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J. Phys. B: At. Mol. Opt. Phys. 28 (1995) L543–L548. Printed in the UK

LETTER TO THE EDITOR

Failure to observe electron circular dichroism in camphor

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Received 3 July 1995

Abstract. *We have searched for evidence of electron circular dichroism, the preferential* transmission of longitudinally polarized electrons through a chiral medium, using stereoisomers of camphor. Such an effect was seen by Campbell and Farago in 1987 for 5 eV electrons. Within our detection limit (~ 0.02%) we have not observed asymmetric transmission at either an incident electron energy of 1 eV or 5 eV. In preparation for this inquiry, we also measured the total scattering cross section for camphor in the energy range 0.5–5 eV.

Optical activity is the rotation of the plane of polarization of linearly polarized light as it passes through a chiral medium. A complementary phenomenon is circular dichroism: the preferential absorption of left- or right-handed circularly polarized light in a chiral medium. Farago (1980, 1981) pointed out that symmetry allows similar phenomena to be observed with electrons. Thus 'electron optical activity' is the rotation of a transverse electron spin vector in a plane perpendicular to the momentum in a chiral medium. Similarly, 'electron circular dichroism' is the preferential absorption of left- or right-handed longitudinally-polarized electrons in a vapour of chiral molecules. These parity violating effects arise because the target molecule lacks inversion symmetry.

Electron circular dichroism also causes scattered electrons that were initially unpolarized to develop a polarization component in the plane of scattering. Beerlage *et al* (1981) first searched for this effect but failed to see it within their experimental limits. A different experiment, performed by Campbell and Farago (1987), looked for preferential transmission of longitudinally polarized electrons through stereoisomers of camphor. They measured the asymmetry

$$\mathcal{A} \equiv \frac{(I_\uparrow - I_\downarrow)}{(I_\uparrow + I_\downarrow)} \tag{1}$$

where $I \uparrow (\downarrow)$ is the transmitted intensity of electrons for a given incident current with spins aligned (anti-aligned) with their momenta. Note that symmetry requires $\mathcal{A}$ to change sign when the target handedness is reversed. Campbell and Farago found $\mathcal{A}$ to be $23(11) \times 10^{-4}$ for D-Camphor and $-50(17) \times 10^{-4}$ for its enantiomorph (L-Camphor) at an incident electron energy of 5 eV and polarization of 0.28.

These results are intriguing, given that they would constitute the first evidence for an electronic analogue of the basic phenomenon of optical circular dichroism. Moreover, they lend credence to the Vester–Ulbricht theory (see Walker 1979) describing the origins of biological homo-chirality, which postulates that irradiation of primordial achiral molecules by beta-radiation caused a preferential production of one enantiomorph of, for example, amino-acids over the other enantiomorph. The subsequent amplification by self-replicative biological systems could lead to complete chiral purity of biological component amino acids (all L) and sugars (all D) in the biosphere (Walker 1979, Avetison *et al* 1991).

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However, the magnitude of $\mathcal{A}$ measured is much larger than that expected from present dynamical models. One mechanism, proposed by Kessler (1982), involves plural scattering of the incident electrons within the structure of the molecule. In this picture, the electron is first transversely polarized by spin–orbit interactions (Mott scattering). A final collision within the molecule projects some component of polarization along the electron's momentum. This non-zero longitudinal polarization does not average to zero over all orientations of the target molecule since its structure is chiral. Kessler estimated the largest polarization for a carbon chiral centre to be about 10^{-4}. One would then expect the transmission asymmetry $\mathcal{A}$ be of the same order.

Another approach to this problem is the bound helical electron model put forth by Hegstrom (1982) and co-workers (Rich *et al* 1982). Here, the singlet ground-state wavefunctions of the chiral molecule are mixed with higher-lying triplet states by spin–orbit interactions. The chiral molecule develops a net 'helical density', i.e. the bound electron's spin and momentum are correlated. From this model, Hegstrom obtains $\mathcal{A} \cong \eta(\alpha Z)^2$, where α is the fine structure constant, Z is the charge of the nucleus at the chiral centre of the molecule and η is a geometrical parameter which accounts for the degree of chirality in the molecule, and is typically about 10^{-2}. Thus, for most carbon-based chiral molecules $\mathcal{A} \sim 10^{-5}$.

