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POLARIZED X-RAY ABSORPTION NEAR EDGE STRUCTURE

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Abstract - Polarized measurements of oriented single crystals can be used to simplify the interpretation of X-ray absorption near edge structure (XANES) spectra by permitting a direct determination of the symmetry properties of a particular transition. We have utilized this technique to study the XANES spectra for several first-row transition metal complexes. Applications to the weak, 1s→3d transition, to intense near edge features, and to continuum transitions are discussed.

INTRODUCTION

It is well known that X-ray absorption near edge structure is sensitive to the electronic and geometric structure of an absorbing site and can provide information complementary to that obtained from EXAFS. However, in comparison with EXAFS, there have been relatively few attempts to apply XANES as a tool for structure elucidation. This stems, in part, from the difficulties involved in predicting ab initio the XANES structure expected for a particular site. Recent years have witnessed a dramatic improvement in the theoretical treatment of XANES spectra. We have adopted a complementary empirical approach to this problem, in which polarized XANES spectroscopy of small, crystallographically characterized molecules is utilized as an approach toward understanding the physical basis of XANES spectra. Measurement of polarized spectra is relatively straightforward, given the nearly completely plane polarized nature of synchrotron radiation and the availability of oriented samples.

Polarized spectra often provide enhanced resolution of features having different polarization properties. More importantly, they permit direct determination of the symmetry properties of a particular transition. The symmetry properties can be used, in turn, to test more stringently the predictions resulting from various theoretical models. We present here a brief discussion of the methodology for measurement of polarized single crystal absorption spectra and a discussion of recent applications of the technique to the study of Cu complexes.

EXPERIMENTAL

Data are measured as fluorescence excitation spectra. The beam is collimated to just slightly larger than the size of the crystal in order to minimize background scatter. Crystals are mounted on the end of a glass fiber or in a thin-walled glass capillary and are oriented using conventional diffraction techniques. In order to obtain the accurate energy calibration necessary for comparing spectra recorded in

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different orientations, we used an internal energy-calibration standard. Typically, this consisted of a foil of the element of interest, with the foil absorption spectrum being recorded simultaneously with measurement of the crystal fluorescence.

A problem unique to single crystal fluorescence measurements is the presence of Bragg diffraction peaks. The intensity of these peaks can be quite large compared to the intensity of the fluorescent radiation. In order to preserve the angular information, while eliminating contributions from diffraction peaks, we have used a spatially resolving array of fluorescence detectors. Since the diffraction peaks are spatially well resolved, they will contribute to the signal of at most one detector at any given energy. The diffraction peak is then removed from a detector's signal by linear interpolation or, if necessary, that detector is excluded from the average.

APPLICATIONS

ls+3d transition. Although the ls+3d transition is forbidden (\(\Delta l=2\)) for centrosymmetric complexes, this transition is observed to be weak, but not absent, for all first row transition metal complexes having vacancies in the 3d shell [1]. Possible mechanisms to account for this intensity are vibronically allowed dipole coupling and direct quadrupole coupling. These mechanisms can be distinguished on the basis of the polarization properties of the ls+3d transition. If a square planar complex is oriented with the metal-ligand plane parallel to the polarization (\(e\)) and propagation (\(k\)) vectors and is rotated about an axis perpendicular to the \(e\cdot k\) plane, the ls+3d transition strength will be angle independent for dipole coupling and will show four-fold periodicity for quadrupole coupling. Polarized measurements on the creatinium salt of Cu(II)Cl₄ show that for this molecule, the ls+3d transition results primarily from quadrupolar coupling [2].

If the \(x\) and \(y\) axes are defined to be parallel to \(e\) and \(k\), the quadrupole operator transforms as \(xy\). Since \(\langle s|xy|d_{x^2-y^2}\rangle=0\) while \(\langle s|xy|d_{xy}\rangle\neq0\), the half-filled Cu 3d orbital must transform as \(xy\) in the coordinate frame of the radiation in order to have non-zero quadrupole transition probability. The observed maximum in the ls+3d transition occurs for the orientation in which the \(e\) vector bisects the Cu-Cl bond directions. The theoretical and experimental orientations which correspond to the maximum ls+3d transition strength (in the coordinate frame of the radiation) are shown at the right. From a comparison of these orientations, it is obvious that the half-filled Cu 3d orbital must transform as \(x^2-y^2\) in the coordinate frame of the molecule. Polarized XANES measurements can thus be used to probe the detailed electronic structure of an absorbing atom.

