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RESONANT INELASTIC X-RAY SCATTERING FROM MOLECULES AND ATOMS

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X-ray fluorescence spectroscopy is one of the most powerful methods for the understanding of the electronic structure of matter. We report here on fluorescence experiments in the 2 to 6 keV photon energy range using tunable synchrotron radiation and the resulting experimental programs on resonant inelastic scattering in atoms and on polarization measurements in resonant molecular excitations.

1 Introduction

Before synchrotron radiation was commonly applied, mainly two methods were used to ionize a deep-inner-shell: X-ray tubes and electron beams. In most experiments both were used with excitation energies far above threshold, often leaving the target in an undefined multi-vacancy state, which led to satellites in the emission spectrum. To study and understand these x-ray satellites it is necessary to excite with tunable photons close to threshold. This was achieved by applying many different anode materials in laboratory sources in a study of the $K\beta$ spectra of argon, and of potassium and chlorine in KCl ^{1,2}.

In many other x-ray fluorescence experiments (see e.g. refs.³⁻⁵) the exciting radiation was not tunable and caused satellites. Tunable synchrotron radiation opened the door to satellite-free x-ray fluorescence spectra, because it was easily possible to continuously tune the exciting photon beam to an energy below the first double excitation threshold⁶. Tunability also allows studies of the creation of satellite transitions by scanning the primary photon energy over a double excitation threshold⁶.

In addition, with tunable synchrotron radiation, resonance and threshold phenomena could be studied. With the improved performance of x-ray beamlines⁷⁻¹¹ it is possible to study the resonant inelastic Raman scattering of x-rays by atoms and molecules¹². Characteristic fluorescence can be explained using a static two-step model, whereas x-ray scattering processes like x-ray resonant Raman scattering have to be explained using one-step models¹², which are based on the Kramers-Heisenberg formalism¹³.

Synchrotron x-rays are highly linearly polarized in the orbit plane of the storage ring, and monochromator crystals at a Bragg-angle close to 45° are also good polarizers¹¹. This leads to the use of x-ray spectrometers to investigate molecular structure through polarization analysis of resonant x-ray fluorescence¹¹.

We will not address experiments on solids because other authors will do that in more detail in this issue. However, we note that several results on resonant inelastic scattering from solids¹⁵⁻¹⁷ have been obtained using the same instrumentation^{7-9,11} described here, and the physical principles are the same.

2 Experiment

The instrumentation is described in refs. ^{7-11,18} and the methods in refs. ¹⁹⁻²¹.

The geometry of the x-ray spectrometer is shown in fig. 1. The focused, narrow-bandwidth, linearly polarized x-ray beam provided by beamline X24A at the National Synchrotron Light Source passes through the target gas cell. Ionization chambers or thin foil photo current detectors are used to measure the intensities of the incident and transmitted x-ray beam, providing

absorption spectra and normalization for variations in beam intensity. Scattered and fluorescent x-rays emitted normal to the propagation direction of the incident x-ray beam are dispersed by a curved crystal spectrometer¹¹ and recorded by a position-sensitive proportional counter (PSPC)²¹. The Bragg angle of the spectrometer is adjusted to detect a particular spectral component ($L\alpha$, $K\alpha$, $K\beta$, or $K-V$), and the acceptance window of the PSPC is typically wide enough to record the entire spectrum simultaneously. Multichannel recording provided by the PSPC is very important for these experiments due to the typically low counting rates.

The beamline's double-crystal monochromator⁷⁻⁹ and the curved-crystal emission spectrometer¹¹ are designed to operate at large Bragg-angles ($\approx 20^\circ$ - 70°) and are usually used with semiconductor crystals (Si, Ge, InSb) to work in the energy range 2-6 keV. The polarization sensitivity of these Bragg-reflections can be quite high. For example, Si(111) crystals have been used in both the beamline monochromator and emission spectrometer for Cl K-edge absorption and Cl K-V and $K\alpha$ emission studies of Cl-containing molecules. The x-ray energies involved are in the range 2.6 to 2.9 keV, for which the Si(111) Bragg-angles are between 43° and 49° , resulting in excellent polarization selectivity.

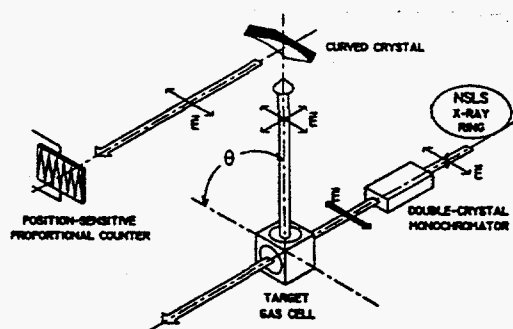


Figure 1. Schematic drawing of the x-ray spectrometer used for the measurement of the angular distribution of polarized x-ray emission.

As described below, this polarization selectivity has allowed observation of strongly polarized and anisotropic x-ray emission from resonantly-excited molecules!⁹⁻²¹.

