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Natural circular dichroism in XANES of chiral transition metal systems

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Abstract: The possibility of natural circular dichroism measurements in XANES and EXAFS is promised by new helical undulators at high brilliance synchrotrons. The study of chiral transition metal sites can provide important structural information on enzyme active sites and synthetic asymmetric catalysts. In the present work the mechanism for the manifestation of rotational strength in core-valence transitions of naturally chiral transition metal systems is considered. The approach taken is to evaluate the effect of pseudoscalar and pseudotensor perturbations in cubic achiral parent geometries. The expected magnitudes of the rotational strengths of K- and L-edge transitions are discussed for the O_h - D_3 system tris(1,2-diaminoethane) Co^{III} in the context of recent rotation measurements. The key problem of the source of core-valence magnetic dipole transition moments is examined. A treatment is outlined incorporating the effects of valence state mixing and core level mixing brought about by the chiral molecular potential. Sum rules and restricted sum rules for rotational strengths are discussed.

1. INTRODUCTION

1.1 Natural Circular Dichroism

The general theory of circular dichroism (cd) is well established [1,2]. The area under a circular dichroism band, $\int \Delta \epsilon d\nu$ ($\Delta \epsilon = \epsilon_l - \epsilon_r$ being the difference in the molar absorptivities for left and right circular polarisations), is related to the rotational strength, R_{if} , of a transition $i \rightarrow f$. The rotational strength is given by the imaginary part of the pseudoscalar product of the electric dipole (μ) and the magnetic dipole (m) transition moments,

$$R_{if} = \text{Im} \{ \langle i | \mu | f \rangle \langle f | m | i \rangle \} \quad (1)$$

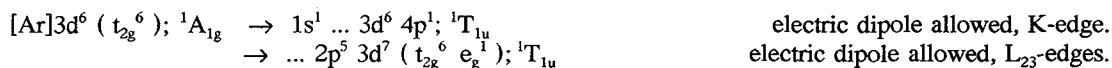
, for a randomly oriented sample. The use of circular dichroism in the study of natural chirality has provided invaluable information concerning the mechanisms by which chirality is manifested in electronic and vibrational transitions and the relation of spectroscopic observations to absolute stereochemical structure. Such measurements have been made for valence state electronic transitions throughout the ultraviolet, visible and near infrared regions and have been extended into the vacuum uv and the vibrational infrared more recently. There have been no measurements as yet of *natural* cd in the X-ray region although there have been a number of studies of *magnetic* X-ray cd, notably in ferromagnets [3]. The complementary measurement of the rotation of plane polarised radiation (related to the cd via the Kramers-Kronig transformation) has shown encouraging results in a study [4] at the Co K-edge in the coordination compound $[Co(en)_3]Br_3 \cdot H_2O$ ($en = 1,2$ -diaminoethane). The present paper will concentrate on the mechanism of cd in this system which represents a paradigm of transition metal coordination complexes.

The development of helical undulators producing modulated circular polarisation promises the possibility of systematic investigations of natural chirality in the X-ray region, involving the measurement of circular dichroism in absorption near-edge structure (XANES) and in EXAFS. It is expected that this will lead to an enhancement of the structural information obtainable for metal ions at chiral sites in metalloenzymes and synthetic asymmetric catalysts. However it seems likely that natural cd will be a weak effect inasmuch as the core electrons, especially in heavy atoms, have little experience of the molecular chirality. It is therefore timely to provide some theoretical guidance as to the likely magnitude of the effect and the possible choices of chemical systems which will maximise the chances of experimental success.

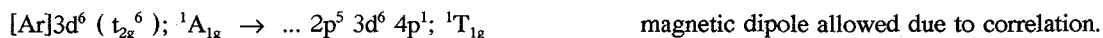
2. TRANSITION METAL SYSTEMS

In metal complex systems a useful approach is to consider the metal ion/atom as an achiral (symmetric) chromophore in a dissymmetric environment provided by the ligands. This approach is the natural one for essentially metal-localised transitions (eg in d-d or f-f valence level spectroscopy) and is an appropriate starting point for the consideration of core \rightarrow valence excitations. In the 'three-bladed propeller' complex ion $[\text{Co}(\text{en})_3]^{3+}$, the dissymmetric environment is provided by a perturbation of D_3 symmetry acting on the states of an octahedral chromophore. Let us begin by considering the available excitations in the parent octahedral symmetry.

