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Detection Limits for Natural Circular Dichroism of Chiral Complexes in the X-ray Range

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Whereas both Magnetic Circular Dichroism and Faraday Rotation studies have been successfully carried out at the K-, L- and M- absorption edges of metal atoms in ferromagnetic systems, *Natural optical activity* of chiral complexes has not yet been detected quite unambiguously in the X-ray range. We review a number of theoretical arguments which confirm that the optical asymmetry factor g_σ should be very small in the X-ray range for unoriented powdered samples, especially at the K-absorption edges. This stimulating challenge prompted us to start an intensive programme of measurements aimed at detecting natural circular dichroism in both the soft and "firm" X-ray ranges. Although some of our experiments look consistent with the presence of the expected effect, our conclusions cannot be taken yet as definitive due to the presence of a weak residual signal which, unfortunately, could not be eliminated.
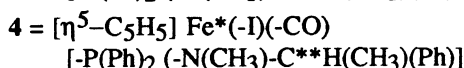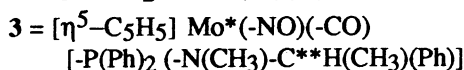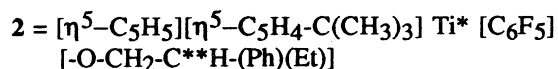
Keywords : XAFS, Soft-X-ray Spectroscopy, Natural C.D., Rotatory Strength, Optical Asymmetry

1. INTRODUCTION

Since the pioneering experiment reported by Schütz *et al.*[1], the interest in X-ray Magnetic Circular Dichroism and Faraday Rotation has grown rapidly, not only for ferromagnetic materials but also for paramagnetic systems investigated at very low temperature under very high magnetic fields. However, the chemists have known for a long time that optical activity can be observed in the absence of any magnetic field with *chiral molecules* which do not possess a rotation-reflection axis of any order (S_n). Unfortunately, previous attempts to observe natural optical activity in the X-ray region have met with very little success and, even in the case of the ellipsometric measurements reported recently by Siddons *et al.*[2], the conclusions remain ambiguous.

We will first identify the terms that may contribute to a rotatory strength in X-ray absorption spectroscopy. The corresponding optical asymmetry (*i.e.* the Kuhn Factor "g_σ") can, however, be predicted to be very small, especially near a K-absorption edge, and for unoriented samples. Our predictions are supported by *ab initio* calculations on a model disulfide compound (H_2S_2). This is contradicted by the "large" asymmetry factor ($g_\sigma \approx 1\%$) that can be derived from the ellipticity data reported by Siddons *et al.*[2] for a powdered sample of 1 = tris-[ethylen-diamine] Cobalt (III) investigated at the Cobalt K-edge. This exciting result prompted us to launch an intensive campaign of X-ray CD measurements on several stereogenic metal complexes where the metal is itself a well proven center of asymmetry :

$$2 = [\eta^5\text{–}C_5H_5][\eta^5\text{–}C_5H_4\text{-}C(CH_3)_3]\ Ti^*\ [C_6F_5]$$
$$[\text{-O-}CH_2\text{-}C^{**}H\text{-(Ph)(Et)}]$$

$$3 = [\eta^5\text{–}C_5H_5]\ Mo^*(\text{-NO})(\text{-CO})$$
$$[\text{-P(Ph)}_2\ (\text{-N(}CH_3)\text{-}C^{**}H(CH_3)(Ph))]$$

$$4 = [\eta^5\text{–}C_5H_5]\ Fe^*(\text{-I})(\text{-CO})$$
$$[\text{-P(Ph)}_2\ (\text{-N(}CH_3)\text{-}C^{**}H(CH_3)(Ph))]$$

Each one of these compounds has 2 centers of optical asymmetry, so-that there are 2 stereoenantiomeric couples with opposed rotation angles at optical wavelengths :

$$[\alpha]_D^{25}\ (2: \text{-/+; s/r}) = \pm 168° ; \pm 151°$$

$$[\alpha]_{365}^{20}\ (3: \text{-/+; s/r}) = \pm 2845° ; \pm 2570°$$

$$[\alpha]_{436}^{20}\ (4: \text{-/+; s/r}) = \pm 780° ; \pm 560°$$

With such huge specific rotations[3,4], species **3** and **4** were very attractive candidates for our programme. Note that the ligand field at the metal is truly asymmetric in the coordination shell, while this is not the case for species 1. All stereoisomers have been isolated and purified at the University of Dijon. The preparation of species **3** and **4** followed closely the original synthesis described by Brünner *et al.*[3,4]. No significant enantiomorphic impurity could be

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detected from the NMR spectra.

