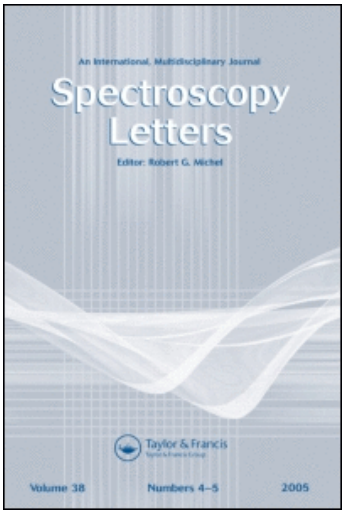

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Åke Davidsson[a]; Bengt Nordén[a]
[a] Department of Inorganic Chemistry 1, University of Lund, Lund, Sweden

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ELECTRIC DICHROISM SPECTROSCOPY

Åke Davidsson and Bengt Nordén

Department of Inorganic Chemistry 1, University of Lund,
Chemical Center, P.O.B. 740, S-220 07 Lund, Sweden.

Legrand-Grosjean circular dichroism spectrometers are easily converted to detect electric dichroism (ELD), i.e. anisotropic absorption due to an external electric field. The sensitivity enables the studying of small molecules with dipole moments or anisotropic polarisabilities. The observed ELD is in part due to the orientation of the absorbing transition dipole (the orientational distribution being given by the interaction between the dipole and the electric field) but contributions due to perturbations (type Stark) may generally not be neglected. The method is predicted to become an important complement to LD studies in oriented matrix, to evaluate directions of transitions moments, but other applications are also possible. The experimental qualifications are demonstrated on two different species, nitrobenzene and Cu(II) ethylenediamine(acetylacetone)$_2$.

The Kerr effect, i.e optical birefringence (of e.g liquid nitrobenzene) due to an applied electric field, discovered one hundred years ago by the Reverend Kerr in Glasgow, [1] is well known for its use in light modulators. It is generally referred to as an effect of molecular alignment by the action of the electric field on permanent dipoles. Actually this explanation is not quite true for small molecules (like nitrobenzene) but holds for macromolecules with large permanent dipole moments or anisotropic polarisabilities, so let us first introduce the concept of electric linear dichroism, ELD, for such a case.

Then, ELD = $A_{||}-A_{\perp}$ (|| being the direction of the electric field vector $\vec{F}$) arises from the interaction between the transient electric field $\vec{E}$ of the incident electromagnetic radiation and the electric transition moment, $\vec{\mu}_{ab}$, (electronic transition a → b)

due to non random molecule distribution. ELD/A (A = absorption in absence of field) is obtained by averaging $[(\mu_{ab})_{\parallel}^2 - (\mu_{ab})_{\perp}^2]/(\mu_{ab})^2$ over all orientations weighted by the Boltzmann factor of the interaction energy $U = \mu F \cos\phi$, where ϕ is the instantaneous angle between the dipole moment $\vec{\mu}$ ($\equiv \vec{\mu}_{aa}$) and $\vec{F}$:

$$\frac{ELD}{A} = f(x)[(3\cos^2\theta_{ab} - 1)/2]$$

$$f(x) = 1 - \frac{3\coth x - 3/x}{x} \approx x^2/15 \text{ for } x \ll 1$$

$$x = \mu F/kT \quad (= 2.42\cdot10^{-7}\ \mu F/T \text{ with } \mu \text{ Debye, } F \text{ V m}^{-1} \text{ and } T \text{ K}) \qquad (1)$$

θ_{ab} the angle between $\vec{\mu}_{aa}$ and $\vec{\mu}_{ab}$ gives us the direction of $\vec{\mu}_{ab}$ since the direction of $\vec{\mu}_{aa}$ is generally easily obtainable, either from symmetry or from charge considerations. This is a very important additional information about a molecule, beyond that obtained from $|\mu_{ab}|^2$ (= dipole strength), about electronic structure, conformation and interactions.

The advantage of ELD to other LD methods is the unambiguous orientation (the single orientation axis in the molecule is known and the orientational distribution purely uniaxial). However, two difficulties arise with ordinary small molecules: 1. As seen from eq. (1), the typical effect (let μ be 5 Debye and $F = 2\cdot10^7$ V m^{-1} = the highest field that can be applied to liquid solvent without break-through) is thousends of times smaller than those of e.g. stretched film experiments. 2. Eq. (1) is not true at high fields, but contributions arise by perturbed electronic states and dipole moments. Thus e.g. also the random case (a rigid isotropic glass) exhibits ELD, though then the orientation factor $f(x) = 0$ by definition. The first of these problems is the reason for why few experimental results have been reported.