3 Results

The beamline-spectrometer system has been operated successfully for several years, and we will give a short overview of selected results and refer to cited articles for more detailed information.

3.1 Multivacancy Effects in Atomic Argon

Exciting an atom using an x-ray source far above threshold causes additional multivacancy structures to appear in the fluorescence spectrum. Deslattes *et al.*^{6,22} studied the origins of multivacancy processes by measuring argon $K\beta$ spectra below the $1s \rightarrow 4p$ resonance, above the $1s$ threshold but below the $1s3p$ double ionization threshold, above the double ionization threshold and far above thresholds. Fig. 2 illustrates the results. Spectrum 2a) was obtained at high excitation energy and shows three prominent features, labeled $K\beta_{1,3}$, $K\beta'$, and $K\beta''$.

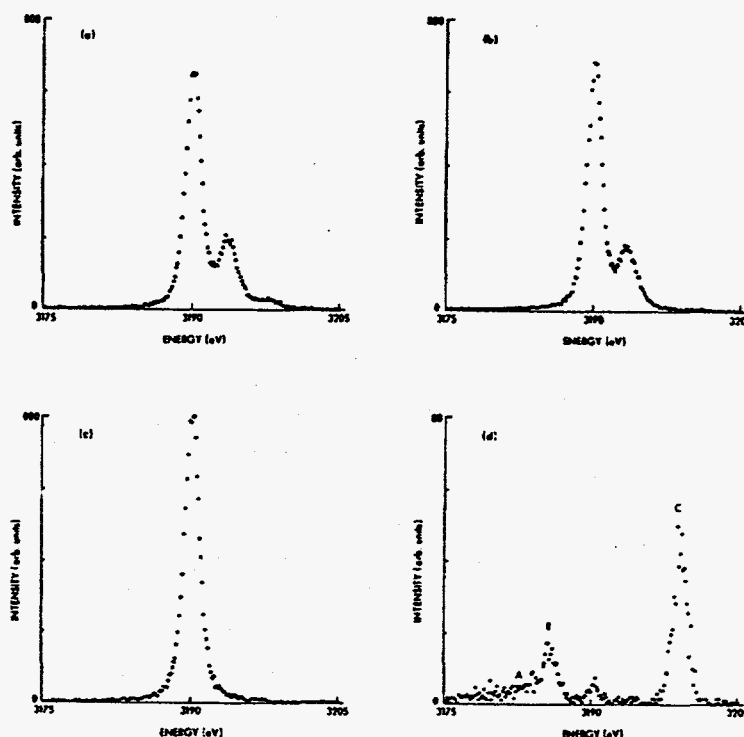


Figure 2. Sample Ar $K\beta$ emission spectra obtained with incident photon energy at a) 3281.4 eV, b) 3245.9 eV, c) 2113.1 eV, and d) 3199.2 eV.

At excitation energies between ~ 20 and ~ 60 eV above threshold the $K\beta''$ features disappear [Fig. 2b]. Between the $1s$ threshold and $+20$ eV both satellites are absent, leaving only the $K\beta_{1,3}$ diagram line [Fig. 2c]. Below threshold, several features dominate the emission spectrum due to Compton (A), resonant Raman (B), and Rayleigh \odot scattering [Fig. 2d].

The argon fluorescence spectrum changes dramatically as the energy of the incident x-ray beam is changed, evolving from a typical Raman scattering structure below threshold, over a normal satellite-free x-ray fluorescence spectrum into a spectrum containing many additional structures created through multivacancy processes.

3.2 Inelastic X-Ray Scattering in Atoms

There are relatively few experiments done in the field of resonant x-ray Raman scattering or resonant inelastic scattering. The first reported observation of x-ray resonant Raman scattering was done by Sparks²³ using x-ray anodes. Eisenberger *et al.*²⁴ used tunable synchrotron radiation and observed linear dispersion and linewidth narrowing for resonant inelastic x-ray scattering near the Cu K edge of copper metal. They also presented a theoretical formulation. Briand *et al.*²⁵ observed resonant Raman scattering from both bound and continuum intermediate states. Åberg and Tulkki have developed a detailed theoretical formulation²⁶, and applied their theory to model observed results²⁶⁻²⁸.

Åberg and Tulkki^{12,26,27} described the evolution of inelastic scattering from the Ar $1s \rightarrow np$ Rydberg-resonances and the continuum threshold into "normal" fluorescence. Cowan^{17,29}