2. ROTATORY STRENGTHS IN XAS :

2.1 General Formulation :

In contrast to MCD, *Natural* CD does not exist under the strict Electric Dipole approximation. This is because optical activity refers to the *cross terms* that couple the electric transition dipole $E1_{(i \to f)}$ either to the transition magnetic dipole $M1_{(i \to f)}$, or to the electric transition quadrupole $E2_{(i \to f)}$ in the complete expression of the X-ray absorption cross sections. One may define therefore two different rotatory strengths[5] :

$$R^{11} \propto 2q \, [kA_d]^2 \sum_{m''} \mathcal{D}^1_{m''q} \cdot \mathcal{D}^1_{-m''-q}$$

$$.\text{Im} \, [\langle i \, |E1| \, f \rangle . \langle f \, |M1| \, i \rangle] \qquad (1)$$

and :

$$R^{12} \propto q \, [kA_d]^2 \sum_{m'} \frac{k\sqrt{3}}{6} \, \mathcal{D}^1_{m'q} \cdot \mathcal{D}^2_{m'-q}$$

$$.\text{Re} \, [\langle i \, |E1| \, f \rangle . \langle f \, |E2| \, i \rangle] \qquad (2)$$

$\mathcal{D}^j_{mq}(\alpha,\beta,\gamma)$ being a standard notation for the irreducible Wigner rotation matrices specifying the direction of propagation of the incoming photon (of helicity q and wave- vector k) in the internal coordinate system of the absorbing atom. From the orthogonality of the Wigner matrices :

$$\int \text{Sin}\beta \, d\alpha d\beta d\gamma \, \mathcal{D}^1_{mq}(\alpha,\beta,\gamma) . \mathcal{D}^2_{m-q}(\alpha,\beta,\gamma) = 0 \qquad (3)$$

one may immediately anticipate that the E1.E2 cross term will vanish unless the orientational isotropy of the medium is broken. This condition leaves no hope to detect any significant contribution of the quadrupolar term R^{12} in solutions nor in powdered samples.

In practical applications dealing with oriented systems, it may be more convenient to resort to the compact cartesian tensor notations introduced by Barron many years ago [6] :

$$\mathbb{R} = \{ \mathbb{R}_{\alpha\alpha} - \mathbb{R}_{\alpha\beta} \mathbb{S}_{\alpha\beta} \} \qquad (4a)$$

where :

$$\mathbb{R}_{\alpha\beta} = \frac{1}{2} \{ R^{11}_{\alpha\beta} + R^{11}_{\beta\alpha} + \varepsilon_{\alpha\gamma\delta} R^{21}_{\gamma\delta\beta} + \varepsilon_{\beta\gamma\delta} R^{21}_{\gamma\delta\alpha} \} \qquad (4b)$$

$\mathbb{S}_{\alpha\beta}$ being the Saupe ordering matrix used to characterize anisotropic media. It is noteworthy that the contribution of the R^{12} terms is traceless, so-that *for isotropic media* Eq. (4a) simply reproduces the Rosenfeld equation.

Although M1 and E2 are usually associated with different irreducible representations and thus contribute to different electronic transitions, the corresponding rotational strengths involved in Eq. (4b) have identical transformation properties

with respect to spatial symmetries or time-reversal. In practice, this means that the sign of the CD effect will change *for both* R^{11} or R^{12} when a chiral system is replaced by its true enantiomer. On the other hand, it is easy to show that both terms change sign on applying the time-reversal Kramers operator, so-that the latter does not commute anymore with the Hamiltonian.[7]

2.2 Selection rules and non-orthogonality :

There are several reasons that may cause the cross terms R^{11} and R^{12} to vanish :

(i) The selection rules for E1, M1 and E2 being intrinsically different, some transitions may be symmetry forbidden and the corresponding transition matrix elements are zero ;

(ii) The pseudoscalar term R^{11} will also vanish whenever the transition dipoles $E1_{(i \to f)}$ and $M1_{(i \to f)}$ are orthogonal.