Yet another model is analogous to the conventional optical model developed by Condon (1929). Essentially, the incident electron induces both an electric and magnetic dipole moment in the target. While an electric dipole moment can be induced in any molecule, the magnetic dipole moment arises only in chiral molecules from lack of inversion symmetry. The combined interaction of the electron with these induced moments can give rise to electron circular dichroism. Using this approach, Walker (1982) estimated the strength of these interactions for camphor based on its optical rotatory power. From this, $\mathcal{A}$ was inferred to be $\sim 10^{-23}$. Recently Gallup (1994), using the same model, has calculated *ab initio* the strength of this interaction and finds $\mathcal{A} \sim 10^{-4}$.

Since the results of Campbell and Farago are 30 to 100 times larger than a general result of 10^{-4}–10^{-5} based on disparate models, the origin of their result is unclear. To gain insight into this problem, we have repeated Campbell and Farago's experiment. We have also used stereoisomers of camphor and have measured $\mathcal{A}$ with an incident electron energy of 5 eV. At the suggestion of Burrow (1988), we have also measured $\mathcal{A}$ at 1 eV where a negative ion resonance is known to exist. One might expect that by lengthening the collision time as happens in such a resonance, the incident electron and target molecule could 'sample each other's handedness', thus enhancing $\mathcal{A}$.

Our apparatus was designed to be as axially symmetric as possible to reduce possible instrumental asymmetries. It is composed of three main components: a polarized electron source, an electron polarimeter and a camphor target chamber. We have minimized the effect of the earth's magnetic field by orienting the beam line along magnetic north and cancelled the remaining transverse component with large rectangular Hemholtz coils. With the exception of small steering fields, essentially all electromagnetic fields encountered by the electrons are axially symmetric about the beam axis.

The polarized electron source is based on photoemission of GaAs. The rudiments of this type of source can be found in Pierce *et al* (1980), so we only give information relevant to describing its axial symmetry. The photoemission laser light enters the apparatus almost collinear (4° deviation) with the electron-beam axis. The light undergoes a reflection from a polished stainless steel electron aperture in the beam line and illuminates the photoemitter at near-normal incidence. The electrons are extracted axially and are thus almost completely longitudinally polarized ($\cos(4°) = 0.997$). The electron helicity is controlled via the laser's

circular polarization with a liquid crystal variable retarder.

The electron polarization is measured with an 'optical' polarimeter. This device is based on impact exchange excitation of an atomic target by the polarized electrons and measuring the circular polarization of the subsequent optical decay. We used the $3p\,^3D_3 \rightarrow 3s\,^3P_2$ (640.2 nm) transition in Ne, and observed the decay at a polar angle of 135° from the beam axis. From these measurements, the electron polarization was found to vary between 27% for bulk GaAs and 45% for thin, epitaxially grown crystals. Details on optical electron polarimetry can be found in Furst *et al* (1993), Gay *et al* (1995) or Trantham *et al* (1995).

In the target chamber, the electron beam is transported from the polarimeter and focused into a vapour target cell. Following the target is a retarding field energy analyser (RFA) and an electron multiplier for single-particle detection of the transmitted electrons. We have used both continuous dynode multipliers ('channeltrons') and discrete dynode multipliers for particle detection. The target cell has two ports for the introduction of camphor and for monitoring the pressure with a capacitance manometer. The RFA uses a screen placed immediately after the target exit aperture. With its potential set properly, only those electrons that have suffered no more than 200 meV energy loss will be transmitted to the detector. We used the computer program SIMION (Dahl 1988) to determine that the geometry of the detector and target apertures allow only forward-scattered electrons within a half-angle of 2° to be detected.

The correct RFA potential is found by decreasing its applied voltage to reject the electron beam and identifying the threshold of transmission. The RFA is then set 200 mV above this threshold. The gas cell potential is set in a similar manner, for a given energy, $\mathcal{V}$ eV, its potential is set $\mathcal{V}$ volts above the lowest potential that transmits the electron beam.

