

## POLARIZATION EFFECTS IN MOLECULAR X-RAY FLUORESCENCE

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## Abstract

Highly polarized x-ray fluorescence has been observed following K-shell excitation of several Cl-containing molecules. Monochromatic synchrotron radiation (SR) with a high degree of linear polarization was used to resonantly excite Cl 1s electrons in  $\text{CH}_3\text{Cl}$ , and the three Freons,  $\text{CF}_3\text{Cl}$ ,  $\text{CF}_2\text{Cl}_2$ , and  $\text{CF}_3\text{Cl}$ . The subsequent Cl K $\beta$  fluorescence was found to be strongly linearly polarized. The direction of polarization of the K $\beta$  fluorescence is determined in part by the symmetry of the valence-orbital electron involved in the fluorescence decay which fills the Cl 1s hole. Our results illustrate that the core-level resonance lifetimes are short enough to preclude substantial disorientation of the molecule prior to fluorescence decay. Measurements of this type may prove to be a sensitive probe of orbital symmetry in more complicated molecular systems, condensed matter, and adsorbates.

X-ray emission spectroscopy has been useful in understanding core-level phenomena in a wide variety of systems and environments [1]. Recently, the application of synchrotron radiation has added a new dimension to x-ray spectroscopy; the capability to selectively tune the exciting radiation in the near-threshold region [2]. Coupling this tunability with polarization analysis of the x-ray fluorescence has opened a new approach to studies of molecular electronic structure. While previous work has used fluorescence polarization to study molecular alignment in the valence shell [3], we report here the first observation following core-level excitation. Using core levels provides the advantages of atomic specificity, and very short lifetimes which mitigate the effects of disorientation by nuclear motion.

The present measurements were performed at beamline X24-A at the National Synchrotron Light Source at Brookhaven. A high-energy-resolution primary monochromator [4] focuses the incident beam into a cell containing the sample gas. Ionization chambers before and after the cell are used to obtain relative absorption cross-section curves (see Fig. 1). The molecular x-ray fluorescence emitted upward from the gas cell is collected by a curved-crystal [5] secondary spectrometer with position-sensitive detection [6]. Polarization sensitivity is accomplished by using a Si(111) crystal in the spectrometer (and in the primary monochromator), for which the Bragg angle is  $44.6^\circ$  for Cl K $\beta$  fluorescence. Rotation of the secondary spectrometer, and hence the crystal dispersion plane, by  $90^\circ$  suffices to detect orthogonal fluorescence-polarization components.

As an example of the high-degree of polarization observed, Fig. 2 contains two Cl K $\beta$  fluorescence spectra of  $\text{CF}_3\text{Cl}$ . Both spectra were taken with incident excitation of 2823.1 eV, on the large peak (D) below threshold, but with orthogonal polarization detection. Parallel and perpendicular refer to the orientation of the K $\beta$  fluorescence polarization with respect to the polarization of the incident radiation. The initial excitation to the molecular resonance state is of a symmetry, and thus selects preferentially those  $\text{CF}_3\text{Cl}$  molecules

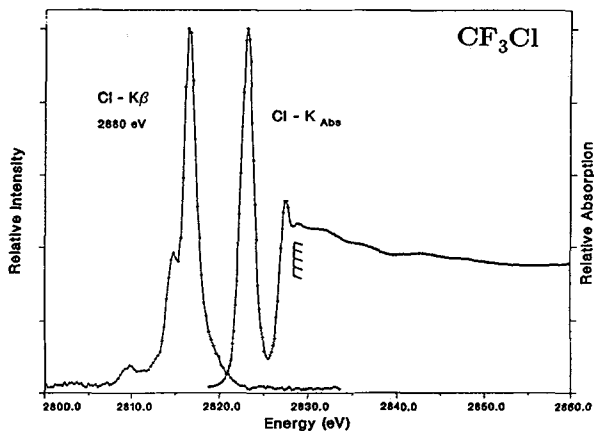


Fig. 1 Absorption spectrum of  $\text{CF}_3\text{Cl}$  near the Cl 1s threshold (hatched mark), and Cl K $\beta$  fluorescence spectrum taken with 2880 eV photon energy excitation, well above threshold. The K $\beta$  spectrum at 2880 eV is independent of the polarization of fluorescence. These results for  $\text{CF}_3\text{Cl}$  and the results for the other molecules agree well with previous measurements [7,8].

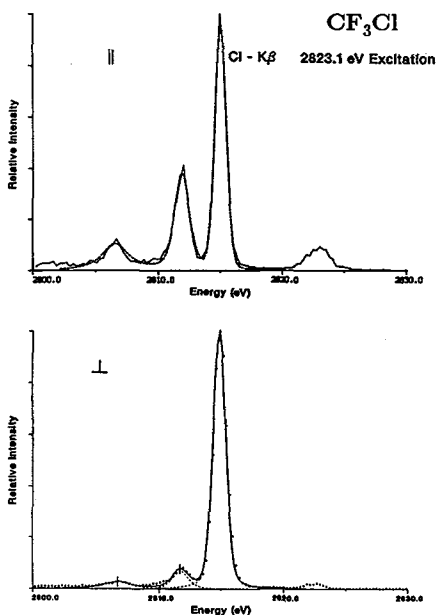


Fig. 2  $\text{CF}_3\text{Cl}$  Cl K $\beta$  spectra using 2823.1 eV photon energy, on peak D in the absorption spectrum (see Fig. 1). The two spectra were taken under conditions to detect fluorescence polarization parallel (top) or perpendicular (bottom) to the  $\mathbf{E}$ -vector of the incident radiation. The peak at 2823.1 eV is due to elastic scattering.

with their C-Cl bond axis parallel to the E-vector of the synchrotron radiation. If no disorientation occurs prior to radiative decay, then one expects that the valence orbitals which are involved in producing the K $\beta$  fluorescence will produce parallel- or perpendicular-polarized radiation depending on whether they are of a<sub>1</sub>-symmetry (along C-Cl bond) or e-symmetry (perpendicular to C-Cl bond) symmetry, respectively. New *ab-initio* calculations by P.W. Langhoff et al. [9] confirm this qualitative picture, and agree quantitatively with the relative fluorescence peak intensities observed.

Other Cl-containing molecules, CH<sub>3</sub>Cl, CF<sub>2</sub>Cl<sub>2</sub>, and CFC1<sub>3</sub>, also have been studied and exhibit very similar effects [10]. These preliminary results suggest the usefulness of fluorescence polarization to the assignment of resonant features both below and above threshold, and of the final valence-hole-state symmetry. Beyond this straightforward spectroscopic utility, more general applications might include the study of molecules, ions, or molecular fragments in different environments and phases to determine spectroscopic or geometrical parameters. Furthermore, we suspect that the atomic specificity of this phenomenon may permit its use to study adsorbate orientations on surfaces:

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