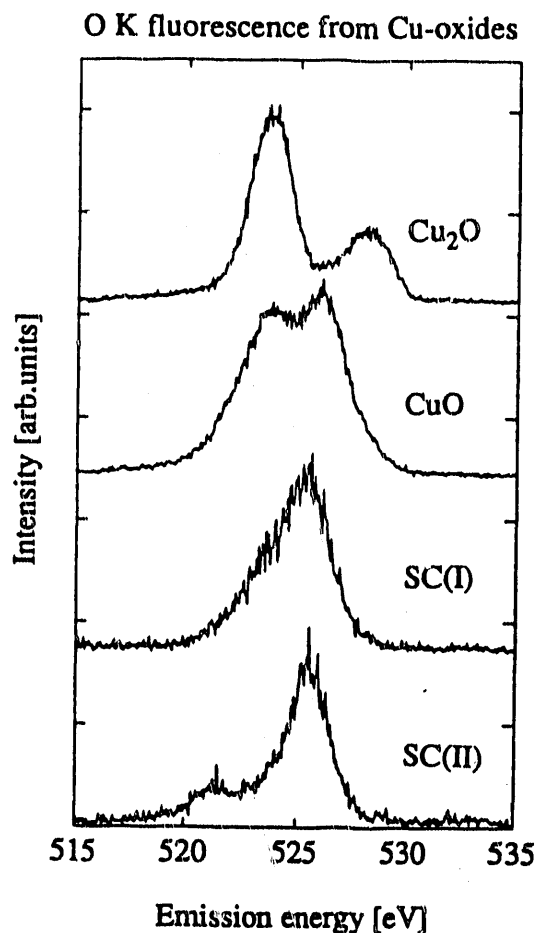
density of states. One notices, comparing the spectra of the metal and the oxide, that the satellite intensity changes, presumably reflecting a quenching of the Coster-Kronig decay of  $L_2$  holes induced by the modification of the valence band in forming the oxide.

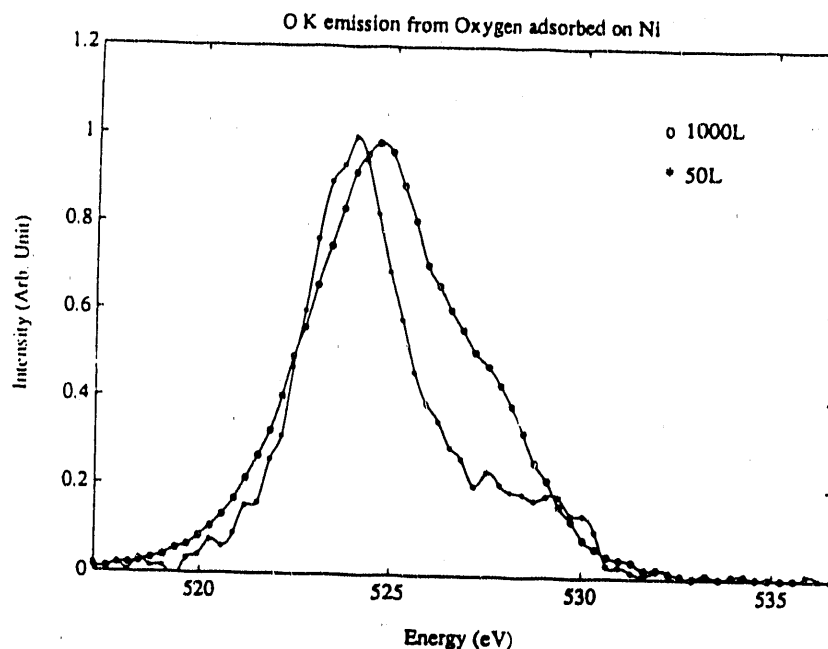
More detailed information on the dynamics of the excitation processes is offered by studying the excitation energy dependence of the satellites /1/. The inherent selectivity of x-ray transitions and the feature of separating initial and final state satellites in terms of emission energy are valuable assets in this context.

Tuning of the excitation to certain resonance energies allows studies of the dynamics of excitation processes /2/ and also focussing on details in the electronic structure. In Fig.2 is shown an example where this latter ability is used. Two of the samples studied were 1-2-3 superconductors differing slightly in oxygen content, leading to a minute change in critical temperature (SCI and SCII in the figure,  $T_c$  differing 1.3K). For most excitation energies, and in particular for non-selective excitation, the two samples show almost identical oxygen K emission spectra. At two distinct energies, though, differences appear, namely at 535 eV, where a structure above the fermi level appear, and at 541 eV (shown in the figure), where a dramatic change of the valence band spectrum is observed.

The large information depth offered by the penetration of x-rays, as compared to electrons, is a useful property whenever bulk properties are being studied. However, this does not mean that soft x-ray emission can not be used in the study of extreme surface problems. As a matter of fact, it has recently been shown that high resolution fluorescence spectra can be obtained from fractions of monolayers of adsorbed atoms and molecules on surfaces by using grazing incidence excitation /3/. Fig.3 shows oxygen K emission spectra of a Ni (100) surface exposed to respectively 50 L and 1000 L of oxygen. In the former case a  $c(2 \times 2)$  structure is formed, giving rise to a spectrum with a distinct fermi edge, and in the latter case, a different spectrum is observed, similar to previous recordings of NiO. The ability of SXES to probe the local partial density of states is of great value in this kind of study, and it allows a direct means to investigate the bonding of the adsorbate in terms of orbital hybridization.

Given the ability to record soft x-ray emission spectra from sub-monolayer systems it is clear that the proper use of the polarization of synchrotron radiation used for excitation adds





an important element of selectivity. Such studies have not been made yet, but are being planned for the near future. Generally, the use of polarization and angular resolved SXES is expected to promote this spectroscopic method, and an experiment station for angular resolved soft x-ray fluorescence spectroscopy using monochromatized synchrotron radiation is presently being built for installation at the Bypass laboratory at the DORIS storage ring in Hamburg. One goal set out in that project is to study angular resolved L emission spectra from 3d transition element systems, thereby obtaining m-resolved 3d decomposition of the valence band.

The expected performance of the third generation synchrotron radiation sources will make the novel use of SXES, briefly presented above, even more feasible. With band passes of 0.1 eV at fluxes allowing high resolution emission spectra to be recorded, one should be able to make very detailed studies, for instance by separating spectra pertaining to chemically shifted atoms of the same species in compounds or molecules, or by tuning the excitation energy to different vibrational levels in the primary core excitation. In conclusion, we feel that the new possibilities of soft x-ray emission spectroscopy, which have been demonstrated, will contribute to make this method a wide spread and useful one at the third generation synchrotron radiation facilities coming up in the near future.

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## ANISOTROPY AND POLARIZATION OF X-RAY EMISSION FROM ATOMS AND MOLECULES

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Strongly anisotropic and polarized K-V x-ray emission has been observed from gas-phase molecules following resonant excitation with a linearly polarized x-ray beam.<sup>1-3</sup> Distinctively different polarizations and angular distributions are observed for x-ray emission involving molecular orbitals of different symmetries. These observations are attributed to the strong angular and polarization dependencies of the x-ray absorption and emission processes when transitions occur between states having well-defined symmetries. A simple classical model well describes the observed radiation patterns.<sup>2,3</sup>

Anisotropic x-ray emission from molecular crystals and solids has been attributed to the inherent ordering of those samples,<sup>4</sup> and it has been expected that randomly oriented samples, such as gas-phase atoms or molecules, will display isotropic x-ray emission. However, it is possible to create a spatially anisotropic ensemble of core-excited atoms or molecules from a randomly oriented target via energy- and polarization-selective excitation with x-rays. Anisotropy of x-ray excited molecules occurs when the incident, linearly polarized x-rays are tuned in energy to a resonance involving an unoccupied state with well defined symmetry. In such cases, the photoexcitation probability will be larger for those molecules whose symmetry axes are momentarily in a given orientation with respect to the polarization vector. The anisotropy of the ensemble of core-excited molecules will be reflected in the polarization and angular distribution of the subsequent x-ray emission when transitions involving states of well-defined symmetries are resolved. These ideas are the basis for the classical model<sup>5,6</sup> of the polarization and anisotropy of photon absorption and emission. This simple model has been found to accurately describe the anisotropy of polarized Cl K-V x-ray emission from CF<sub>3</sub>Cl following resonant excitation with a linearly polarized x-ray beam.<sup>2</sup> (See Figs. 1 - 3)

A small anisotropy also has been measured for Ar K $\alpha$  emission following resonant excitation.<sup>3</sup> A quantum theoretical model<sup>7,8</sup> of photon absorption and emission was used to interpret the observed anisotropy. The observation of only a small anisotropy in this case is attributed to the averaging out of the individual anisotropies from unresolved final states.<sup>3</sup>

The measurements were made using narrow bandwidth, linearly polarized x-rays provided by beamline X-24A<sup>9</sup> at the National Synchrotron Light Source. The x-ray fluorescence was analyzed using a polarization-selective, curved-crystal spectrometer,<sup>10</sup> and a position sensitive proportional counter.<sup>11</sup> In order to measure angular distributions, the target chamber and emission spectrometer were mounted on a rotation platform to record x-ray spectra at different emission angles with respect to the polarization vector of the incident x-ray beam.