In an octahedral basis the core-valence transitions available for Co(III) systems are



However, in order to obtain rotational strength a source of magnetic dipole transition moment is required in a randomly oriented sample. This is a major problem for inter-shell excitations due to the selection rule $\Delta n = 0$ applying to matrix elements of the angular momentum operator. In fact correlation effects in the core-excited state are expected to overcome this problem by removal of the radial orthogonality between core and valence orbitals. The correlation effects lead to the induction of magnetic dipole intensity into the $2p \rightarrow 4p$ transition which therefore acts as a magnetic dipole source for L_{23} -edge rotational strengths:



The use of hydrogenic functions gives an estimated $\langle 2p | 4p \rangle$ radial overlap of $\sim 10^{-2}$. In the case of K-edges however the angular selection rule ($\Delta l = 0, l = 0 \rightarrow 1 = 0$) remains and it is necessary to include 1s-2p core mixing to obtain rotational strength. However, due to the large separation between the $1s^1 2p^6 3d^6 4p^1$ and $1s^2 2p^5 3d^6 4p^1$ configurations, it might be expected that K-edge rotational strengths would be weaker by 2 or 3 orders of magnitude than those observed at the L_{23} -edges.

The coupling of the electric dipole and magnetic dipole sources, brought about by the chirality in the environment of the metal ion chromophore, may be expressed through perturbation theory. For example, for the rotational strength an electric dipole allowed transition:

$$R({}^1A_{1g} \rightarrow {}^1T_{1u}) = \langle {}^1A_{1g} | \boldsymbol{\mu}^{(1)} | {}^1T_{1u} \rangle \langle {}^1T_{1u} | V^* | {}^1T_{1g} \rangle \langle {}^1T_{1g} | \mathbf{m}^{(1)} | {}^1A_{1g} \rangle \Delta E^{-1} \quad (2)$$

V^* represents the relevant parts of the D_3 potential which are considered in the next section. The energy denominator, $\Delta E^{-1} = [E({}^1T_{1g}) - E({}^1T_{1u})]^{-1}$, gives equal magnitude but opposite sign to the rotational strength of the complementary magnetic dipole transition, $R({}^1A_{1g} \rightarrow {}^1T_{1g})$, for this two-state model.

3. CHIRAL PERTURBATIONS

3.1 Symmetry Considerations

In considering the origins of circular dichroism it is sufficient to use only those perturbations, V^* , which are capable of mixing the valence basis in such a way as to produce chiral states $|f^*\rangle$ for which the transition $|i\rangle \rightarrow |f^*\rangle$ possesses collinear components of the electric and magnetic dipole moment operators. It is always possible to consider a chiral molecular geometry as derived from a parent achiral geometry by the application of such perturbations. These perturbations must rigorously possess certain symmetry properties [5]:

- A. The representation Γ^* is contained in the direct product $\Gamma_\mu \otimes \Gamma_m$ in the parent achiral symmetry.
 B. $\Gamma^* \rightarrow \Gamma_1$, the totally symmetric irreducible representation in the chiral subgroup of interest.

Γ^* has odd parity, is generally reducible in the parent achiral point group and always contains the pseudoscalar representation. For example, in the case of the trigonal perturbation of an octahedral system: $O_h \rightarrow D_3$, $\Gamma^* = A_{1u} + T_{2u}$; being the only parts of the D_3 potential contained in $\Gamma_\mu \otimes \Gamma_m = \Gamma_{t1u} \otimes \Gamma_{t1g}$ which descend to the A_1 representation in D_3 . There is a large family of trigonal dihedral metal complexes which correspond to this case, eg $[\text{Co}(\text{en})_3]^{3+}$. In accounting for the optical activity of these systems an important fact is that the pseudoscalar representation, $A_{1u}(O_h)$, is first encountered in a spherical harmonic expansion at the ninth rank (transforming like the cartesian product $xyz(x^2-y^2)(y^2-z^2)(z^2-x^2)$). This means that the pseudoscalar perturbation is incapable of providing the appropriate mixing within an $s + p + d + f$ orbital basis. Recourse must be made to the pseudotensor part V_{12u} .