Camphor vapour is supplied from a room temperature vial containing a solid sample. With a vapour pressure of approximately 200 mTorr at room temperature, we experienced little difficulty in maintaining sufficient pressure ($\sim$ 1 mTorr) in the target cell. However, the electron optics and target chamber needed to be warmed slightly ($\sim$ 40 °C) to prevent anomalous tuning effects due to camphor 'plating' of the transport optics. This was accomplished with an ordinary infrared heat lamp. With about 1 mTorr in the target cell the camphor vapour attenuated the electron beam by a factor of four to five. To ensure chiral purity of our camphor supply, the optical specific rotation was checked for each isomer by measuring the degree of rotation of plane polarized light with a known concentration of camphor dissolved in acetone (see e.g. Barron 1982).

Total scattering cross sections (σ_{tot}) were measured first to verify our ability to handle low-energy electrons and to control the flow of vapour into the target chamber. Most of our cross section measurements were taken with a larger half-angle acceptance ($\sim$ 6°) before the target aperture was restricted for asymmetry measurements. The beam attenuation method was used for the σ_{tot} measurements. Hence, for a predetermined electron energy, the gas cell pressure was slowly changed while recording the transmitted intensity. Thus, σ_{tot} was deduced from the Lambert–Beer law:

$$\frac{I}{I_0} = \exp(-\sigma_{tot} n l). \tag{2}$$

The vapour number density n was estimated to be 3×10^{13} mTorr^{-1} and l, the effective target length, was taken to be the geometrical length of the cell.

To lend credibility to a first camphor σ_{tot} measurement, we first measured σ_{tot} for nitrogen near the well established resonance as shown in figure 1. Also illustrated is data from Kennedy (1980), using a much more accurate time of flight technique. Note that our N_2 σ_{tot} data were taken with a 6° acceptance angle. The second graph of figure 1 shows

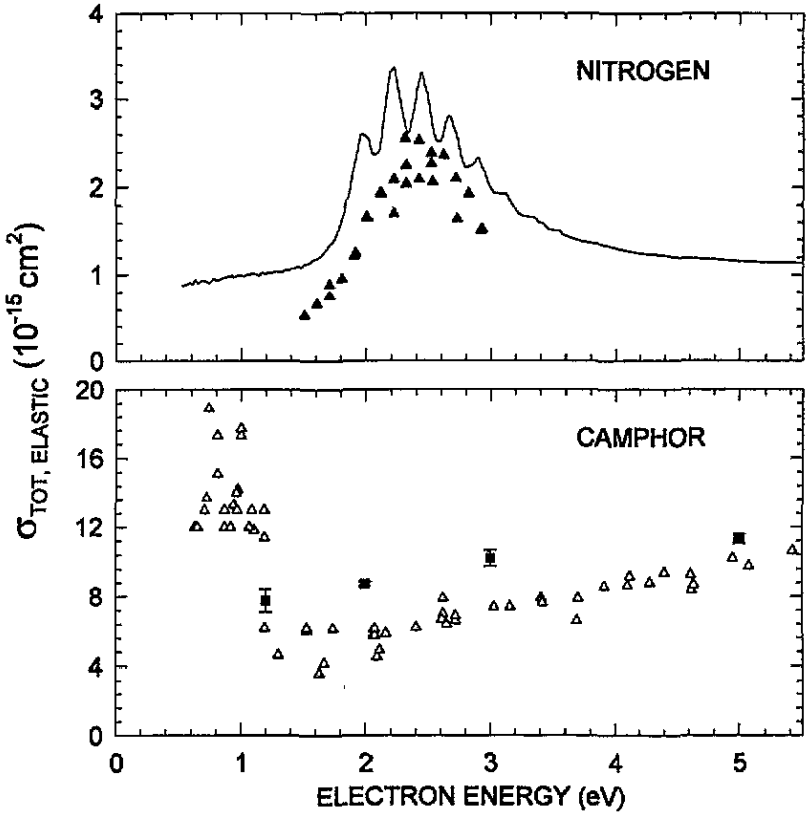

Figure 1. Total scattering cross sections measured for nitrogen (filled triangles) compared with Kennerly (1980) (full curve) and for camphor (see text).

our total cross section results for camphor. The data in open triangles were taken before the target aperture was narrowed, while the filled squares represent data taken with the same geometry as that described for the asymmetry measurements. The general energy dependence of our data compares well to that of Stephen *et al* (1988), who first identified the resonance at about 1 eV by measuring $d\sigma_{tot}/dE$ directly. We have thus confirmed qualitatively the existence of a negative ion resonance in the region of 1 eV, and have shown that our apparatus operates in a reliable fashion at those low energies.