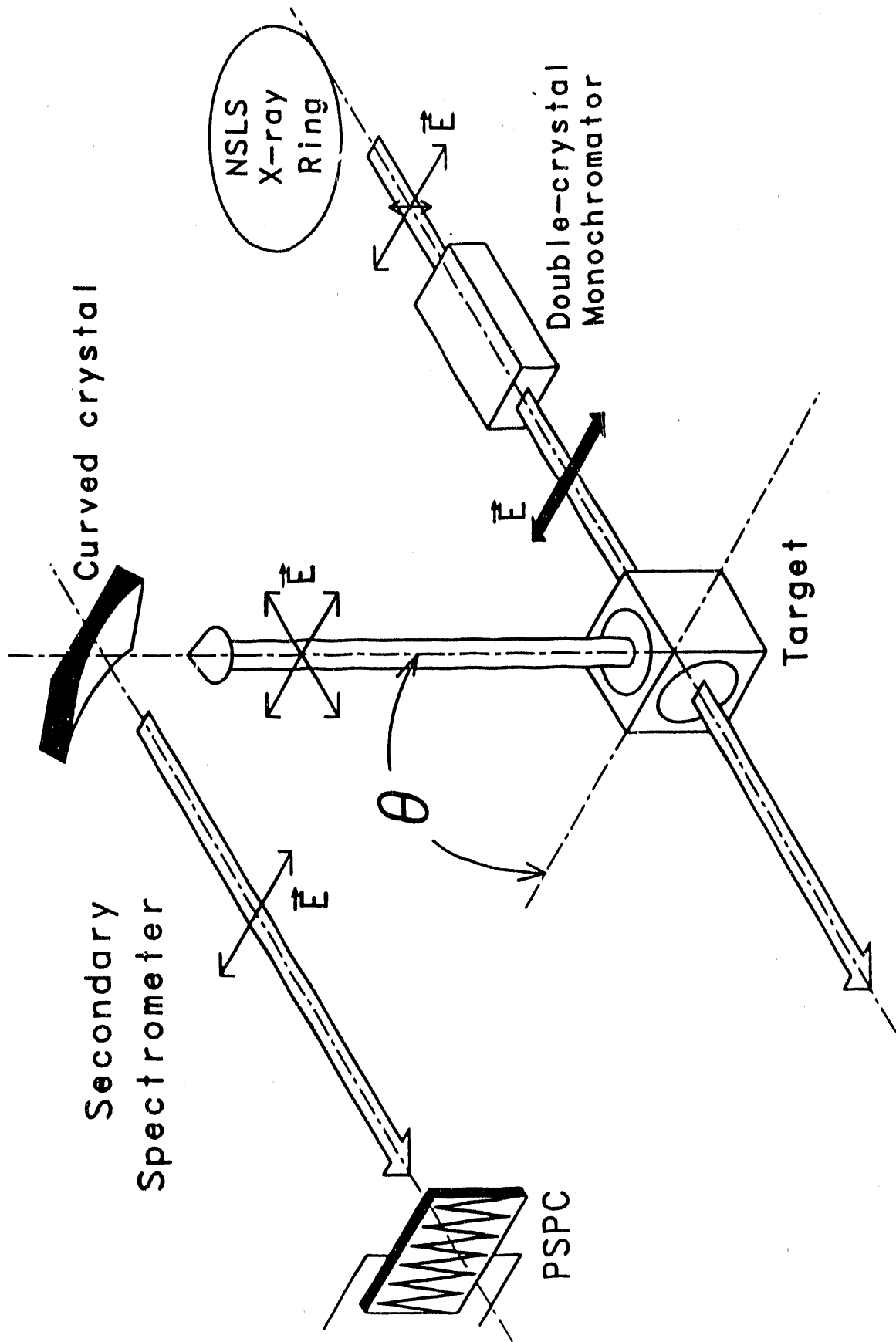
In making use of either the classical model<sup>5,6</sup> or the quantum theoretical model<sup>7,8</sup> to interpret our x-ray absorption/emission measurements, we have adopted a two-step picture in which the absorption and emission are regarded as independent processes. We have also assumed that x-ray absorption and emission may be described as pure electric-dipole processes. It follows that the photoexcited system has symmetry properties which simplify the characterization of the x-ray emission radiation pattern. Consequently, the polarization and angular distribution of the emitted x-rays may be characterized using a single parameter, the "polarization anisotropy,"  $R$ .<sup>2,3</sup> Theoretical values for  $R$  are obtained using either the classical model or quantum theoretical model. Furthermore, there exist "magic angles," where the observed x-ray emission

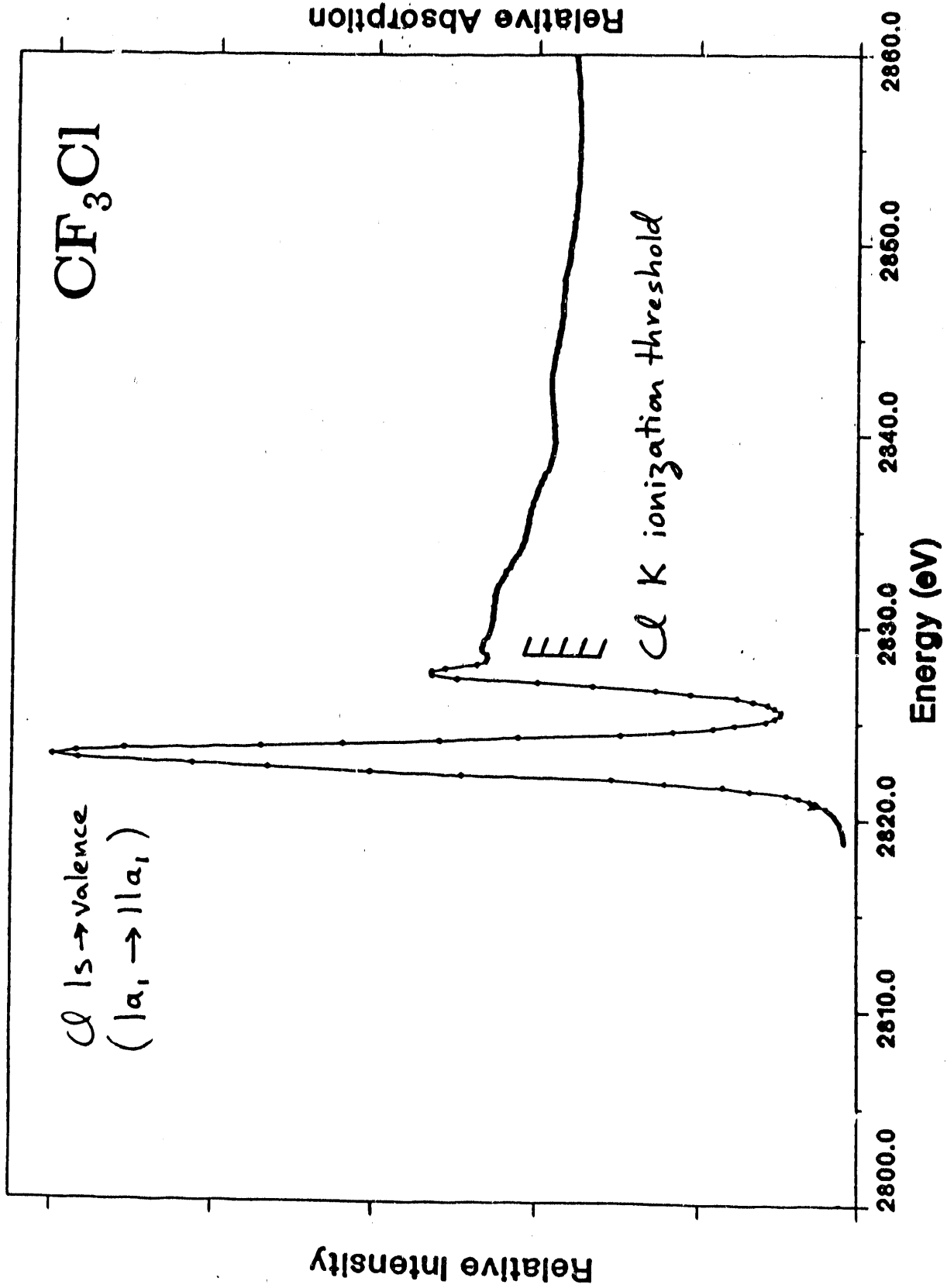
intensities are proportional to oscillator strengths, independent of the polarization and anisotropy.

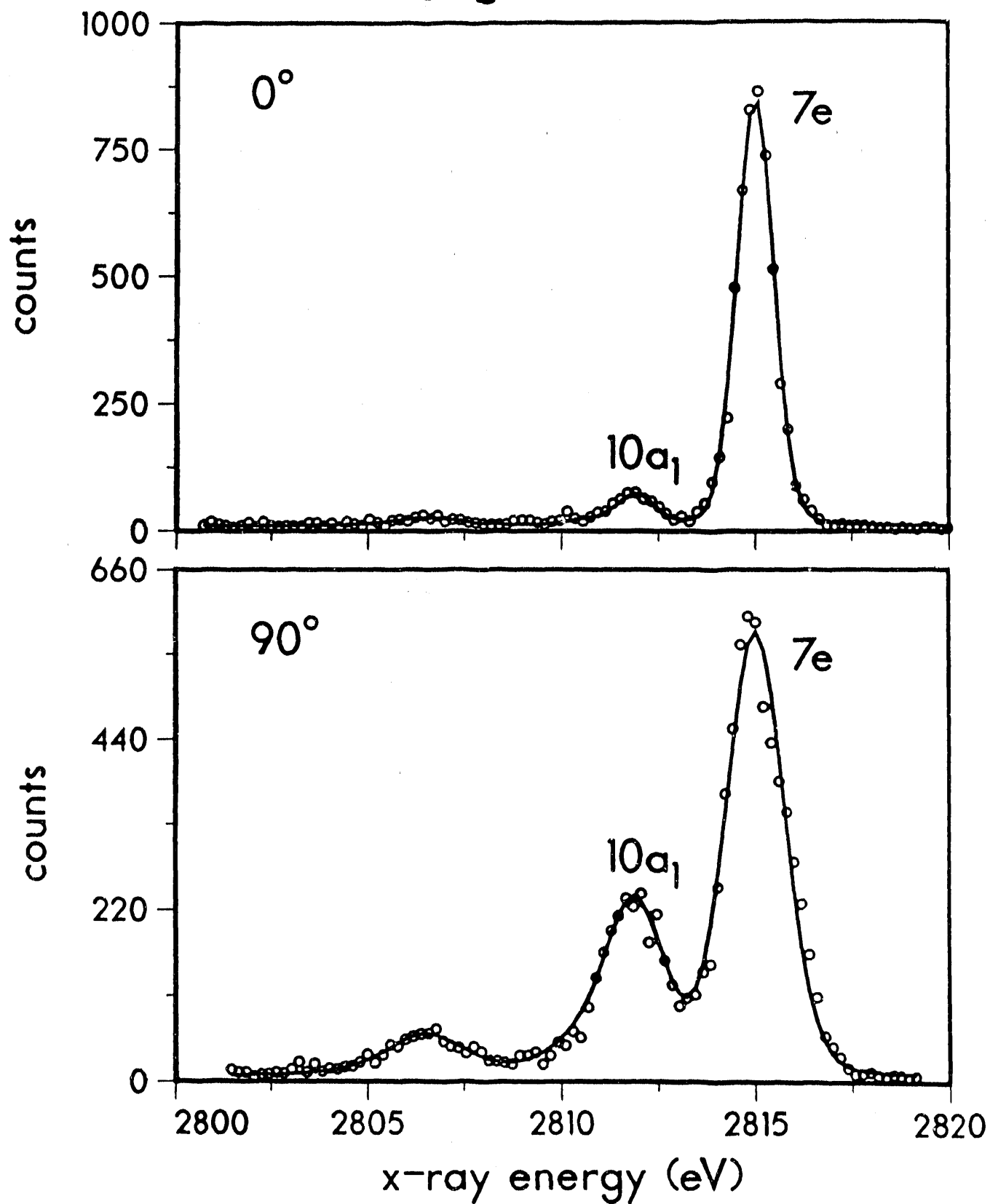
These studies demonstrate that the technique of polarized, angle-dependent x-ray emission spectroscopy, following resonant excitation of randomly oriented samples, provides a sensitive probe of the symmetries of the electronic states involved in the absorption and emission processes. Recently, for example, the polarization of sulfur K-V x-ray emission from H<sub>2</sub>S was used to determine experimentally the symmetries of overlapping absorption resonances.<sup>12</sup> It is expected that such techniques can be applied to studies of increasingly complex samples, perhaps including large polyatomic molecules or molecules in liquid solutions. The increased photon beam intensities and spectral resolutions to be available at third generation synchrotron radiation beamlines will further enhance the range of application of these techniques.