We here describe a method by which the spectral as well as signal resolving powers of a commercial circular dichroism spectrometer can be employed in ELD detection: The photo-

modulator of the CD instrument is disconnected and its oscillator arranged to supply a Kerr cell containing the sample in the light-path with a high tension, sinusoidally oscillating between 0 and some amplitude value V_0. The light incident on the cell is constantly linearly polarised parallel to the field and of constant intensity. If the sample exhibits ELD, the light intensity reaching the photomultiplier will contain an ac component (of the same frequency as the excitation voltage) which, by the locked-in electronics, will lead to a recorder deflection ELD = $A_{||}$-A (technical details described elsewhere [2]). If the measurement is performed instead with an angle χ between $\vec{E}$ and $\vec{F}$ we shall write $ELD_\chi = A_\chi - A$. If orientation of transition moments were the only determining factor, $ELD_{54.7^o} = 0$. We found two alternative methods of measuring ELD (static field perpendicular to light propagation + LD detection unit described earlier, [3] or oscillating field parallel to direction of propagation + the present unit but with unpolarised light) unsuitable for studying small molecules.

At converting a JASCO J-40 to ELD spectroscopy we employed $V_0 = 2 \cdot 10^4$ V (370 Hz); Kerr-cell with optical path of 1.0 cm; two planar Pt-electrodes 0.10 cm apart; lens f = 10 cm, focusing the light through the electrode gap; two cell positions yielding ELD_0 and $ELD_{54.7^o}$. Special precautions had to be made to eliminate two strongly disturbing effects due to contaminating orientable large particles (dust, crystallites) and to oscillating coronas at the high tension conductors.

Following the nomenclature in an outline recently given by Lin [4] we now consider ELD including the above mentioned field perturbations. An electric field applied along the Z axis in a laboratory-fixed coordinate system gives the absorption coefficient

$$k^Z_{ab}(\omega) = \frac{4\pi^2\omega}{\alpha_s \hbar c} \sum_\nu \sum_{\nu'} P_{a\nu} D_Z(a\nu, b\nu') \delta(\omega_{b\nu' a\nu} - \omega)$$

$$D_Z(a\nu, b\nu') \equiv |\langle a\nu | Z | b\nu' \rangle|^2$$

$$k^X_{ab}(\omega) = \cos^2\chi k^Z_{ab}(\omega) + \sin^2\chi k_{\chi ab}(\omega) \qquad (2)$$

In $k^{Z}_{ab}(\omega)$ light of frequency ω impinges with $\vec{E}$ parallel to Z i.e. parallel to $\vec{F}$, in $k^{\chi}_{ab}(\omega)$ we have an angle χ between $\vec{E}$ and $\vec{F}$. P_{av} is the normalised Boltzmann factor, $\delta(\omega_{bv'av} - \omega)$ is the delta function centered around the frequency of the electronic transition $a \rightarrow b$ (av and bv' are the ground and excited vibronic states). α_s is a factor considering medium effects. Other symbols have their usual meaning. By the perturbation method on the delta function, the dipole strength and the Boltzmann factor, changes of wavefunctions and energies are calculated and the subsequent effect on the absorption, which for an allowed electronic transition yields the expression:

$$
\begin{aligned}
(A_\chi - A)_\omega = {} & \frac{\beta F^2}{10}(3\cos^2\chi - 1)A(\omega) \times \\
& \times \{[\vec{p}_{ab}\cdot\boldsymbol{\alpha}(a)\cdot\vec{p}_{ab} - \tfrac{1}{3}\,\mathrm{Tr}\{\boldsymbol{\alpha}(a)\}] + \beta[(\vec{p}_{ab}\cdot\vec{\mu}_{aa})^2 - \tfrac{1}{3}|\vec{\mu}_{aa}|^2]\} + \\
& + \frac{\omega F^2}{10\hbar} \times \frac{\partial}{\partial\omega}\left\{\frac{A(\omega)}{\omega}\right\} \times \{[(2-\cos^2\chi)\mathrm{Tr}\{\Delta\boldsymbol{\alpha}(b,a)\} + \\
& + (3\cos^2\chi - 1)\vec{p}_{ab}\cdot\Delta\boldsymbol{\alpha}(b,a)\cdot\vec{p}_{ab}] + 2\beta[(2-\cos^2\chi)\cdot\vec{\mu}_{aa}\cdot\Delta\vec{\mu}(b,a) + \\
& + (3\cos^2\chi - 1)(\vec{p}_{ab}\cdot\vec{\mu}_{aa})\vec{p}_{ab}\cdot\Delta\vec{\mu}(b,a)]\} + \\
& + \frac{\omega F^2}{10\hbar^2} \times \frac{\partial^2}{\partial\omega^2}\left\{\frac{A(\omega)}{\omega}\right\} \times \{(2-\cos^2\chi)|\Delta\vec{\mu}(b,a)|^2 + \\
& + (3\cos^2\chi - 1)|\vec{p}_{ab}\cdot\Delta\vec{\mu}(b,a)|^2\} \qquad (3)
\end{aligned}
$$