2.2.1 Atomic selection rules :

Let us start with the basic atomic selection rules *for a single electron* without L-S coupling :

E1 : $\Delta \ell = \pm 1$; $\Delta m = 0, \pm 1$

M1 : $\Delta \ell = 0 \quad (\ell_0 \neq 0)$; $\Delta n = 0$,

E2 : $\Delta \ell = 0, \pm 2 \quad (\Delta \ell \neq 0 \text{ if } \ell_0 = 0)$; $\Delta m = 0, \pm 1, \pm 2$

This would leave no hope to observe any E1.M1 interference term, especially at the K absorption edge. It is well known, however, that M1 transitions cannot be detected without a substantial amount of spin-orbit interaction[7] (j-j coupling being the most favourable scheme). The appropriate selection rules are therefore :

E1 : $\Delta J = 0, \pm 1$; $\Delta M = 0, \pm 1$

M1 : $\Delta J = 0, \pm 1 \quad (J_0 + J_f \geq 1)$; $\Delta M = 0, \pm 1$

E2 : $\Delta J = 0, \pm 1, \pm 2 \quad (J_0 + J_f \geq 2)$; $\Delta M = 0, \pm 1, \pm 2$

Nevertheless, as concerns core level spectroscopy, the main handicap to observe magnetic dipole transitions remains with the condition $\Delta n = 0$ which takes its origin in the fact that M1 does not act on the radial part of the wave-function.[8] Keeping in mind that the radial parts of $|i\rangle$ and $|f\rangle$ are orthogonal if $\Delta n \neq 0$, then it is obvious that the $M1_{(i \to f)}$ matrix elements will be all zero. For valence electron spectroscopy, C.I. between $|i\rangle$ and $|f\rangle$ are sufficient to break down the selection rule $\Delta n = 0$, but this becomes unrealistic for deep core level spectroscopy because the energy difference between the core state and the valence electrons is too large. There are, at least, two possibilities to relax the critical condition $\Delta n = 0$:

(i) the initial and final state wavefunctions $|i\rangle$ and $|f\rangle$ are multielectron wavefunctions and the core hole left behind with a charge , a spin and a finite angular momentum may strongly perturb the final state, so-that the orthogonality of

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the wavefunctions may not be anymore relevant.

(ii) relativistic corrections including spin-orbit coupling become very substantial for high Z elements (Z ≥ 70) and can break down the selection rule $\Delta n = 0$. Edlabadkar and Mande[9] have calculated that, in the case of the fluorescence lines of atomic Hf (Z=72), the ratio $\langle .N_{II} |M1| L_{II} \rangle / \langle M_{IV} |E1| L_{II} \rangle$ would be of the order of $\sim 0.1\%$.

Nevertheless, eventhough M1 and E2 transitions have the same scaling factor $[Z_{eff}/137]^2$, the atomic selection rules suggest that the detection of R^{12} (for oriented species) should be easier than the detection of the R^{11} cross term.

2.2.2 Molecular selection rules :

Only very few molecular point groups (C_n, D_{n+1}) are compatible with chirality, the key criterion being the absence of roto-reflexion (S_n) axes of any order. In coordination chemistry, any metal atom placed in a chiral ligand field (or crystal field) will also become optically active : the Wigner-Schellman theorem states that the ligand field will be chiral if the induced perturbation transforms like a cartesian *pseudo-scalar*.