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## Valence-hole Fluorescence from Molecular Photoions as a Probe of Shape Resonance Ionization: Progress and Prospects

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Molecular photoionization provides a natural means of studying the correlation of electronic and nuclear motion, as the electron energy can be continuously adjusted and the nuclear motion can be probed sensitively using appropriate detection schemes. Moreover, photoionization exhibits characteristics of molecular scattering that are of central importance in chemical physics [1-4], yet is sufficiently simple to be theoretically tractable. I will describe studies of resonant molecular photoionization that employ dispersed fluorescence from valence-hole states of photoions as an experimental tool. Several recently studied examples are presented to highlight current topics of interest, and also to demonstrate the utility of dispersed fluorescence for studies of molecular photoionization. These case studies show how fundamental resonant phenomena facilitate the conversion of electronic and nuclear motion. In so doing, they underscore a central and recurring theme in molecular ionization studies, namely, that a qualitative microscopic understanding of the scattering dynamics requires probes that provide information on molecular aspects (e.g., vibration, rotation, alignment, etc.) of the ionization process. In retrospect, this is hardly surprising, as many of the processes of interest are molecular in origin. However, there are subtleties in obtaining the relevant experimental data, and useful experimental approaches are described.

A central goal is to understand the response of the resonance complex to changes in the molecular geometry. Progress in fundamental studies — as well as the application of molecular photoionization as an analytical tool — requires insight into how the ionization dynamics are affected by changes in the molecular geometry. For this reason, it is essential that experiments selectively sample alternative vibrational levels of the photoion, as different vibrational levels probe alternative internuclear configurations. This requirement for vibrationally resolved data is a strong motivation for dispersed fluorescence measurements, as they can provide highly resolved (including rotationally resolved) data on the photoions over a wide range of incident photon energies.

Vibrationally resolved data obtained as a function of electron kinetic energy illuminate the correlation of electronic and nuclear motion. In particular, resonant ionization phenomena, such as shape resonant ionization, frequently induce coupling between nuclear and electronic motion [1-4,12]. However, variable photon energy is needed to tune to and through the resonant excitation, and this requirement can be a serious obstacle using traditional tools involving photoelectron spectroscopy. Typically, the necessity of a large range of photon energies dictates that synchrotron radiation be used as the source of ionizing radiation. While synchrotron radiation sources are tunable, they do not simultaneously provide high resolving power and high flux, so traditional photoelectron measurements have been unable to probe the molecular motion (i.e., vibration and rotation) while varying the photoelectron energy continuously over a wide range. Dispersed fluorescence measurements circumvent this difficulty because the detection bandwidth is uncoupled from, and therefore not limited by, the excitation bandwidth [5]. As a result, dispersed fluorescence measurements have been used to investigate a variety of resonant photoionization phenomena [5-16], including those noted below. (See Figs. 1-3)

- Vibrationally resolved partial photoionization cross section data have illustrated the behavior of a polyatomic shape resonance ( $N_2O$ ) for the first time [12]. These results have important implications for surface and materials science, as well as for their intrinsic significance. Recently, we have extended this program to the study of  $SiF_4$  photoionization [16].

- Continuum channel coupling effects have been observed following shape resonant excitation [5,10,11,14,15]. When used for core-hole processes, these studies probe aspects of core electron excitation that depend of the internuclear separation via the channel coupling of the core-hole complex to valence-hole continua of the ion [10,11,14]. (See Figs. 4-5)
- Rotationally resolved fluorescence spectra have been generated for molecular photoions [8] which reveal the partitioning of angular momentum between electronic and nuclear motion. (See Figs. 6-7)

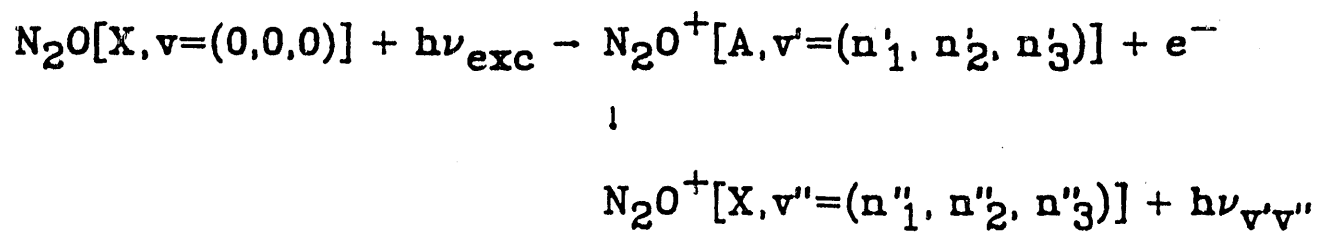
These studies are described in order to demonstrate that discerning molecular vibration and rotation over a broad electron energy range provides a window into fundamental ionization processes. More specifically, we describe the utility of third generation synchrotron radiation sources for such investigations, and it is clear that there are many possible benefits. First, it will be possible to extend the existing studies to more complex polyatomic systems given the higher brightness and consequent optimization of interaction volumes. More enticing perhaps, is the possibility of ir/xuv double resonance experiments, where a laser is used to state select a vibrational and rotational level in the ground electronic state manifold to undergo photoionization using the tunable synchrotron radiation source. Such future developments are sketched out, and these outgrowths illustrate that there are many exciting possibilities for future applications of dispersed fluorescence as a probe of resonant ionization processes.

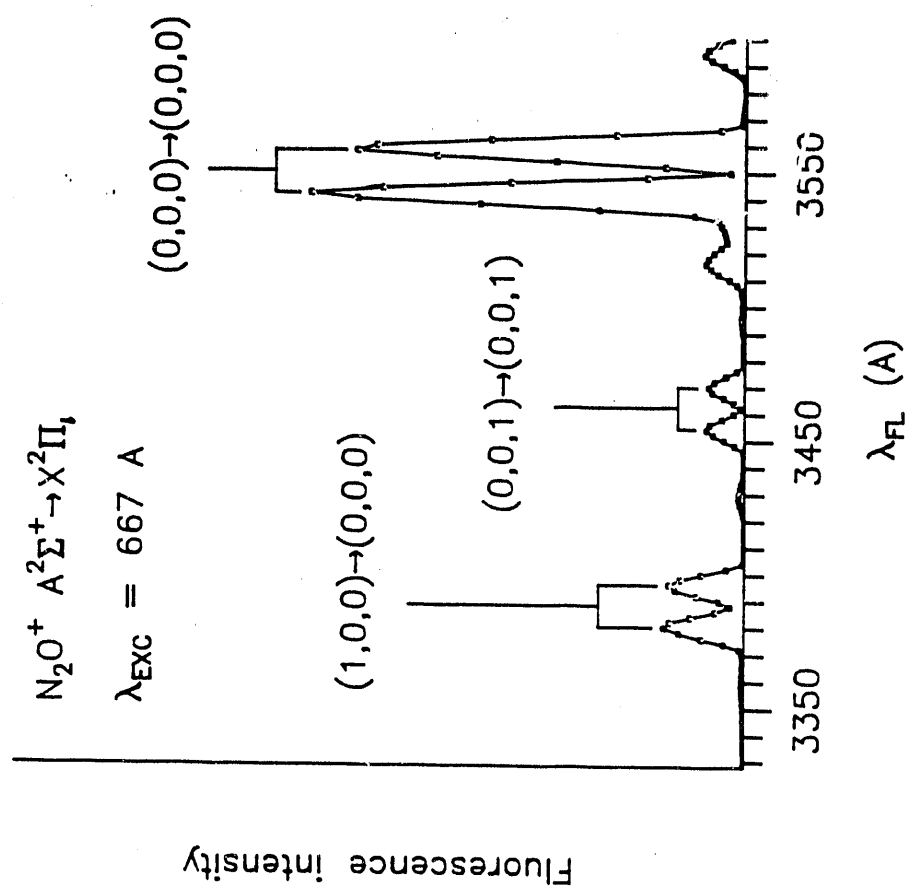
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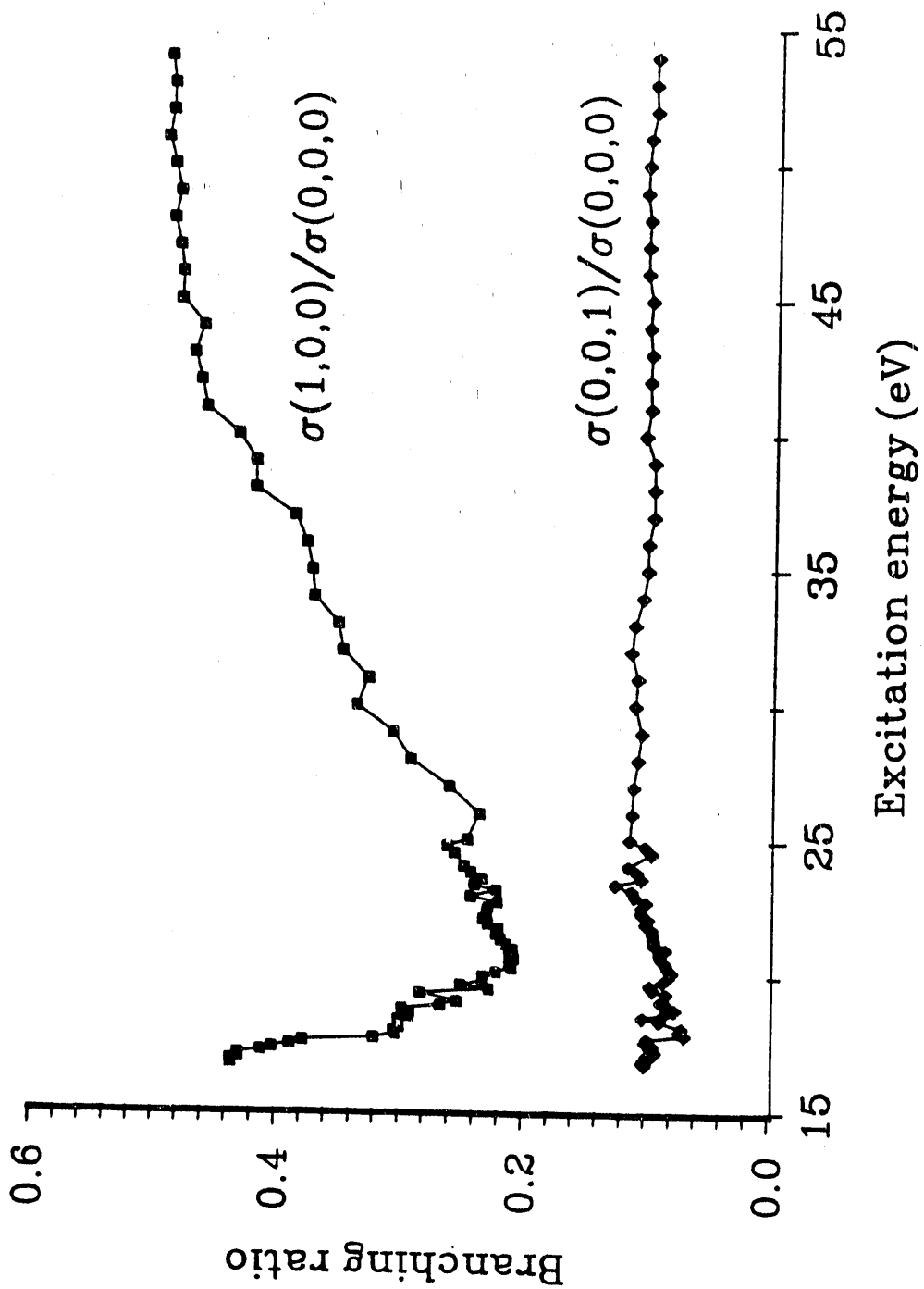
Vibrationally resolved polyatomic studies:

