Experimental Verification of Electron Optic Dichroism

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Electron optic dichroism, i.e., the spin-dependent attenuation of electron beams transmitted through the vapor of chiral molecules, was investigated. No transmission asymmetry was found for longitudinally polarized electron beams of opposite helicity passing through enantiomeric camphor vapor. The experiment was carried out at electron energies of 0.9, 4.0, and 5.0 eV with an accuracy much better than 10^{-4}. Asymmetries up to 1.5×10^{-4}, which was clearly above the detection limit, were, however, observed for $Yb(hfc)_3$, a camphorlike molecule containing an ytterbium atom.

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When electrons are scattered from chiral molecules, spin-polarization phenomena can occur which one does not find in scattering from nonchiral molecules, where they are not compatible with reflection symmetry [1,2]. To name a few of these effects appearing with such optically active molecules, the scattered electrons may have polarization components lying in the scattering plane and the transmission of longitudinally polarized electrons through a target of chiral molecules may depend on the helicity of the electrons (electron optic dichroism). Equivalently, a beam of unpolarized electrons passing through such a target should acquire longitudinal polarization. These are a few simple examples of a larger number of polarization effects that are produced by the regular electromagnetic (not parity-violating) forces in conjunction with the chiral structure of the molecule.

As the experimental and theoretical [3–5] work done so far has shown, the polarization effects should be rather small if the target consists of nonoriented chiral molecules. This is the main reason why the experimental results existing so far are not unequivocal. This holds in particular for the great number of experiments where the decomposition of chiral molecules by polarized electrons has been studied. This effect is closely related to the above mentioned phenomena and is considered to be a possible explanation for the origin of the chiral dissymmetry of the terrestrial biosphere, a problem that has intrigued scientists since the time of Pasteur. Of the numerous experiments on this topic we will quote only the one paper [6] which, in our opinion, is the most convincing and which showed that, within the detection limit of $\sim 10^{-3}$, such an effect does not exist, thus contradicting a previous experiment with a similar though less perfect technique [7].

A different experiment was performed by Farago and collaborators [8] who searched for polarization components in the scattering plane after scattering of unpolarized 25 eV electrons through 40°–70° from right-handed (D) unoriented camphor vapor ($C_{10}H_{16}O$). They found that these in-plane components were below the detection limit of 5×10^{-3}.

A positive result was, however, reported by Campbell and Farago [9] who studied the attenuation of a longitudinally polarized electron beam traversing optically active camphor vapor. From the transmitted beam intensities $I(P)$ and $I(-P)$ for electron polarization P parallel and antiparallel to the beam axis the transmission asymmetry

$$A = \frac{I(P) - I(-P)}{I(P) + I(-P)} \tag{1}$$

was determined. For the right-handed enantiomer the result was $A(\mathrm{D}) = (23 \pm 11) \times 10^{-4}$ while for the L enantiomer the authors found $A(\mathrm{L}) = (-50 \pm 17) \times 10^{-4}$. The quoted uncertainties are single standard deviations. The measured values differ from one another by more than three standard deviations. Accordingly, the authors conclude that the existence of electron optic dichroism has been confirmed with a confidence limit exceeding 95%.

This has stimulated activities of several groups because the asymmetries are much larger than could be anticipated from the theoretical estimates used so far. One can speculate that resonant temporary-ion formation that would lengthen the time over which spin-orbit interaction takes place could enhance the polarization effect. In fact, the aforementioned result has prompted search for such resonance features which have, indeed, been found in the transmission spectrum of slow electrons in camphor [10], though at energies smaller than the 5 eV used in Ref. [9].

The present paper gives experimental results of much higher accuracy and on a broader scale. We happened to be well equipped for such measurements because one of our projects in the past years was focused on reliable measurements of small asymmetries and polarizations [11]. A detailed study of the proper position of the monitor detectors [12] in the Mott detector, which correct for instrumental asymmetries, turned out to be an important improvement just as the increased stability of our polarized electron beam.

This enabled us to perform experiments that were improved in three respects: (i) The uncertainty limits were smaller by more than 1 order of magnitude. (ii) We

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made measurements not only at 5 eV, as Ref. [9] but at energies down to 0.5 eV, so that we measured in the range where the resonances appear which are supposed to enhance the polarization. (iii) We not only used camphor as the target but aimed at chiral molecules containing atoms of higher atomic number Z so that the effect should be much larger [13].