ls+4p transition. If the square-planar Cu complex discussed above is rotated so that \(e\) is parallel to the \(x\) axis (i.e., \(e\) perpendicular to the Cu-Cl plane), a dramatically different absorption spectrum is observed [3,4]. For Cu(II) complexes, the \(e|z\) XANES spectra show absorption maxima at 8986 and 8995 eV. In isotropic Cu(II) XANES spectra, the 8986 eV transition appears as a poorly resolved shoulder, with the principal absorption maximum occurring at 9000 eV. The 8986 eV feature has previously been assigned as the ls+4s transition [1]. As an experimental approach to understanding the physical basis of this transition, we have measured the polarized (\(e|z\)) XANES spectra for a series of square-planar Cu(II) complexes.

The spectra for four Cu(II) complexes which have different distances from the Cu to the nearest axial atom are shown in Figure 1. It is clear that the intensity of the 8996 eV transition is strongly dependent on the separation between the Cu and the nearest axial atom, while the energy of this transition depends only slightly on the structure of the Cu site. This is the qualitative behavior which would be
Fig. 1. Experimental \( e \parallel z \) spectra for selected Cu(II) complexes. The distance to the nearest axial atom is varied by choice of counter ion. Expected for a predominantly metal-centered transition. On the basis of MSW-Xa calculations [4], this transition is assigned as predominantly \( 1s^2 4p \). The inverse dependence of intensity on axial-atom distance can be understood, in a molecular orbital sense, as resulting from increased overlap of the metal 4p orbital with the ligand orbitals.

\( 1s^2 \)-continuum transition. The isotropic XANES spectra for Cu(II) compounds generally show a broad principal absorption maximum at \(-9000\) eV. Since this structure is not observed in the \( e \parallel z \) spectra (Fig. 1), it must arise from orientations in which \( e \) is parallel to the Cu-ligand plane. This is confirmed experimentally, as shown in Fig. 2. The spectra in Fig. 2 represent trans-CuN\(_2\)Cl\(_2\).

Fig. 2. \( e \parallel Cu-N (\ldots) \) and \( e \parallel Cu-Cl (\ldots\ldots) \) experimental spectra for mixed-ligand complexes. [Reproduced from Ref. 4]

Plastocyanin. The measurements discussed above have provided a relatively complete understanding of the structural features which are empirically correlated with specific XANES features. This understanding can now be used to interpret the XANES spectra for the blue copper protein plastocyanin. The Cu site in plastocyanin has been crystallographically characterized [6] and shown to have a \( C_3v \) distorted tetrahedral environment [7], consisting of an N\(_2\)S basal plane and an apical S(Met) ligand at a long distance (2.9 Å) from the Cu. Single-crystal EPR measurements [7] have identified the Cu \( z \) axis as lying approximately parallel to the Cu-S(Met) direction.
The isotropic XANES spectrum for Cu(I) plastocyanin is relatively featureless. In contrast, the polarized XANES spectra [8] show several distinct absorption features and striking dichroism (Fig. 3). For the orientation with e||Cu-S(Met), there are intense features at -8986 and 9005 eV, with an unresolved shoulder at lower energy. The 8986 eV feature is reminiscent of the ls+4p transition discussed above. On the basis of the model compound spectra, the intensity of this feature can be taken as an indication that the Cu-S(Met) interaction is quite weak. This is consistent with the long Cu-S(Met) distance observed in the crystal structure.

The isotropic ls+3d intensity in Cu(I) plastocyanin is greater than that observed for centrosymmetric Cu(I) complexes. This intensity enhancement arises from mixing of the Cu 3d and 4p orbitals [1]. Since the ls+3d transition is only observed (Fig. 3) for orientations having e perpendicular to the Cu z axis, it is clear that this mixing must involve 3d+4p y or 3d+4p z. This supports the EPR determination [7] that the symmetry of the Cu site is approximately C3v rather than D3d. Previous studies of Cu model compounds [9] had shown that small A|| hyperfine coupling constants, could be explained by 3d+4p orbital mixing. The polarized XANES spectra show that this explanation cannot account for the small A|| values observed for plastocyanin.

CONCLUSIONS

Polarized measurements can be used to enhance both the sensitivity and the resolution of XANES spectra. By permitting an empirical determination of the polarization properties of specific edge features, polarized XANES measurements provide a stringent test of potential theoretical models. By probing the valence orbitals, polarized XANES spectra can be used to study the electronic structure of the metal center.

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REFERENCES