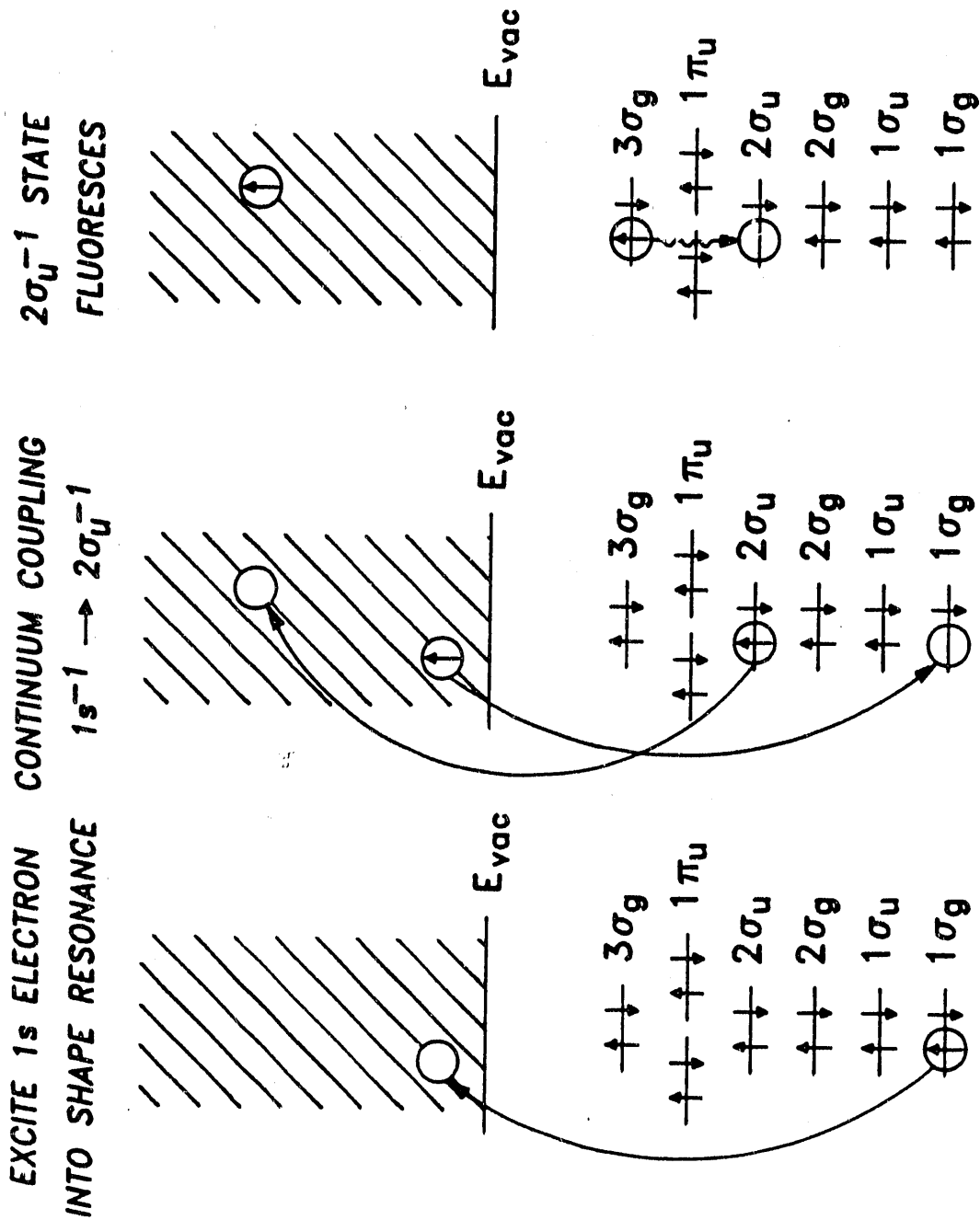
$\text{N}_2\text{O}$  shape resonant photoionization