2.2.3 Non-orthogonality condition :

At this stage, one may like to calculate the R^{11} cross term within the usual Multiple Scattering Wavefunction approach. The Kuhn asymmetry factor g_σ is defined as :

$$g_\sigma = \frac{2.[\sigma^+(\omega) - \sigma^-(\omega)]}{[\sigma^+(\omega) + \sigma^-(\omega)]} = \frac{2.\Delta\sigma(\omega)}{[\sigma^+(\omega) + \sigma^-(\omega)]} \quad (5)$$

where :

$$\Delta\sigma(\omega) = \frac{2\alpha}{3} \sum_{M0,\mu} (-1)^\mu \langle i | rC_\mu^1 | f \rangle \langle f | J_{-\mu} + S_{-\mu} | i \rangle \quad (6)$$

The inital and final state wavefunctions can be expressed as :

$$| i \rangle = \underline{R}_{\ell 0}^c (r) | J0\, M0 \rangle \quad (7a)$$

$$| f \rangle = \sum_{\ell m \sigma} B_{\ell m \sigma}^{\Gamma \gamma} \cdot \underline{R}_{\ell m \sigma}(r) \sum_{JM} | J M \rangle \langle J M | \ell m; \tfrac{1}{2} \sigma \rangle \quad (7b)$$

$B_{\ell m \sigma}^{\Gamma \gamma}$ being the scattered wave amplitude.

Injecting the E1 selection rules into Eq. (6):
$\ell = \ell_0 \pm 1$ and $J = \ell_0 \pm 1/2 = \ell' \mp 1/2$
it is rather straigthforward to show that :

$$\Delta\sigma = \frac{2\alpha}{3} \sum_\ell M_{\ell \ell 0}^1 M_{\ell 0 \ell 0}^0 [(2\ell +1)(2\ell 0 +1)]^{1/2} \, \text{Im} \sum_m \Delta Q_m \quad (8)$$

where :

$$\Delta Q_m = \left\{ [(\ell -m)(\ell 0 +1+m)]^{1/2} [B_{\ell m}\uparrow B_{\ell 0 m}^*\uparrow - B_{\ell -m}\downarrow B_{\ell 0 -m}^*\downarrow] \right.$$

$$\left. + [(\ell -m)(\ell 0 -m)]^{1/2} [B_{\ell m}\uparrow B_{\ell 0\, m+1}^*\downarrow - B_{\ell -m}\downarrow B_{\ell 0 -m-1}^*\uparrow] \right\} \quad (9)$$

and :

$$M_{\ell \ell 0}^1 = \int_0^\infty r^3 dr\, \underline{R}_\ell (r).\underline{R}_{\ell 0}^c (r) \quad (10a)$$

$$M_{\ell 0 \ell 0}^0 = \int_0^\infty r^2 dr\, \underline{R}_{\ell 0} (r).\underline{R}_{\ell 0}^c (r) \quad (10b)$$

Let us assume provisionally that the radial integral (10b) does not vanish as a consequence of the condition $\Delta n \neq 0$. It was first pointed out by Natoli[10] that the summation over M0 in Eq. (6), or over m in Eq. (8), yields zero unless the scattered wave amplitudes are spin-dependent. An alternative way to relax this condition is again to break the orientational isotropy of the medium. This suggests that, for a powdered sample, the Kuhn asymmetry factor g_σ can hardly exceed 10^{-3} under the most favourable conditions, excluding K-edge spectra.

The latter condition may be still reformulated differently : eventhough individual transitions in the whole set of M0 values exhibit a non-zero rotatory strength, the dichroism signal will cancel out unless the energy degeneracy of the corresponding transitions is removed by some strong enough perturbation (core hole, ligand field or crystal field etc...). This seems unrealistic for very deep core levels but quite possible for the outer shells close to the valence electrons. In the latter case, even the initial state is to be represented with scattered waves generated by a non spherically symmetric potential. This seems consistent with some of our results discussed in section 2.3.

2.2.4 Sum rule for rotatory strengths :

It has been known for a long time that the rotatory strengths are subject to the following sum rule :

$$\sum_f R_{i \to f}^{1n} = 0 \quad (11)$$

because :

$$\sum_f \langle a|E1|f\rangle\langle f|N|i\rangle = \langle i|E1.N|i\rangle = 0 \quad (12)$$

owing to the orthogonality of the multipole moments Note that this sum rule is valid for both R^{11} and R^{12}.