Here $\beta = 1/kT$; $\vec{p}_{ab}$ is a unit vector along the transition moment $\vec{\mu}_{ab}$; $\boldsymbol{\alpha}(a)$ and $\vec{\mu}_{aa}$ is the polarisability tensor and the permanent dipole moment of the ground state, respectively; $\Delta\boldsymbol{\alpha}(b,a)$ and $\Delta\mu(b,a)$ is the difference in polarisability and the difference in dipolemoment, respectively, between ground and excited states. $A(\omega)$ is the random absorption at frequency ω. F denotes the effective field. Obviously the measurable quantity $(A_\chi - A)_\omega$ is proportional to F^2, it is further composed of one orientation term weighted by the random absorption, and two disturbance terms of polarisability and dipole moment

expressions weighted by first and second derivatives of A(ω). The shapes of these contributions are shown in FIG 1. The first derivative represents the apparent energy perturbation (because its unsymmetry around absorption max.), the second derivative broadens the apparent absorption.

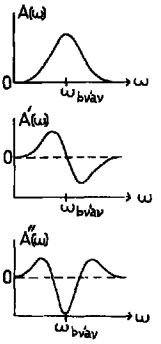

FIG 1.
Typical absorption-band and its first and second derivatives versus frequency.

Studying molecules with predominating dipole moments, polarisability effects can be neglected. Thus for polar molecules in a rigid medium of random orientation eq. (3) simplifies to (let $\chi = 0$):

$$(A_{||}-A)_\omega = \frac{\omega F^2}{5\hbar^2}\frac{\partial^2}{\partial\omega^2}\{\frac{A(\omega)}{\omega}\}[\frac{1}{2}|\Delta\mu(b,a)|^2 + |\vec{p}_{ab}\cdot\Delta\vec{\mu}(b,a)|^2] \quad (4)$$

A possible application of this special case is to use the fine structure of the second derivative to resolve bands obscuring each other in the usual absorption. This is exemplified for nitrobenzene, where the ELD spectrum in EPA (-190°C) shows at least three bands. However, if we want to determine their transition moment directions we need two linearly independent ELD spectra at two angles χ and an accurate resolution of the second derivatives into contributions from the individual transitions. This is often impossible due to strong overlaps.

When relative polarisations are available (from stretched sheet LD or by photo-selection methods) a more qualitative ELD evaluation is often sufficient to remove remaining directional ambiguities. Thus, Labhart [5] defined a system of molecules with molar absorption coefficients ε_x, ε_y, ε_z, all oriented and interacting with x,y and z polarised radiation (the dipole moment

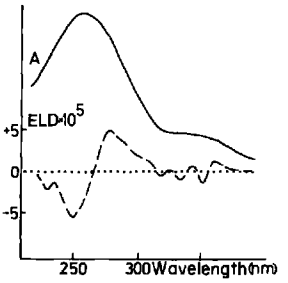

FIG 2.
Absorbance ___, $ELD^{F=120\ kV/cm}_{=0}$ --- and baseline ... of Nitrobenzene in EPA at -190°C. Sensitivity $1.5\cdot10^{-5}$ absorbance units/an.

$\vec{\mu}_{aa}$ is oriented along the z axis). He identified the effect of the field on the absorption with the following expansion, assuming the dipole moment be oriented along e.g. the z-axis and the transition moment be oriented independently of the field along either x, y or z.

$$\varepsilon_k^{Field} = \varepsilon_k^{F=0} + \sum_i \frac{\partial \varepsilon_k}{\partial F_i} F_i + \frac{1}{2} \sum\sum_{ij} \frac{\partial^2 \varepsilon_k}{\partial F_i \partial F_j} F_i F_j$$

$$i,j,k = x,y,z \qquad (5)$$

He assumes $\frac{\partial \varepsilon_k}{\partial F_i} = \frac{\partial^2 \varepsilon_k}{\partial F_i^2} = 0$, $k \neq i$, that is only longitudinal perturbation is considered while transversal effects are neglected. From measurements at two angles χ we may get two pieces of the (diagonal) absorption tensor $(A_x, A_y, A_z)/C \cdot d = (\varepsilon_x, \varepsilon_y, \varepsilon_z)$, viz. ε_z (parallel to the dipole) and $\varepsilon_x + \varepsilon_y$:

$$A_{\chi=0}/C \cdot d = (\varepsilon_x+\varepsilon_y+\varepsilon_z)/3 + \frac{2\beta^2F^2}{45}|\vec{\mu}_{aa}|^2(\varepsilon_z - \frac{\varepsilon_x+\varepsilon_y}{2}) +$$