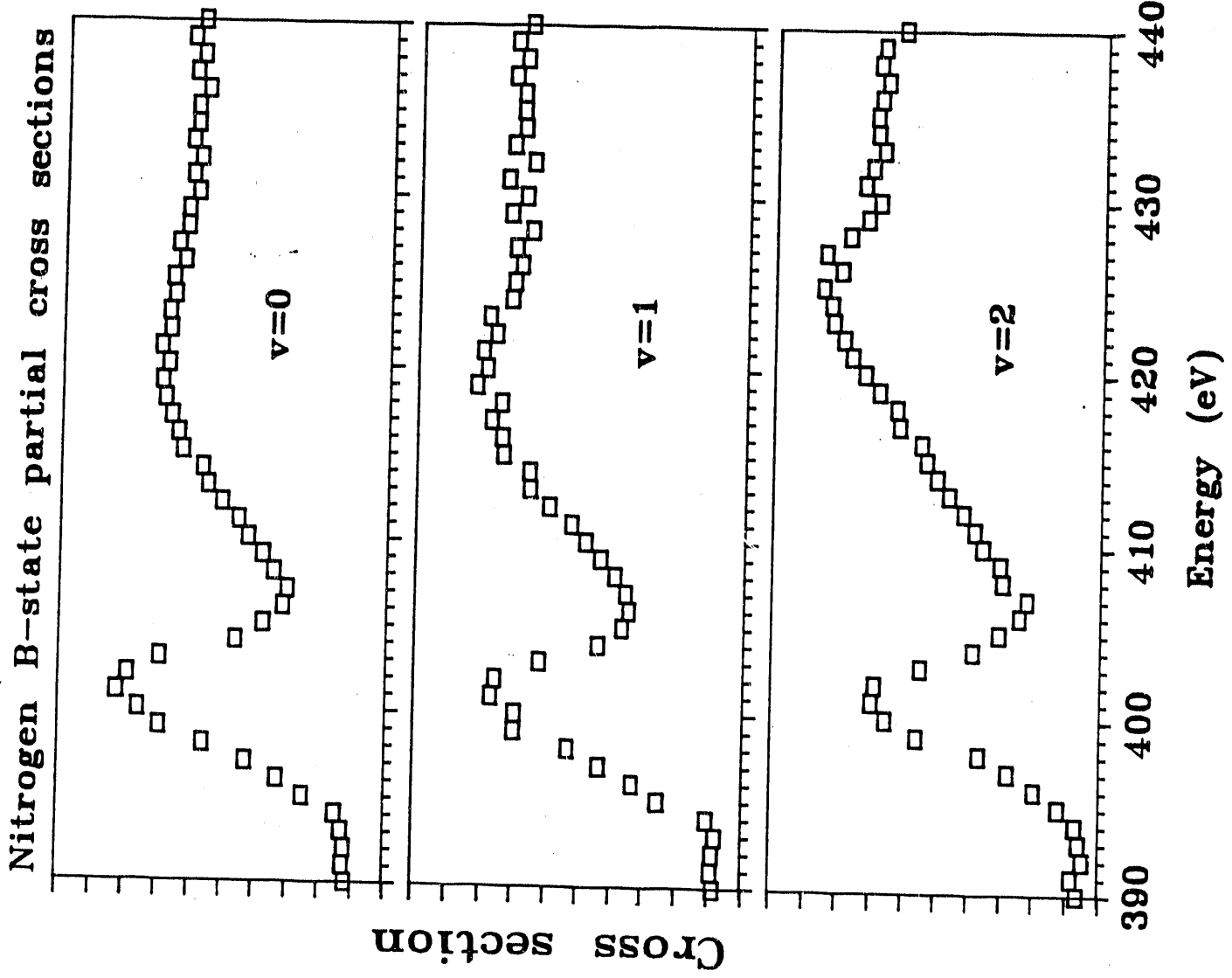


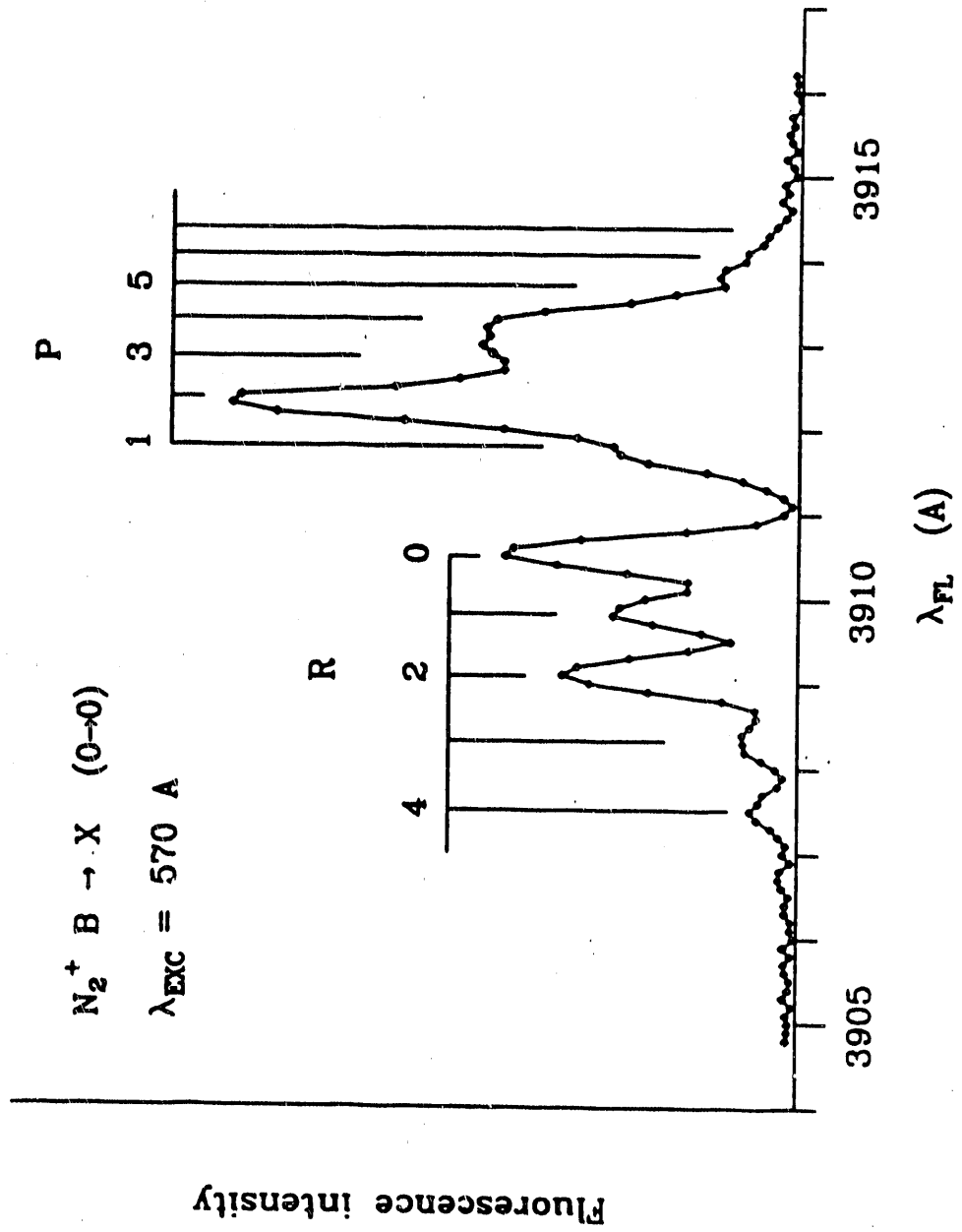
$N_2O^+ A^2\Sigma^+$  vibrational branching ratios



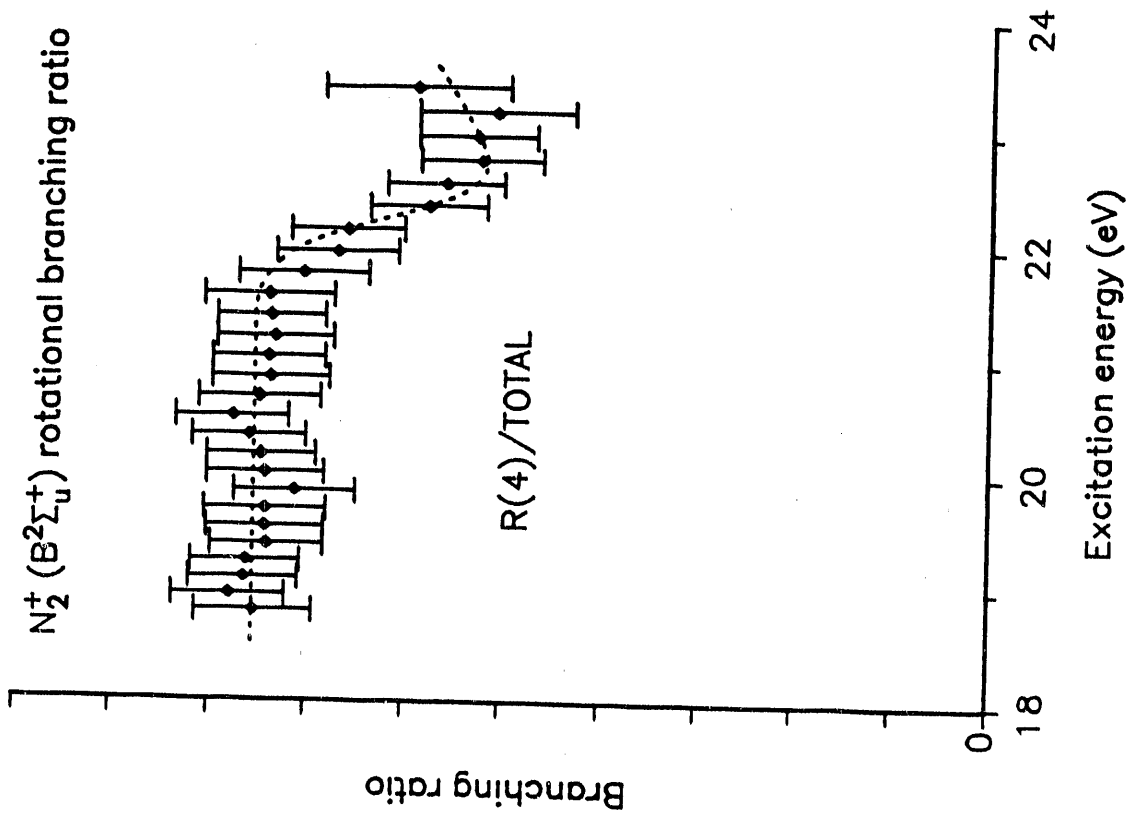


CONTINUUM CHANNEL COUPLING IN  $N_2$ :  $1s^{-1} \leftrightarrow 2\sigma_u^{-1}$









## **Structural Biophysics on Third Generation Synchrotron Sources**

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### **Extended Abstract**

Synchrotron radiation has much to offer structural biophysics, particularly when used in conjunction with recombinant DNA technology. Site directed mutagenesis allows the experimenter to selectively alter the amino acid sequence of proteins (by tinkering with the DNA that codes for them) and to study the ensuing effects from structural and functional perspectives. Advances in higher dimensional NMR technologies and high performance computing also are important complements to synchrotron radiation.

Diffraction and XAFS studies using second generation sources have been very productive for static structural and time resolved studies on relatively long time scales. Third generation sources potentially can reduce the time scale of experiments by two or more orders of magnitude, permitting the study of reaction dynamics and transient structures with short lifetimes. Novel insertion devices potentially offer the possibility of x-ray circular dichroism of proteins and advanced linear dichroism (polarized XAFS). X-ray raman spectroscopy is an intriguing possibility but its practical application to dilute biological specimens remains to be demonstrated.

## Representative problems in structural biophysics

### Regulation

conformational changes – allosteric effects  
subunit association/dissociation  
supramolecular assemblies  
DNA/protein interactions

### Protein folding problem

how does linear sequence uniquely determine 3D structure?  
what are structural intermediates in folding pathway?

### Binding and catalysis

what are the structures of catalytic sites of enzymes?  
how do the structures change upon binding of ligands?  
how do they change during the reaction?  
energetics  
allosteric effects

### Structures

single crystals  
viruses, membranes, LB films, filaments, tubules, solutions

### Structure and electronic structure of transition metal centers

Mn, Fe, Co, Ni, Cu, Zn, V, Mo...  
hemes, B<sub>12</sub>  
non-heme Fe, binuclear centers (e.g. Fe-O-Fe, Cu-S-Cu)  
Fe-S proteins

### Electron transfer reactions

photosynthetic reaction center  
intra- and intermolecular transfer (e.g. cytochromes)

## Structural techniques currently used

### Diffraction

provides more information as sample long range order ↑  
tremendous amounts of information for good single crystals  
useful amounts of information from membranes, fibers etc.  
limited information from solutions  
can do time resolved diffraction & Laue

### XAFS

provides local structural information regardless of LRO  
 $N, R, \sigma^2(T)$   
polarized XAFS gives more information on oriented systems  
bond angles, symmetry  
XANES can provide chemically useful information  
polarized XANES picks out transition dipole M.E.  
Time resolved XAFS made *practical* on 3rd generation sources

### 2D and higher D NMR

permits solution studies approaching atomic resolution  
multidimensional NMR slow → ~~time-resolved studies~~

### Strategy

use crystallography and 2D NMR to map out 3D structures  
time resolved diffraction and XAFS to study *dynamics*

## **Advantages of third generation sources**

- High flux on small samples with low angular divergence  
pushes time domain of experiments into interesting regions
- Tailor source properties to expt using novel insertion devices

## Diffraction

anomalous diffraction  
time resolved studies  
samples with very long range spatial periodicities (~3000Å)  
samples with small ordered domains  
diffuse scattering

## XAFS

time resolved studies  
fast-scan XAFS  
rapid mixing/flow systems  
photolysis experiments  
pressure and T-jump  
high pressure expts  
polarized XAFS

## Hybrid diffraction/spectroscopy techniques

DAFS  
other

## Other possibilities

x-ray circular dichroism and MCD of metal centers  
x-ray raman spectra (low-Z XAFS in high Z matrix)  
e.g. S-XAFS and L-edges of first row elements  
S/N ratio & sample radiation damage questions  
...

## Technical Challenges

Fast time framing 2D Detectors  
Fast energy resolving detectors (1000 channel)  
Radiation damage to specimens

# Ultra soft x-ray fluorescence yield XAFS: An *in situ* photon-in photon-out spectroscopy

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Exxon

Ultra soft fluorescence yield XAFS is an important extension of a traditionally hard x-ray technique for structural determination of low Z elements (C,N,O,F) in materials. Until recently soft x-ray XAFS studies have been accomplished solely by electron yield methods which usually must be done under ultra high vacuum conditions [1]. Although the fluorescence yield for low Z elements is very small (e.g. .0012 for carbon) the technical challenge of the technique opens an opportunity (especially using third generation sources) for the development of an *in situ* photon-in photon-out structural probe. The technique is particularly useful in surface chemistry applications for *in situ* monitoring (kinetics) of transient surface species under real reaction conditions of temperature and pressure [2,3,4,5]. We have developed a UHV compatible system for measuring low Z fluorescence XAFS over a broad pressure range; 10<sup>-10</sup> Torr to several atmospheres [6]. Such a system allows the XAFS technique to address a range of materials problems from monolayers to bulk materials (including insulators such as polymers and diamond) even in the presence of a reactive gas atmosphere. Our experimental apparatus shown in figure