2.3 Ab-initio simulations on H2S2

We found highly desirable to start with a tentative evaluation of the order of magnitude of the optical asymmetry factor g_σ to be measured in the X-ray range with a chiral compound. The model disulfide H_2S_2 was a good candidate for such a test calculation because this is a small molecule for which the computation time is minimized. On the other hand, the absorbing elements, *i.e.* the two sulfur atoms, are intrinsic centers of asymmetry.
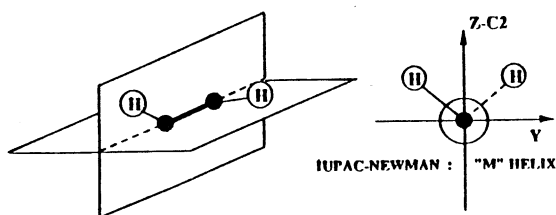
Fig.1 Stereogeometry of the model disulfide H_2S_2. According to IUPAC recommendations, the absolute configuration illustrated by the Newman projection is designated as a "M" helix

As illustrated by Fig. 1, the optical asymmetry results from the (dihedral) twist angle defined by the S1-S2 axis and the adjacent Hydrogen atoms. For this molecule, the point group is C_2, *i.e.* one of the chiral groups. For more simplicity, we have frozen the hindered internal rotation around the S1-S2 axis. Note that the disulfide chromophore is known to exhibit a fairly large rotatory strength (*ca.* 3.2 DBM) at optical wavelengths (240-350 nm). The importance of the disulfide fragment stems from its ability to bridge polypetide chains in a variety of biological compounds.

Ab-initio calculations were performed in the virtual orbital approximation using the QCPE HONDO-7.0 program[11,12] and a standard 4-31 G* basis in C.I. Eventhough the creation of the core hole could not be taken properly into account with this program, some useful information can already be gained concerning the relative order of magnitude of the E1 and M1 matrix elements. We have identified 17 occupied Molecular Orbitals (MO) + 3 antibonding excited states. Forgetting about the transitions initiated from the valence shell, we found that the only transitions that contribute to a significant rotatory strength systematically concern 2 excited states denoted respectively $\sigma^*2(B)$ and $\sigma^*3(A)$. Their energy splitting is of the order of ~75 meV. For the sake of simplicity, we may also restrict the discussion to the cases where the polarization vectors (Y,Z) are perpendicular to the helical screw axis (X)

K and L_I shells :

Owing to the molecular symmetry, the deep core levels are best represented with two MOs that are either antisymmetrical (B) or symmetrical (A) with respect to the C_2 rotation. Their energy splitting (~10 meV) is however much smaller than the life-time broadening. Transitions from the *sub*-states B to the excited states $\sigma^*2(B)$ and $\sigma^*3(A)$ are both allowed and optically active : the corresponding asymmetry factors g_σ are indeed very small and have opposite signs. Note that the optical activity is even smaller for the transitions initiated from the *sub*-states A. As these various transitions cannot be resolved experimentally, one is left with differential contributions :

$$g_\sigma \text{ (K -edge) } \leq 5.3 \ 10^{-8} \qquad g_\sigma \text{ (}L_I\text{-edge) } \leq 1.8 \ 10^{-5}$$

L_{II} and L_{III} Edges :

Again the corresponding core states may be best represented by six MOs : four of them : $\{A_5 ; B_7\}$ and $\{B_9 ; A_{10}\}$

were found to initiate optically active transitions to the low lying excited states. The most intense optical activity was found to be associated with the transitions :

$$A_5 \rightarrow \sigma^*3(A) \qquad A_5 \rightarrow \sigma^*2(B)$$
$$B_7 \rightarrow \sigma^*2(B) \qquad B_7 \rightarrow \sigma^*3(A)$$

our simulation predicting asymmetry factors as large as :

$$g_\sigma \ [A_5 \rightarrow \sigma^*3] \approx 3.1 \ 10^{-3}$$

Unfortunately, the energy splitting of the final states $\sigma^*2(B)$ and $\sigma^*3(A)$ is not large enough to leave any hope to resolve the corresponding transitions, so-that, again, one is left with "differential" asymmetry factors :

At the L_{II} - Edge : $g_\sigma \ [A_5 \rightarrow \{\sigma^*3, \sigma^*2\}] \approx 4.6 \ 10^{-4}$