Figure 1 is a schematic diagram of the apparatus. A beam of transversely polarized electrons is extracted from a GaAs photoemission source (not shown in Fig. 1). Electron sources of this type have frequently been described in the literature, e.g., in Ref. [14]. The GaAs cathode is irradiated with circularly polarized light from a diode laser. A low-voltage Pockels cell is used to switch the sign of the circular light polarization in order to reverse the electron polarization. The source delivers an electron current of ~100 nA at the target, even at energies below 5 eV. The electron polarization was measured to be 40% ± 1%.

The electron beam passes through a Wien filter which rotates the polarization into the longitudinal direction. For the camphor experiment the beam is then directly focused into a gas cell of 46 mm length. The angular divergence of the incident beam is restricted to ±2°. Camphor vapor of L or D handedness is admitted into the cell from two containers outside the vacuum via leak valves. The camphor pressure in the cell is adjusted to attenuate the transmitted beam by a factor of 10. A Baratron capacitive manometer serves as a pressure monitor. The electrons transmitted through the gas cell enter a filter lens [15] with an angular acceptance of ±2°. The filter lens eliminates inelasticity scattered electrons which have suffered an energy loss >250 meV from the beam.

For polarization measurements the adjacent transport optics focuses the transmitted beam through a second Wien filter into a Mott analyzer [11] of high precision. The Wien filter serves for rotating the longitudinal polarization into the transverse direction. In order to determine the intensities $I(P)$ and $I(-P)$ the transport optics can be used as a Faraday cup. In this case the electrons are not allowed to pass through the optics but are deflected onto the walls where the current I_t is measured with an electrometer amplifier. The current I_s scattered onto the walls of the gas cell is measured with a second electrometer. The outputs of the amplifiers are digitized and fed into a computer where the asymmetry A is calculated according to Eq. (1) from the transmitted currents $I_t(\pm P)$ normalized to the sums $I_s(\pm P) + I_t(\pm P)$. This normalization eliminates spurious asymmetries caused by fluctuations of the incident intensity. Spurious asymmetries were also caused by minute changes in the position or angular spread of the incident beam occurring when the Pockels cell was switched. These asymmetries are not eliminated by the above mentioned normalization procedure and turned out to easily reach values $>10^{-3}$ if no measures were taken to further reduce them.

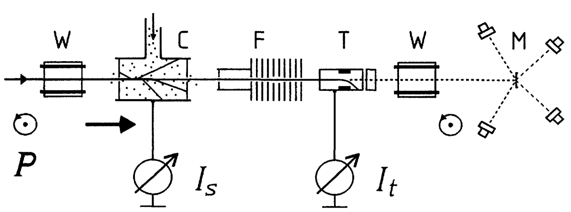

FIG. 1. Schematic diagram of the apparatus. (W) Wien filters, (C) gas cell, (F) filter lens, (T) transport optics/Faraday cup, and (M) Mott analyzer.

In order to find methods for a further reduction of spurious asymmetries, we made numerous tests with nonchiral molecules or empty gas cell. Among the necessary improvements the most important ones were temperature stabilization of the diode laser, thorough adjustment of the Pockels cell, selection of a nonbirefringent vacuum window for entrance of the laser beam, and adjustment of the electron optics for maximum transmission. We finally succeeded in performing asymmetry measurements with an accuracy much better than 10^{-4}.

The camphor experiment was made at electron energies of 0.9 and 4.0 eV, where the resonances appear, and at 5.0 eV for comparison with Ref. [9]. The electron energy in the gas cell was calibrated by observing the vibrational resonances of the total cross section of N_2 [16]. At each energy, 30 measurement runs were taken for both L- and D-camphor. The handedness of the target was changed before every second run. During each run the polarization was reversed with a frequency up to 270 Hz, limited by the rise time of the electrometers. The more than 10 000 asymmetries measured in a single run show a Gaussian distribution and were averaged for each run. As can be seen in Fig. 2, these averages are randomly distributed around zero. The mean value of A evaluated for all the runs at a fixed energy does not differ from zero by more than 3×10^{-5}, regardless of the electron energy and the handedness of the target molecules. The nonzero asymmetry reported in Ref. [9] could not be reproduced. Figure 2 shows the improvement in accuracy of the present experiment. The negative result for camphor has also been confirmed by Gay [17].