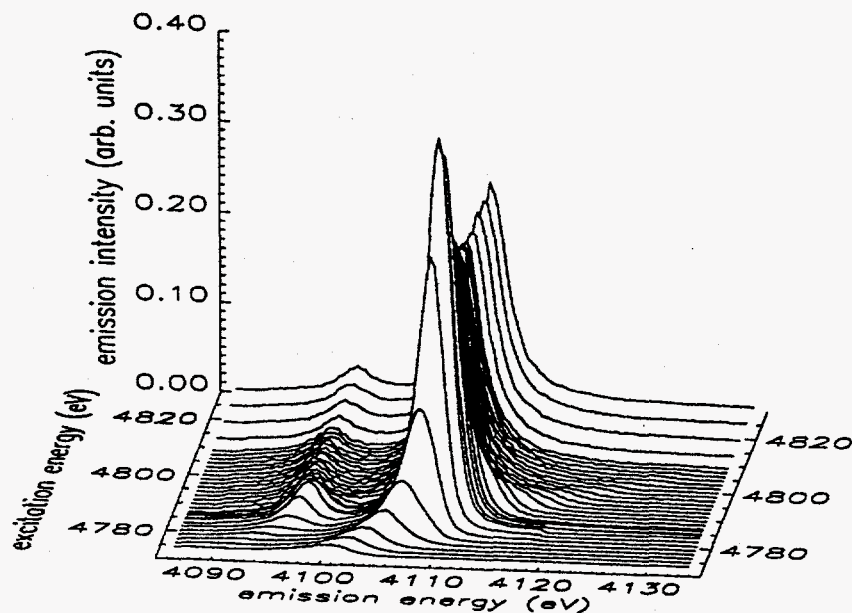


Figure 3. Variation of the Xe $L\alpha_{1,2}$ emission spectrum as the incident x-ray energy is scanned across the L_1 edge region to illustrate resonance inelastic scattering and the onset of fluorescence.

and coworkers observed linewidth narrowing and lineshape variation in the Ar $K\alpha$ x-ray spectrum recorded at several energies below, on and above the $1s - 4p$ resonance. Southworth *et al.*³⁰ reported a small anisotropy effect in the Ar $K\alpha$ emission recorded on the $1s - 4p$ resonance.

Recently MacDonald *et al.*³¹ reported a resonant scattering experiment at the xenon L_3 edge. They investigated the evolution of x-ray resonance Raman scattering into x-ray fluorescence while scanning the excitation energy through the L_3 edge region. Fig. 3 shows the resulting spectrum as a surface plot over the energy of the exciting x-rays and the emission energy. The evolution from a strongly asymmetric profile into the normal fluorescence is clearly shown, in good qualitative agreement with theory²⁶⁻²⁹.

3.3 X-ray scattering in molecules

Cowan²⁹ and Southworth³² summarized the work on the polarizations and anisotropies in molecular x-ray fluorescence. Large polarizations and anisotropies have been observed in x-ray scattering from molecules which were selectively excited at strong subthreshold resonances^{18-20,33,34}. Resonant excitation can select a spatially aligned set of molecules from a randomly oriented gas phase target, resulting in strongly polarized and anisotropic x-ray scattering¹⁸⁻²⁰.

The classical version of the two-step model shows that large anisotropies and polarizations are expected for x-ray absorption/emission processes involving molecular states of well defined symmetries^{20,30}. In this model^{36,37} the absorption and emission dipole moments are replaced by classical dipole oscillators treated as rigidly attached to the molecular framework. In fig. 4 we show the parallel polarized Cl K-V emission spectra from CF_3Cl recorded on resonance at emission angles $\theta = 0^\circ$ and 90° (from ref²⁰). The variation of the x-ray emission spectrum with angle of observation is in good qualitative agreement with the classic two-step model²⁰. Alternatively, the effects of alignment by resonant excitation can be observed in the polarization dependence of x-rays emitted at fixed (90°) emission angle^{18,19,33,34}.

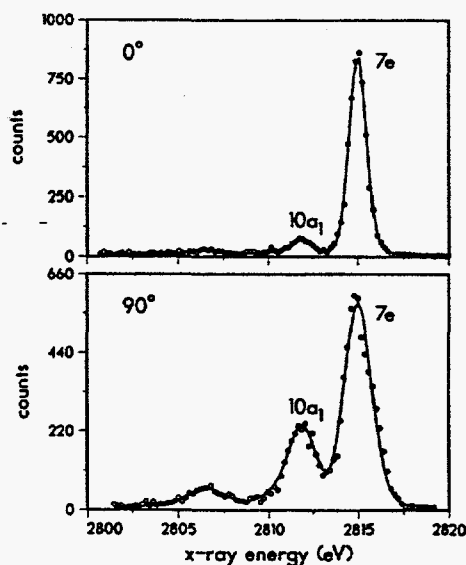


Figure 4. Parallel polarized Cl K-V emission spectra from CF_3Cl recorded on resonance at emission angles $\theta = 0^\circ$ (top) and 90° (bottom). The solid curves are the results of a peak fitting procedure used to obtain relative intensities for transitions involving the $10a_1$ and $7e$ molecular orbitals.

4 Conclusions

We have briefly described several results obtained using tunable synchrotron radiation and a curved-crystal spectrometer for resonance and threshold studies of atoms and molecules. Special emphasis was given to studies of multi-vacancy effects, resonant Raman scattering, and the polarization and anisotropy of emitted x-rays.

Significant advances in this field are expected using the improved flux and resolution available at third-generation synchrotron beamlines. For example, the investigation of vibrationally-dependent effects should provide further insight into resonant x-ray scattering from molecules.

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