At the L_{III} - Edge : $g_\sigma \ [B_7 \rightarrow \{\sigma^*2, \sigma^*3\}] \approx 7.8 \ 10^{-4}$

As our calculation does not take into account the creation of the core hole with a finite angular momentum and spin-orbit coupling, the energy splitting between *sub*-states A_5 and B_7 is very small and not significant. This is why the present results are still preliminary and the above figures are only indicative of the following trends :

(i) the predicted asymmetry factors associated with R^{11} are very small at the K- and L_I-edges so-that practically no natural dichroism should be detectable at these edges;

(ii) the asymmetry factor decreases rapidly with Δn, but small effects should remain detectable at the L_{II-III} or M_{IV-V} edges of transition metals in the soft X-ray range.

3. EXPERIMENTAL RESULTS

3.1 Ellipsometric measurements on species 1

We find useful at this stage to come back rapidly on the exciting but puzzling results reported by Siddons *et al.*[2] for a powdered sample of 1 = tris-[ethylendiamine] Cobalt (III) Whereas the rotation angle is quite small ($\delta\Phi \leq 250\mu$rad), the measured ellipticity is surprisingly large ($\psi \leq 6.4$ mrad) while the absorbance μd is *ca.* ~ 2.6. From standard definitions :

$$\psi = \pi \frac{d}{\lambda} [k^- - k^+] \ ; \ \mu d = 4\pi \frac{d}{\lambda} k^\pm \Rightarrow \frac{\psi}{\mu d} = \frac{\Delta k}{4k} = \frac{1}{4} g_\sigma \quad (13)$$

so-that we end up with an asymmetry factor ($g_\sigma \approx 0.98\%$) that is, within a factor of 2, as large as what was measured for the optical transitions[13] : $A_1 \rightarrow A_2$, E_{1a} . Such a "large" asymmetry should be easily detectable with standard instrumentation, especially at the L-edges where the CD is expected to be even larger. Unfortunately, any attempt to measure any signal in the soft X-ray has, up-to-now, failed.

Clearly, this result obtained at the K-edge of Cobalt can hardly be interpreted as a contribution of the Rosenfeld rotatory strength R^{11}. One has therefore to look for another mechanism. Even if we assume that the powdered sample was textured or non-randomly oriented, the effect seems too large to be due to the quadrupolar cross terms R^{12}.

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3.2 CD study of species 2 at the Ti* L-edges

We wish to report next the preliminary results of a study aimed at detecting natural CD in the soft X-ray range. The corresponding experiments have been carried out in 1991 at the NSLS (Brookhaven National Laboratory) using the "Dragon" spectrometer installed on the beamline port U4-B[14]. We looked at all the various stereo-isomers of species 2 :
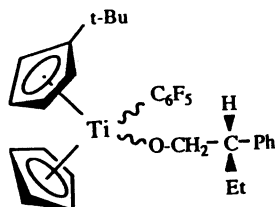
The absorbing Ti* atom is clearly an intrinsic center of asymmetry because it is π-bonded to 2 non-equivalent cyclopentadienyl (Cp) rings and σ-bonded to a pentafluorophenyl ligand + to the oxygen atom of an optically active alcoolate. Note that the t-Butyl substituent of the Cp ring is a bulky repulsing group that induces both a significant charge delocalization and steric effects[15]. Among the various diastereoisomers investigated in this programme, the best results were systematically obtained with the (R+)Ti* / (S-) alcoolate or its true enantiomer that could be prepared as perfectly homogeneous oily samples featuring a low vapour pressure compatible with high vacuum experiments.