1 consists of three distinct elements: a photon-in window system to isolate the experimental region from the UHV synchrotron beamline, a sample/reaction chamber for *in situ* studies, and a sample preparation chamber containing LEED, Auger, quadrupole, sputtering, and gas dosing apparatus. The photon-in window system consists of two window gate valves with a turbo pumped ballast region in between. The window material can be boron, diamond, aluminum or tin, in general 0.1 to 0.4 microns thick, supported on a mesh substrate and capable of withstanding atmospheric pressures in the case of diamond. The choice of window material clearly depends on the experiment, e.g. a diamond window is quite useful for the fluorine K edge but highly absorbing just above the carbon K edge. In practice a highly versatile system would incorporate a series of soft x-ray window gate valves allowing rapid window exchange depending on the edge energy of the material under study. The reaction/sample chamber contains a differentially pumped ultra-high vacuum compatible proportional counter for collecting the photon-out radiation (fluorescence) in an energy dispersive mode which is described in detail in ref. 6. This type of detection turns out to be very useful in eliminating background fluorescence from atoms not under study e.g. CO/Ni(100) [3,4,5] and CO/Fe(100) [7], separating C  $K_{\alpha}$  (277 eV) from NiL $_{\alpha}$  and FeL $_{\alpha}$  (851 eV and 705 eV excited in 3rd order), and also in high temperature superconductors separating O  $K_{\alpha}$  (525 eV) from Cu L $_{\alpha}$  (930 eV excited in 2nd order) [8]. Although an energy dispersive photon detector has been shown useful in enhancing the fluorescence signal of widely spaced emission lines, separating C  $K_{\alpha}$  from O  $K_{\alpha}$  is

only possible by setting a single channel analyzer on the low or high energy tails respectively of the detector photon energy distribution [9]. One approach to this problem, currently under study is the use of a normal incidence focussing multilayer mirror collector. The problem of a multilayer's low reflectivity is counterbalanced by its large area, ability to concentrate flux in a narrow band pass, and particularly, its ability to discriminate between fluorescent and scattered light (about 7 eV at the carbon K edge!). This subject is detailed in reference [6]. With the development of third generation synchrotron radiation sources the use of multilayer mirror detection would become a practical choice for optimum signal to background enhancement. To that end we have designed a prototype normal incidence multilayer system shown in fig. 2. The useful solid angle is roughly equivalent to our current proportional counter, however with a reflectivity of 5% the overall system efficiency will drop by a factor of 20 or more. Of course with an incident intensity gain of 100 or 1000 this will provide a significant advantage over our current ability to make low Z XAFS measurements. This is particularly important in the case of surface chemistry kinetics where the signal to background sets a severe limit on the time domain that can be measured. In general the measurements are made by monitoring the fluorescence yield of a characteristic molecular near edge resonance (e.g.  $\pi^*$  in CO see ref 3,4,5) as a function of time, temperature, and pressure. For example we have recently studied the kinetics of sulfur carbon bond cleavage of methylthiolate on Pt(111) in the presence of hydrogen [10]. The time evolution (intensity of carbon fluorescence yield at 315 eV) of this



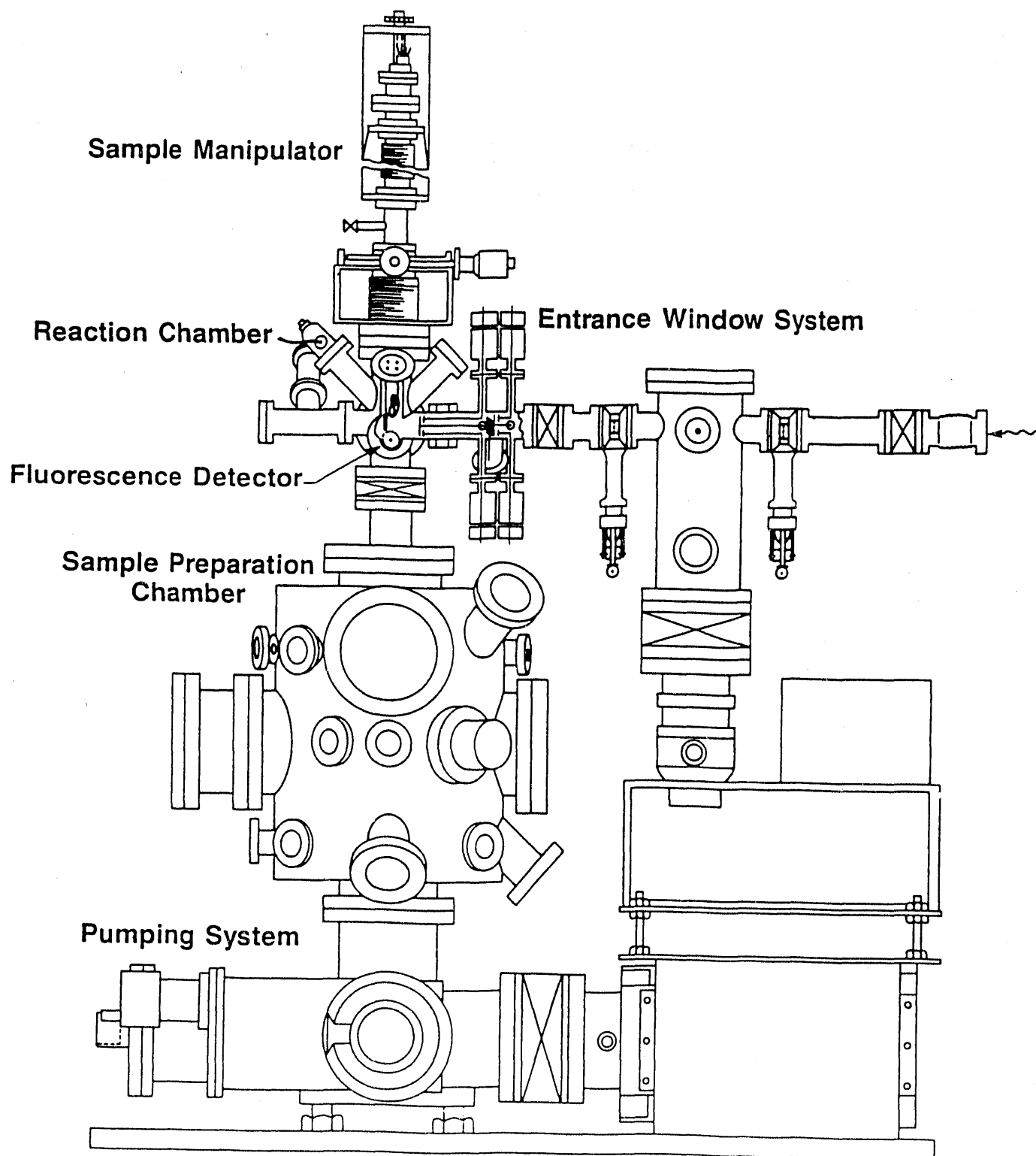
reaction is shown in fig. 3 for several temperatures. These measurements are particularly difficult because methylthiolate doesn't have a strong resonance like carbon monoxide (see inset to fig 3). This study revealed the kinetics of an elementary reaction step, producing methane in the hydrogenolysis of methylthiolate. The reaction was found to be first order in methylthiolate and half order in hydrogen gas pressure as expected. From the figure it is obvious that improved signal to background using a third generation system as described above would allow measurements over a much broader temperature range. In general we would expect that third generation sources will provide a statistical enhancement to our technique because of the very small fluorescence yield of low Z materials like CO on surfaces.

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**Fig. 1. System for in situ low Z (C,N,O,F) fluorescence XAFS under atmospheric pressure conditions**



**Fig. 2. Prototype normal incidence multi-layer mirror carbon K reflector with a collection efficiency of 11.5%**

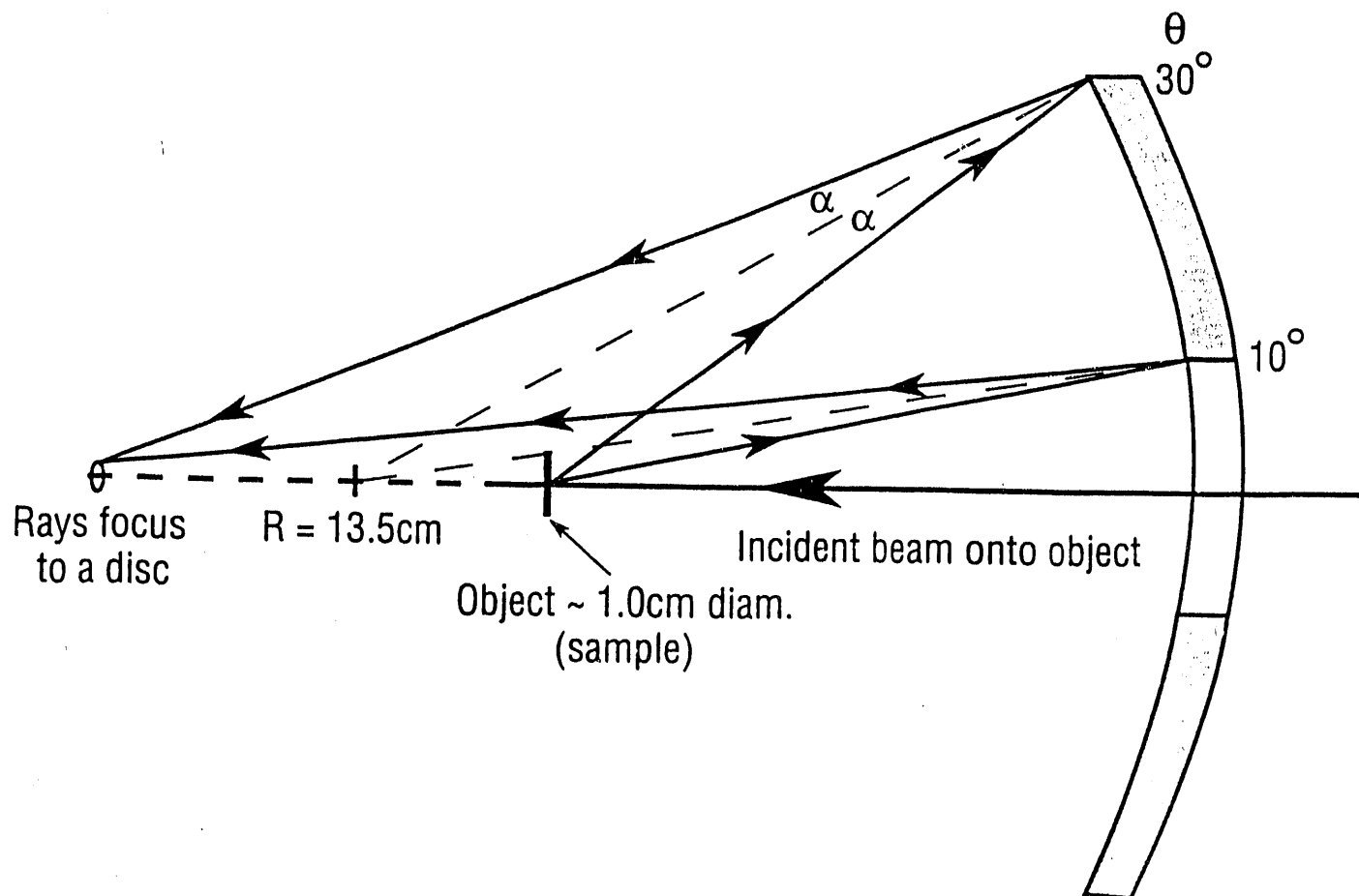
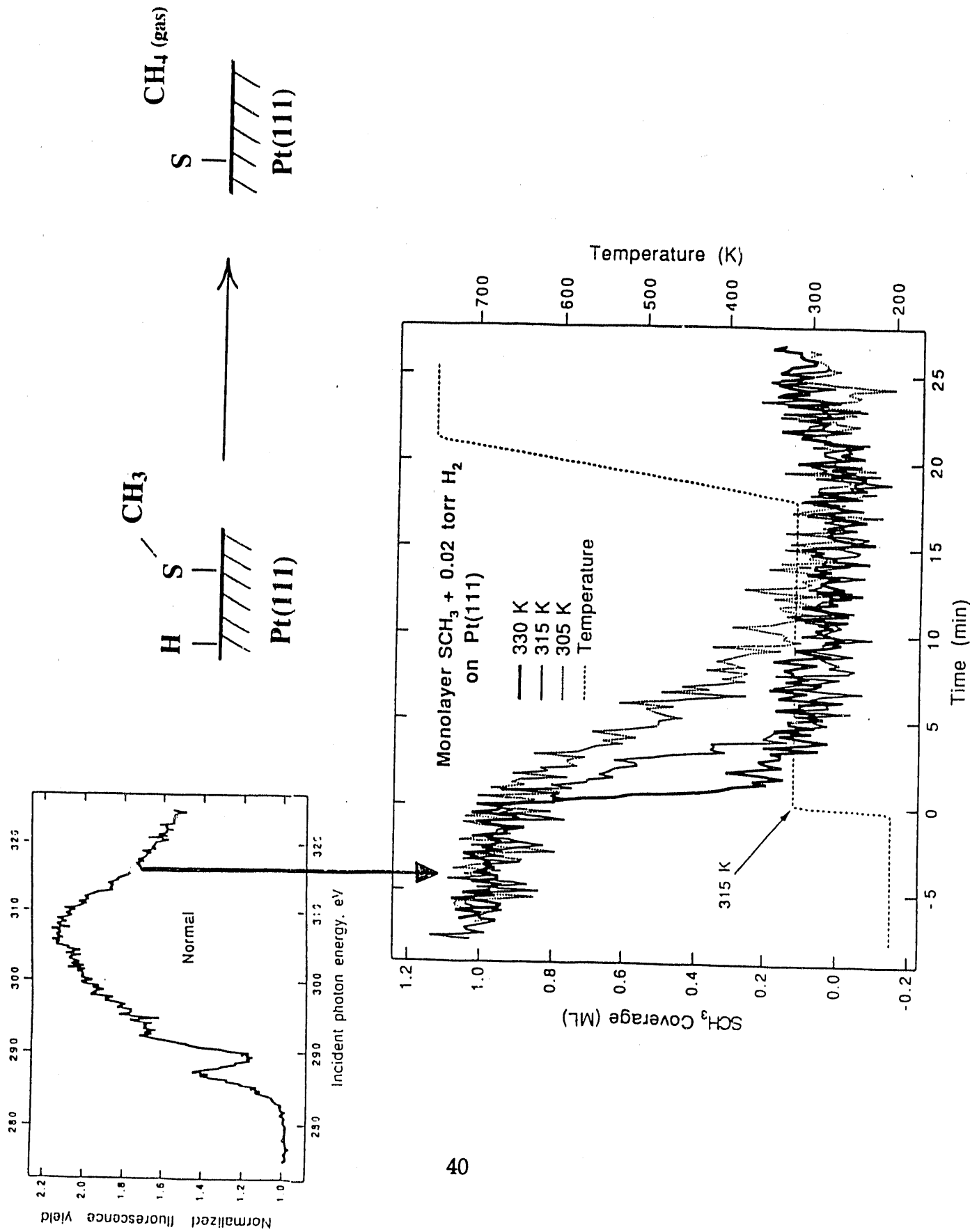