As a cross-check we also measured the longitudinal polarization which the transmitted beam may acquire if the incident beam is unpolarized. For this purpose the GaAs source was replaced by a conventional thermal emission source and the polarization of the beam transmitted through the camphor vapor was measured with the Mott analyzer. Table I shows the results in comparison with the averaged results of the asymmetry measurements. At 4.0 and 5.0 eV we did not find any polarization exceeding the detection limit of $<8 \times 10^{-4}$. Only at 0.9 eV the measured values are larger than their single statistical uncertainties. Since the two values for L- and D-camphor do not differ significantly from each other, they can,

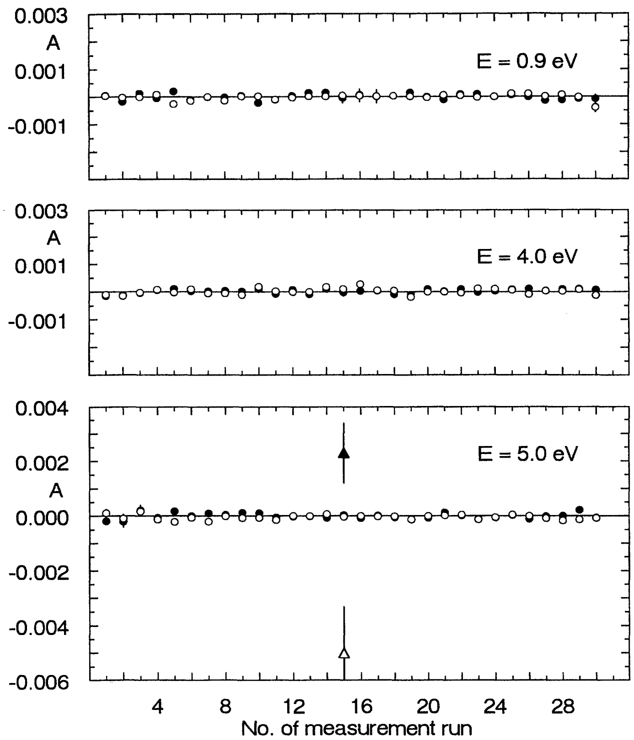

FIG. 2. Transmission asymmetry A measured for D-camphor (filled symbols) and L-camphor (open symbols) at different values of the electron energy E. The error bars indicate the statistical uncertainty. Where no error bars are given they are smaller than the symbols denoting the measured asymmetries. The triangles are results from Ref. [9].

however, not be caused by the chirality of the molecules, but they reflect the limits of the correction for instrumental asymmetries.

In a second step we have extended our experiment towards chiral molecules containing heavy atoms. While no asymmetries were observed with iodo-methylbutane ($C_5H_{11}I$), we found a significant effect with Yb(hfc)$_3$ [18]. The substance is available in L and D handedness and contains ytterbium ($Z = 70$) as a high-Z atom surrounded by three camphorlike ligands. The structure of the molecule is shown as an inset in Fig. 3. The Yb atom is not a chiral center, but the chirality of the molecule is locked up in the details of the ligands. In order to maximize the electron optic dichroism it would have been desirable to investigate molecules containing a heavy chiral center, but evaporable molecules of this type were not available as pure enantiomeric substances.

Since Yb(hfc)$_3$ must be heated to 120 °C in order to reach a sufficient vapor pressure the apparatus had to be considerably modified. The gas cell was replaced by a target chamber which was heated to 150 °C by halogen lamps. It consists of two electron deflectors, differentially pumped electron optics, and a gas cell followed by a

TABLE I. Results of the camphor experiment. The differences between the L and D values do not exceed the given statistical errors. The nonzero asymmetries and polarizations can therefore not be caused by the chirality of the molecules but reflect the systematic errors. The transmission asymmetries are the averages of the values shown in Fig. 2.

	Asymmetry A ($\times 10^5$)		Polarization ($\times 10^4$)	
E (eV)	L-camphor	D-camphor	L-camphor	D-camphor
0.9	0.0 ± 1.8	1.7 ± 1.8	16.5 ± 7.1	12.0 ± 7.1
4.0	2.0 ± 1.3	2.4 ± 1.3	1.9 ± 6.8	4.5 ± 6.8
5.0	−2.0 ± 1.2	−1.1 ± 1.2	7.5 ± 7.6	2.6 ± 7.9

Faraday cup. Such an arrangement is necessary to prevent the target molecules, which leave the gas cell through the electron entrance aperture, from contaminating colder parts of the electron optics, particularly in the electron source. Yb(hfc)$_3$ is evaporated in an oven connected to the gas cell by a valve. The cell can also be supplied with nitrogen for energy calibration.