Total e⁻ yield excitation spectra were recorded at the Ti* L$_{II-III}$ - edges. The circular polarization rate was varied by collecting the X-ray photons emitted above or below the symmetry plane of the machine. The detector was a low noise channeltron. Experimentally, the main difficulty arised from a severe charging effect which depended critically on the sample preparation but was stabilized after a few scans so-that reproducible differential spectra could be obtained. The background substraction in the data processing was another critical matter : the effects on the differential spectra were minimized by treating the crude spectra strictly in the same way.
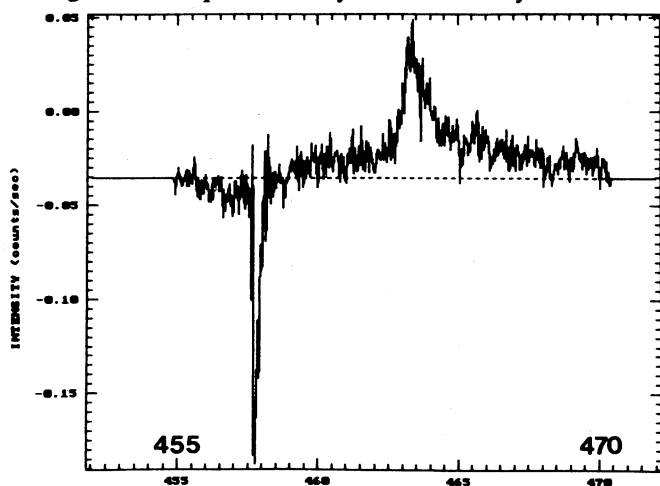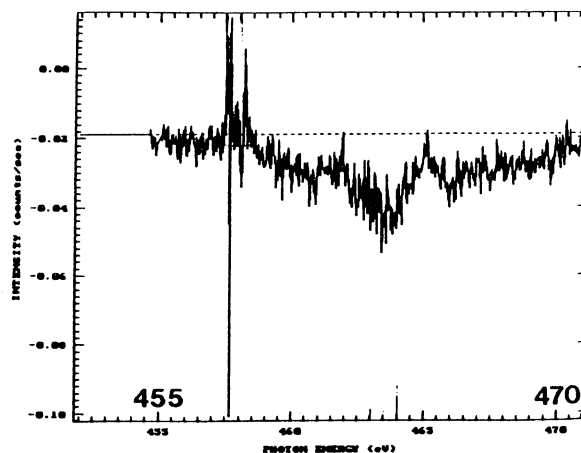
Fig. 3 : Racemic mixture : Difference spectrum derived from two absorption spectra recorded with reversed circular polarization.
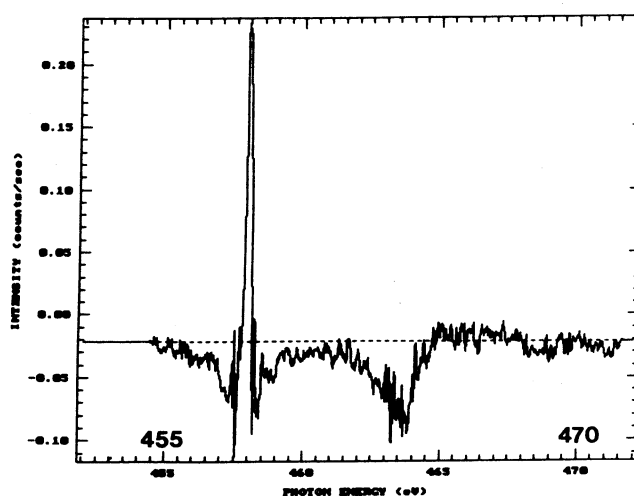
Fig.4 : Difference spectrum derived from the absorption data of the (R+) Ti* / (S-) Alcoolate and its enantiomer (R-) Ti* / (S+) Alcoolate with the same circular polarization.

The point at issue is to know whether the CD spectrum reproduced in Fig. 2 is real or not. Several arguments can be put forward to support the reality of the "measured CD " :

(i) the systematic reproducibility of the effect ;

(ii) the reversed sign at the L$_{II}$ and L$_{III}$ edges

(iii) the "measured CD" largely exceeds the residual non-random error between two successive scans ($\leq 0.2\%$);

(iv) no comparable signal is detected with the inactive racemic mixture containing the enantiomers in equal proportions (See Fig. 3).

(v) a similar difference spectrum is obtained on subtracting the spectra of the two enantiomers recorded with the same polarization. (See Fig.4)

Unfortunately, the last argument remains ambiguous as the sign of the difference did not change on flipping the polarization. One may therefore suspect the contribution of a systematic error that would not cancel out in the subtraction. For instance, the measurements are inherently very sensitive to sample heterogeneity when flipping the circular polarization.