Fig. 3. Hydrogen induced carbon sulfur bond activation on the Pt(111) surface



# X-RAY MICROPROBE: AN ANALYTICAL TOOL FOR IMAGING ELEMENTAL COMPOSITION AND MICROSTRUCTURE

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## 1. Abstract

X rays have many advantages over electrons and other charged particles for the microcharacterization of materials. X rays are more efficient in photoejecting inner shell electrons which results in characteristic x-ray fluorescence. X rays also produce less Bremsstrahlung which yields far higher signal-to-background than obtained with electrons.<sup>1</sup> Minimum detectable limits (MDL) for X ray excited fluorescence can be a few parts per billion;  $10^{-3}$  to  $10^{-5}$  less than for electron excitation. The third generation synchrotron radiation sources such as the Advanced Photon Source will, for the first time, provide x-ray sources as brilliant as the most advanced electron probes. It will therefore soon be possible to develop a submicron x-ray probe with unprecedented low levels of detection in diffraction, EXAFS, Auger, Photoelectron, and fluorescence spectroscopies for structural and chemical characterization. Some applications to materials science are shown.

## 2. Advantages of an X-ray Probe

We are at the beginning of a revolution in our ability to microimage elemental composition and structure with x rays. This revolution is the result of vastly more brilliant x-ray sources,<sup>2</sup> new developments in x-ray optics<sup>3-5</sup> and rapidly improving image processing. The superiority of x rays for imaging internal structure and elemental composition has long been recognized, yet efforts to construct x-ray microprobes have been largely dormant for 30 years due to the overwhelming brightness of electron sources. With the construction of third generation synchrotron radiation sources we will, for the first time, have x-ray sources as brilliant as the most advanced electron sources (Fig. 1). With simultaneous advances in x-ray optics it will be possible to deliver the same flux of x-rays to a  $1 \mu\text{m}^2$  spot as with electrons. The fluorescent signal from each x ray on a sample is typically 10-100 times greater than from electrons or ion excitation. Even more dramatic is the signal-to-noise which is typically four to five orders of magnitude greater for x rays than for electrons (Fig. 2). An x-ray microprobe will, therefore, deposit much less power into the sample for the same minimum detectable limit. Conservative estimates for the detection limits with a  $1 \mu\text{m}^2$  x-ray microprobe having  $10^{14}$  8 keV photons/sec far exceed that possible with alternative probes. An x-ray

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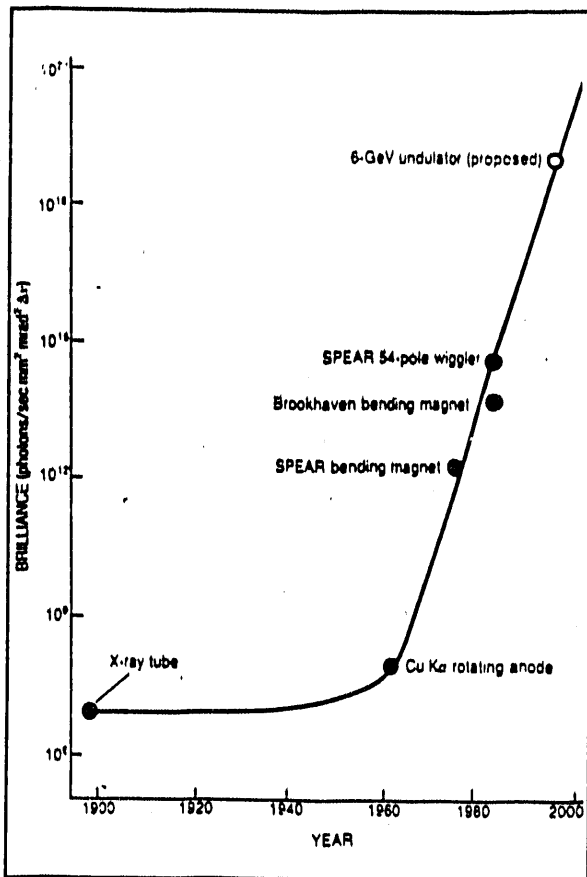


Figure 1. X-ray brilliance has been doubling every 9 months for the last 25 years. At the APS a microprobe beamline will provide  $10^{15}$  x rays/sec/ $\mu\text{m}^2$ .

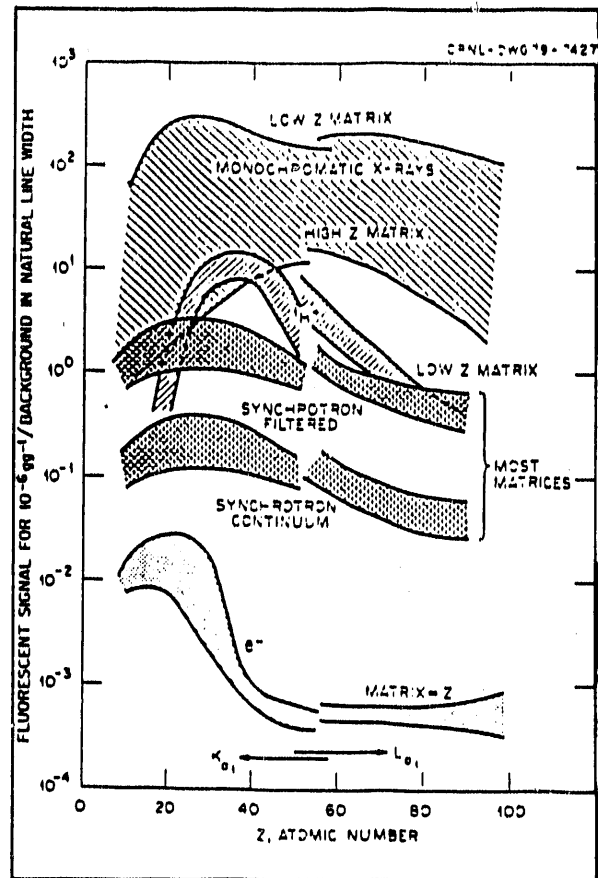


Figure 2. X-ray produced fluorescence has  $10^4$  to  $10^5$  greater signal to background than from electrons.

microprobe will also yield better spatial resolution for thick samples.<sup>6</sup> The ultimate performance for fluorescence detection will be achieved using crystal spectrometers.<sup>7</sup> An x-ray microprobe offers several other advantages compared to charge particle microprobes. The most important of these is the ability to make measurements in the presence of air, water or other gases, and the ability to probe deep into a sample.