In order to enhance the measured intensities we did not use an energy filter for the transmitted beam, and the Faraday cup was directly attached to the gas cell. The signal-to-noise ratio was further improved by carefully shielding the Faraday cup and the gas cell. These measures enabled us to investigate the whole energy range between 0.5 and 10.0 eV in steps of 100 meV within a few weeks. For both L- and D-Yb(hfc)$_3$ more than 400 energy scans of the asymmetry A were taken, each lasting about 3 min. The handedness of the target was changed 3 times. It was not practicable to change the target more often because this could not be done without breaking the vacuum. All measured L scans were averaged as well as the D scans. The results are shown in Fig. 3. The figure shows averaged scans from 0.5 to 6.0 eV overlapping with scans from 5.0 to 10.0 eV. The measured asymmetries differ significantly from zero and have opposite signs for

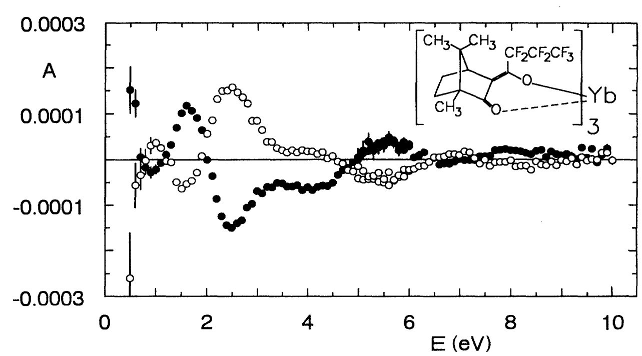

FIG. 3. Transmission asymmetry A measured for D-Yb(hfc)$_3$ (filled symbols) and L-Yb(hfc)$_3$ (open symbols) vs electron energy E. The statistical uncertainty is indicated by error bars, whenever they are larger than the symbols denoting the measured asymmetry. The structure of D-Yb(hfc)$_3$ is indicated in the inset.

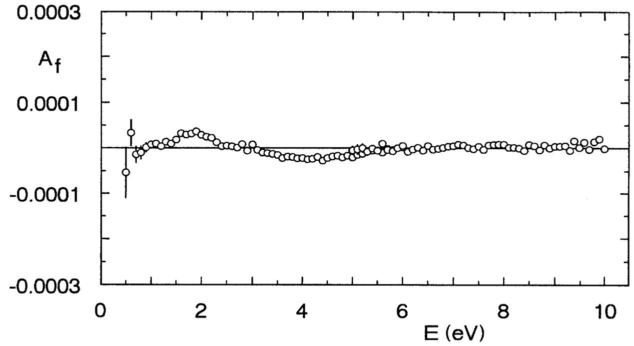

FIG. 4. Estimate of the spurious asymmetry A_f, which limits the accuracy of the measurement shown in Fig. 3, vs electron energy E.

L and D enantiomers, as required by symmetry. Pronounced maxima and minima of the asymmetry A can be seen at 1.7 and 2.6 eV. This is particularly interesting, because in a different experiment sharp resonances near these energies were detected [19]. As an estimate of the spurious asymmetries we have calculated the mean values of the asymmetries measured for both enantiomers. In the absence of spurious asymmetries the mean values should be zero. As can be seen in Fig. 4, the spurious asymmetries do not exceed a level of 5×10^{-5} at energies >0.5 eV.

In conclusion, we neither observed a transmission asymmetry nor chirality-induced polarization for a camphor target even though the accuracy of our experiment was considerably improved compared to Ref. [9]. Although the positive result reported by Campbell and Farago can therefore no longer be maintained, their work had the great merit of stimulating theoretical and experimental work on this fascinating topic. We measured, however, asymmetries clearly above the detection limit when using $Yb(hfc)_3$ as the target. We consider this as the first experimental proof of electron optic dichroism. Our results are in good agreement with theory [4] which predicts asymmetries $\sim 10^{-4}$ only for chiral molecules containing high-Z atoms. A detailed description of the measurements and error assessments will be published elsewhere.

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