Fig. 2 : (R+) Ti* / (S-) Alcoolate : Difference spectrum derived from two absorption spectra recorded with reversed circular polarization.

The most serious argument against the reality of the "measured CD" is to be found in the intensity of the signal : the peak asymmetry factor at the L_{III} edge would be typically in the range : $0.5\% \leq g_\sigma \leq 1.5\%$. which seems unrealistic, even for experiments carried out at the L-edge. A possible explanation could be the partial alignment of the molecules near the surface of the oily sample due to the presence of a strong electric field associated with the charging problem.

3.2   Tentative alignment of chiral compounds

The aim of this project is to detect the contribution of the R^{12} term at a K-absorption edge where the Rosenfeld term R^{11} should be negligible. The most obvious strategy to align chiral molecules is to grow single crystals and this is now being done at the University of Dijon. In the mean time, we tried to investigate another option which consisted in dissolving compounds 3 and 4 in a liquid crystal and to align the latter with an electric or a magnetic field. This is a very old technique which has been extensively used in NMR / EPR since the pioneer work of Saupe et al.[16], but it has apparently never been used in X-ray absorption spectroscopy. For our project, we selected a mixture of nematogens (Merck - LC ZLI 1844) featuring a convenient temperature range of the nematic phase :

Clearing temperature : $T_c = +60°C$

Nematic / Smectic transition : $T_{ns} \leq -20°C$

With a positive anisotropy of magnetic susceptibility ($\Delta\chi > 0$), the optical axis of the liquid crystal is expected to be parallel to the applied magnetic field.

In order to check the alignment of the solute molecules when the liquid crystal is oriented in a strong magnetic field., we substituted first Bromobenzene (symmetry : C_{2v}) to the chiral complexes. The Br* K-edge Xanes spectrum was then recorded at LURE (Orsay) on the Energy Dispersive EXAFS station. As illustrated by Fig.5, a strong linear dichroism appears when the liquid crystal is oriented. This can be explained by an enhanced transition probability towards a quasi-bound excited state that may be either $\pi^*(B_2)$ or $\sigma^*(A_1)$ [17].

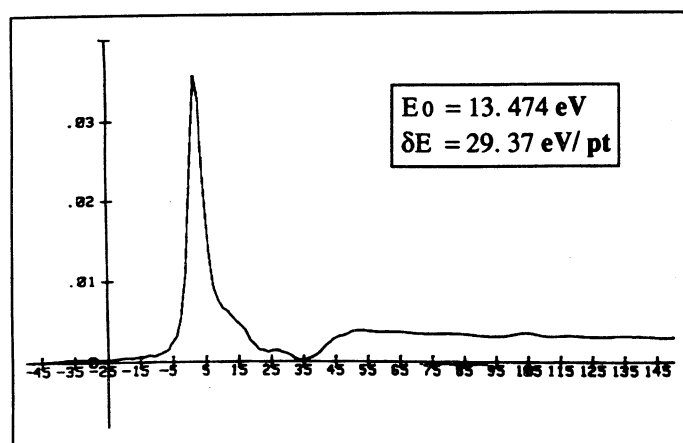$E_0 = 13.474 \, eV$
$\delta E = 29.37 \, eV/pt$

Fig. 5 : Linear Dichroism of oriented Bromobenzene in a magnetically aligned liquid crystal. (Single scan)

We cannot make any definitive assignment until the relative orientation of the solute with respect to the optical axis of the liquid crystal is known. Note that this oriention should depend on the nature of the nematogen[18]. In the present case, the C_2 axis of bromobenzene seems to coincide with the direction of the applied field so that the final state is most probably $\sigma^*(A_1)$, as also suggested by rather large spectral width of the signal. Owing to the C_{2v} symmetry of Bromobenzene, no circular dichroism is to be observed with the aligned Bromobenzene as a consequence of Eq (4a).

We failed to detect any CD dichroism with the oriented solutions of the chiral species 3 and 4. Under the conditions of the experiment, the limit of detection of a CD signal was $\Delta\mu/\mu \leq 0.1\%$. Special efforts are being made in order to push down the detection limits but it seems already well established by our experiments that, even with oriented compounds, the optical asymmetry has to be very small.

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