### 3. Applications of an X-ray Microprobe

An x-ray microprobe on a third generation storage ring will have many important applications to materials science, biology and environmental sciences. The low MDL of an x-ray microprobe will be useful in mapping out trace element distributions in a variety of inhomogeneous samples. Microprobes using pinholes and solid state detectors are presently capable of detecting 100 ppb/sec of metals in plastic with 10-60  $\mu\text{m}$  diameter probe size.<sup>8</sup> The extended range of detectability of a third

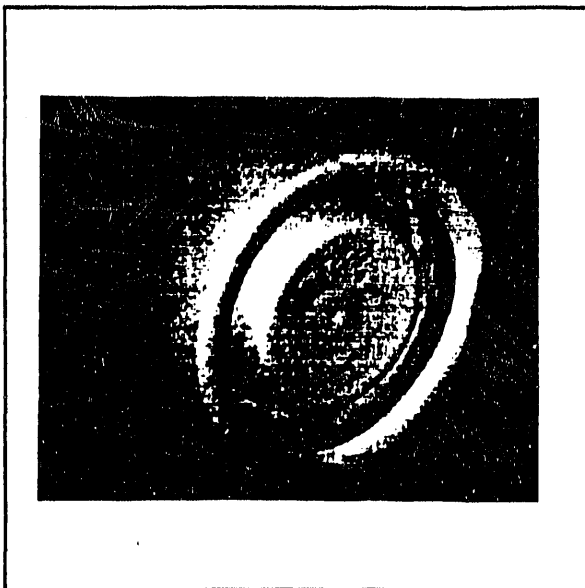
generation x-ray microprobe will be useful in mapping out the elemental distribution in microcircuits, particularly near junctions contacts and at interfaces.

Information about elemental distributions near grain boundaries will help elucidate the role of microalloying in altering grain boundary brittle failure.<sup>9</sup> Similarly at 1  $\mu\text{m}$  resolution we will be able to study diffusion along interfaces and grain boundaries with remarkable sensitivity. Another interesting problem is the effect of microalloying on radiation induced swelling.<sup>10</sup>

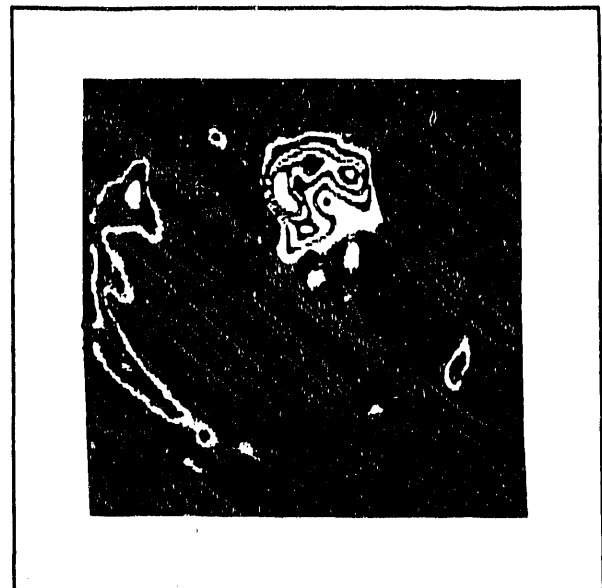
An x-ray microprobe will be particularly valuable for nondestructive studies of microstructure in composite materials. Some possible applications are the radiographic or tomographic study of nuclear fuel particles and fiber reinforced composites (Fig. 3). Tomographic studies using x-ray fluorescence will be particularly sensitive to trace element distributions.

An x-ray microprobe can also be used to study the crystallographic structure at grain boundaries, interfaces, and at composite boundaries. Some early experiments have already demonstrated the usefulness of x rays for studying structure at and near boundaries.<sup>11</sup> Particularly intriguing is the ability to study not only the structure but also the local strain near cracks, precipitates, flaws and other features of importance to materials properties.

An x-ray microprobe will extend the quantitative measurement of toxic materials to small volumes and small concentrations. This will make an important contribution to our understanding and monitoring of pollution and environmental poisoning and will elucidate the response of various organisms to environmental insults. A microprobe will also help identify subtle biological structures with small concentrations of biologically active elements (Fig. 4).



**Figure 3.** X-ray tomographic image of a prototype fuel particle showing a SiC barrier layer. Image made at Exxon beamline X2B.



**Figure 4.** X-ray fluorescent tomograph of the abdomen of a bee showing the iron concentration.



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## CLOSING REMARKS

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As one of the organizers of this workshop, I can state that one of our goals was to invite a slate of speakers that could provide, within the limits of time, the widest possible representation of the many advantages that photon-in, photon-out spectroscopy has for diverse scientific investigations. In most cases, the advantages of the method stem directly from the fundamental characteristics of photons, particularly x-ray and VUV photons, and their interaction with matter. Therefore, to summarize the excellent contributions of our speakers, I have provided a somewhat telegraphic list in Table 1 of some of these fundamental characteristics, upon which I will expand below.

Table 1: Characteristics of Photon-in, Photon-out Techniques

- Penetration
- Wavelength
- Time Scale
- Charge neutrality
- Inner Shells -> Valance -> Unoccupied Levels
- Elemental Specificity
- Dominance of Single Interactions
- Selection Rules and Polarization Effects
- Reduced Damage
- Low Background Signal

At the top of the list is "penetration," because it is historically the first property of x rays to be exploited, and remains the principle reason for the ubiquitous use of x rays in medicine and materials science. Ederer showed us the famous radiograph of Frau Roentgen's hand and wedding ring, which is nearly a century old. The simple importance of the universal ability of x-ray photons to penetrate, to probe the interior of a sample, was illustrated repeatedly in the workshop, ranging from the soft x-ray work of Fisher, through the in situ biological studies described by Bunker, to the hard x-ray tomography illustrated by Ice. There is one important aspect of the penetration power of x rays which was not illustrated, and that is the possibility of extinguishing it to permit surface-sensitive studies. This possibility was anticipated as early as the 1950's by Parratt[1], and in the era of synchrotron radiation facilities, Parratt's dream has begun to be realized starting with the seminal work of Eisenberger et al.[2]

The short wavelength of x-ray and UV photons can also be a critical characteristic for various other measurements. One example is the importance of short wavelengths for imaging and microscopy. Again this feature has been well illustrated by Ice's discussion of x-ray microprobes. Further, examples of the exploitation of short wavelength synchrotron radiation for microscopy—and even holography—are well known[3].

The short wavelength of x rays can have additional significance for photon-in, photon-out spectroscopy, which we were unable to touch upon directly in this workshop. X-ray diffraction measurements, including all of x-ray crystallography, classify as photon-in, photon-out techniques, but these generally fall outside the category of "spectroscopy." Nevertheless, their are interesting examples of x-ray spectroscopy induced during x-ray diffraction. One case is the observation of the x-ray standing wave effect x-ray fluorescence [4,5,6]. Since this effect typically involves x-ray Bragg diffraction, it is essential that the wavelength of the excitation photons is comparable to atomic spacing. Another related example is the observation of the coherent Compton effect [7,8].

Yet another case of x-ray spectroscopy, where the wavelength is critical, falls under the category of x-ray inelastic scattering [9,10]. The regime, where the wavelength is comparable to the Bohr radius of atomic orbitals, is particularly interesting, and it would be informative to include a discussion of this phenomena in any future workshop on the subject.

The time scale of photon interaction with materials can have important ramifications, particularly at synchrotron radiation sources. At least three different time scales can be considered, one being the duration of the photon pulse delivered by the synchrotron, another defined by the core-hole lifetime of an inner shell vacancy, and a third related to the coherence length of the photon. The short pulse length of synchrotron light opens the possibility of timing studies such as the observation of laser excited samples, as studied by Ederer and co-workers. On an even faster time scale is Southworth's example of studies of an isotropy of x-ray emission from molecular gases, where it is essential that the virtual excitation and re-emission of the x rays occurs much faster than the tumbling time of a rotating molecule. The case of resonant Raman scattering, discussed by Isaacs is interesting in that the time scale that determines the lifetime broadening of the spectral features can be either the core-hole lifetime or the x-ray coherence length, depending upon the instrumental resolution of the measurement.

The fact that photons are charge neutral also deserves mention. Charge neutrality of the probing photons in both the initial (photon-in) and final (photon-out) state tends to simplify the interaction of the probe with the sample. To be more explicit, threshold spectra, such as those presented by Nordgren, are less effected by post-collision interaction (PCI) than is the case with near-

threshold electron emission spectra. Charge neutrality also means that sub-threshold excitations are open to study. Furthermore, the environmental influence of applied electric or magnetic fields is unimportant for photon-in, photon-out measurements. X-ray measurements are unique among photon spectroscopies, in that all electron levels of an atom can—in principle—be studied, i.e., even the 1s electrons in uranium can be probed. Furthermore, as illustrated by Poliakoff, photon-in, photon-out methods can be studied, the outer electronic levels of atoms and molecules, often with higher energy resolution than electron spectroscopy.

The cases of inner-shell spectroscopy have an important advantage in providing elemental specificity, i.e., the observed emission spectra can be easily identified as originating at a given atomic element. This is an obvious necessity for the x-ray microprobe analysis described by Ice. It is also an important feature for higher resolution studies of spectra, as discussed by Nordgren and Ederer, in that the local partial density of states can be studied in the vicinity of the ionic core of particular elements. Thus, molecular orbitals—or band structure—in solids can be studied from the point of view of particular constituent atoms.

In almost all examples of photon-in, photon-out spectroscopy, it is safe to assume the dominance of single interactions. This is in contrast, for example, to electron spectroscopy of solids, where a photo-emission peak is always accompanied by a shadow peak at lower energy due to plasma losses incurred by some fraction of the emitted electrons. Self absorption is sometimes in evidence in photon emission spectra, but inelastic scattering, or other secondary interactions of incident, or emitted photons, is too improbable to cause serious difficulties in interpreting spectra.

Selection rules and polarization effects yield advantages which are very similar to those obtained from the elemental specificity of photon spectroscopy, namely the fact that spectra are interpreted in terms which go beyond a simple energy level diagram. As discussed by Ederer and Nordgren, the selection rules for photon absorption and emission dictate that the observed spectra represent a partial density of states. Polarization and anisotropy effects, such as those described by Southworth, also permit the study of orbital symmetry.

Another characteristic of photon spectroscopy, which is traceable to the dominance of single interactions, is reduced damage. This point was particularly emphasized by Bunker's discussion of biological studies and Ice's description of x-ray microprobes.

One other key characteristic of photon spectroscopy is the relatively low background signal. This point was emphasized by Fisher and Bunker in particular. Again the dominance of single interactions, and the concomitant reduction of secondary emission, is the key reason for this advantage over measurements involving electron emission.

To be honest, there are also many disadvantages for photon-in, photon-out spectroscopy, compared to other established methods. The reason that x rays penetrate, and that single interactions dominate the emission process, is quite simply that the cross sections are so low. Also, the state-of-the-art instrumentation for x-ray emission spectroscopy cannot compete with electron spectrometers in their combination of efficiency and energy resolution. These problems have led to the result that, to date, photon-in, photon-out spectroscopy has often been starved for signal, but it is here that the importance of the new, third-generation synchrotron radiation sources becomes evident. The many advantages of the technique listed above, and illustrated in the various excellent contributions to the workshop, can be best exploited by the expected cornucopia of photons provided by the new machines.

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# Photon-In Photon-Out Spectroscopy

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