3.2 Sum Rules

An important consequence of this predominance of the pseudotensor perturbation is *the restricted sum rule*: the net rotational strength vanishes for the sum over D_3 component transitions: $A_1 \rightarrow A_2$ (z polarisation), $A_1 \rightarrow E$ (x,y polarisation). This result, which is found to hold to a good approximation for a large number of cases of intravalence cd, may be obtained by applying irreducible tensor methods [6] to equation (2) using $V^* = V_{12u}$ and employing the symmetry determined linear combinations of O_h basis states:

$$A_2(D_3) = (\sqrt{3})^{1/2} (T_{1x} + T_{1y} + T_{1z}); \quad E_x(D_3) = (1/6)^{1/2} (T_{1x} + T_{1y} - 2T_{1z}); \quad E_y(D_3) = (1/2)^{1/2} (T_{1x} - T_{1y}).$$

$$R(A_1 \rightarrow A_2) = \sqrt{3} \sum_{\alpha,\gamma} V \begin{pmatrix} T_{1u} & T_{2u} & T_{1g} \\ \alpha & \beta & \gamma \end{pmatrix} \mathbf{R} = \sqrt{3} \sum_{\alpha,\gamma} (1/6)^{1/2} |\varepsilon_{\alpha\beta\gamma}| \mathbf{R} = -2 (1/6)^{1/2} \mathbf{R} \quad (3)$$

$$R(A_1 \rightarrow E_y) = 1/2 \sum_{\beta} V \begin{pmatrix} T_{1u} & T_{2u} & T_{1g} \\ x-y & z & x-y \end{pmatrix} \mathbf{R} = (1/6)^{1/2} \mathbf{R} = R(A_1 \rightarrow E_x) \text{ by symmetry.} \quad (4)$$

Here $\mathbf{R} = \sqrt{3} \langle {}^1A_{1g} \| \boldsymbol{\mu}^{T1u} \| {}^1T_{1u} \rangle \langle {}^1T_{1u} \| \mathbf{V}^{T2u} \| {}^1T_{1g} \rangle \langle {}^1T_{1g} \| \mathbf{m}^{T1g} \| {}^1A_{1g} \rangle \Delta E^{-1}$ and $\varepsilon_{\alpha\beta\gamma}$ is the alternating tensor.

Due to the restricted sum rule the magnitude of the trigonal field splitting is likely to be an important factor in the experimental observation of cd in near edge absorption bands.

4. CONCLUSIONS

The predominance of pseudotensor over pseudoscalar perturbations in determining the cd in trigonally chiral metal complexes leads to a sum rule for trigonal component transitions. The observation of cd in xanes is therefore expected to depend on the magnitude of the trigonal field splitting.

Attention is drawn to the importance of core relaxation in overcoming the magnetic dipole selection rule for intershell $\Delta l = 0$ transitions in randomly oriented systems ⁽¹⁾.

In oriented systems however, quadrupole transition moments may give an equally significant contribution to the rotational strengths. Uniaxial oriented single crystals overcome the cancellation effect of the overlapping trigonal component cd, providing an enhancement factor of $\sim 10^2$ in intravalence cd. This technique is likely to be of advantage in xrcd if suitable crystals of sufficient thinness are available.

There is no doubt of the importance of Coulomb and exchange correlation and spin-orbit coupling in determining the details of the $2p \rightarrow 3d$ absorption spectra [7]. However, these interactions have no direct chiral effect, causing changes only in the distribution of rotational strengths. This short paper has followed a simple perturbational approach to obtain essentially symmetry determined conclusions. Further work is under way using LDF and Hartree-Fock methods to examine the detailed mechanism of natural cd in xanes and exafs.

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⁽¹⁾This problem is not encountered in magnetic xrcd where large intravalence magnetic dipole moments are available.