$$\frac{\beta F^2}{5}|\vec{\mu}_{aa}|^2 \frac{\partial \varepsilon_z}{\partial F_z} + \frac{F^2}{10}(\frac{\partial^2 \varepsilon_x}{\partial F_x^2} + \frac{\partial^2 \varepsilon_y}{\partial F_y^2} + \frac{\partial^2 \varepsilon_z}{\partial F_z^2}).$$

$$A_{54.7}/C \cdot d = (\varepsilon_x+\varepsilon_y+\varepsilon_z)/3 + \frac{\beta F^2}{9}|\vec{\mu}_{aa}|\frac{\partial \varepsilon_z}{\partial F_z} +$$

$$+ \frac{F^2}{18}(\frac{\partial^2 \varepsilon_x}{\partial F_x^2} + \frac{\partial^2 \varepsilon_y}{\partial F_y^2} + \frac{\partial^2 \varepsilon_z}{\partial F_z^2}) \qquad (6)$$

Thus we get from the measured A and $ELD_\chi = A_\chi - A$

$$(ELD_{||} - \frac{9}{5} ELD_{54.7}) \frac{45}{2\beta^2F^2|\mu_{aa}|^2} \equiv \Delta$$

$$A = (A_x+A_y+A_z)/3$$

$$A_z = A + \frac{2}{3}\Delta$$

$$A_x + A_y = 2A - \frac{2}{3}\Delta \qquad (7)$$

Cu(II) ethylenediamine(acetylacetonate)$_2$

This complex is distorted from planarity in the ground state and we have recently by stretched film technique been able to make spectral assignments in the UV region. A π-π^* at the C=O group, with polarisation essentially along the permanent dipolemoment (4.5 Debyes), dominates the spectrum. It is expected to couple with the equivalent transition on the second C=O to yield two two exciton bands, one with z and one with x (out of "plane") polarisation. In FIG 3 typical $ELD^{F=0}$, $ELD_{\chi=0}$ and $ELD_{54.7}$ spectra are seen. Obviously, after subtracting $\frac{9}{5}$ $ELD_{54.7}$ a strongly positive LD remains at 300 nm in agreement with a predominant z-polarisation.

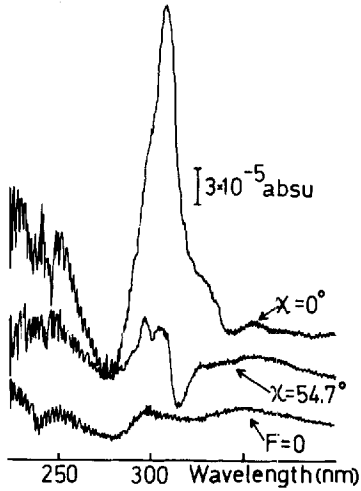

FIG 3.

Cu en(acac)$_2$ in n-hexane at F = 130 kV/cm (curves at different F or χ are for clarity moved apart). Sensitivity: $1.5 \cdot 10^{-5}$ absorbance units/cm. Slit-width: 0.6 m. Time constant: 1 sec.

Nitrobenzene

Though this is a classical molecule in electric field connections and ELD has before been studied by Labhart, our

ELD measurements combined with the stretched sheet method make it possible to identify a number of new bands. The absorption is a mixture of overlapping bands of mutually perpendicular polarisations and A, $ELD_{\chi=0}$ and $ELD_{54.7}$ therefore have very similar shapes. However, careful analysis according to eq. (6) shows one z-polarised region down to 300 nm, then a x and/or y polarised region down to 270 nm, and another (new) band of the same polarisation(s) around 240 nm. These conclusions are in agreement with the results from studies of nitrobenzene in stretched polyethylene film. Here the orientation (with the z-axis as the obvious orientation axis) is large, $(LD/A)_{max} = 7 \cdot 10^{-2}$ as compared to $(ELD/A)_{max} = 4 \cdot 10^{-4}$, and further bands may be distinguished: one with y (or x) at 215 nm, one with z polarisation below 200 nm. The component spectra as obtained from ELD and LD are shown in FIG 4, the final assignments are obtained by excluding the possibility of out of plan (x) polarisations.

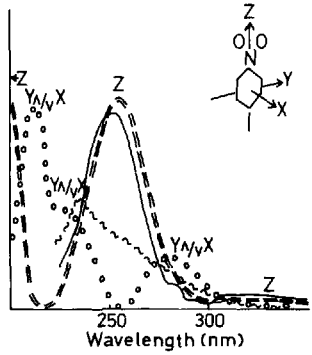

FIG 4.

Componentspectra of nitrobenzene 1) in n-hexane A_z ——, A_x+A_y ∿∿∿, 2) in stretched polyethylene A_z ===, A_y ...

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