Our symmetry measurements are a culmination of many blocks of data taken over the course of several weeks. Each block contains approximately 500 individual asymmetry measurements, each obtained by toggling the electron's helicity and recording $I_\uparrow$ and $I_\downarrow$, as defined above. The temporal order of data acquisition ($I_\uparrow, I_\downarrow$ or $I_\downarrow, I_\uparrow$) was randomly set for each asymmetry. For a given target handedness, around 125 asymmetries were taken, with approximately 2 s of data accumulation time for each helicity setting. The target vapour handedness was changed and about another 125 asymmetries were taken after the preceding vapour had been evacuated. Target handedness was typically switched four times for a given block of data. A mean and standard error were then computed for each isomer from the approximately 250 available asymmetries thus obtaining an $\mathcal{A}_D^{raw}$ and $\mathcal{A}_L^{raw}$ for a given block of data. Now, $\mathcal{A}_D^{raw}$ and $\mathcal{A}_L^{raw}$ should be equal in magnitude and opposite in

sign. Thus instrumental asymmetries were corrected from

$$\begin{aligned} \mathcal{A}_{\mathrm{L}} &= \mathcal{A}_{\mathrm{L}}^{\mathrm{raw}}/2 - \mathcal{A}_{\mathrm{D}}^{\mathrm{raw}}/2 \\ \mathcal{A}_{\mathrm{D}} &= \mathcal{A}_{\mathrm{D}}^{\mathrm{raw}}/2 - \mathcal{A}_{\mathrm{L}}^{\mathrm{raw}}/2. \end{aligned} \tag{3}$$

The instrument symmetry

$$\mathcal{A}_I = \mathcal{A}_{\mathrm{L}}^{\mathrm{raw}}/2 + \mathcal{A}_{\mathrm{D}}^{\mathrm{raw}}/2 \tag{4}$$

was typically 2×10^{-4}, in agreement with asymmetry runs made with argon as the target gas. This procedure was repeated many times at both 5 eV and 1 eV incident target energy. Each asymmetry measurement has been normalized to the electron polarization measured for each data set. Table 1 shows the weighted average of our measurements, along with the results of Campbell and Farago, normalized to their polarization. While we have not been able to verify their results, our findings are consistent with the dynamical models sketched above.

Table 1. Camphor transmission asymmetries taken at 1 eV and 5 eV compared with results of Campbell and Farago (CF) (1987), both normalized to unit electron polarization in units of 1×10^{-4}.

	$\mathcal{A}_{\mathrm{L}}$	$\mathcal{A}_{\mathrm{D}}$
Present 1 eV	−2.1(5.3)	2.2(5.4)
Present 5 eV	−0.9(4.4)	0.9(4.5)
CF (1987) 5 eV	−179(61)	82(39)

It is unclear at present why we have not been able to confirm Campbell and Farago's results. However, Farago's original ideas of electron optical activity and circular dichroism are certainly worth trying to observe and understand. To this end, we are planning to look for both of these effects in other materials, such as 3-Bromocamphor, as this molecule has a higher Z. Also, since it is possible to measure asymmetries more accurately using a phase-sensitive detection scheme, further investigations will most certainly employ a lock-in amplifier and transmitted current detection. Once an effect has been observed, careful investigations should be carried out to determine the physical mechanism(s) responsible.

We have recently become aware of work done by Kessler's group in Münster. They confirm our results with camphor, but have also observed non-zero values of $\mathcal{A}$ with a chiral molecule containing ytterbium.

This work was supported by NSF grant PHY-9504350. The authors wish to acknowledge numerous useful conversations with G A Gallup.

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