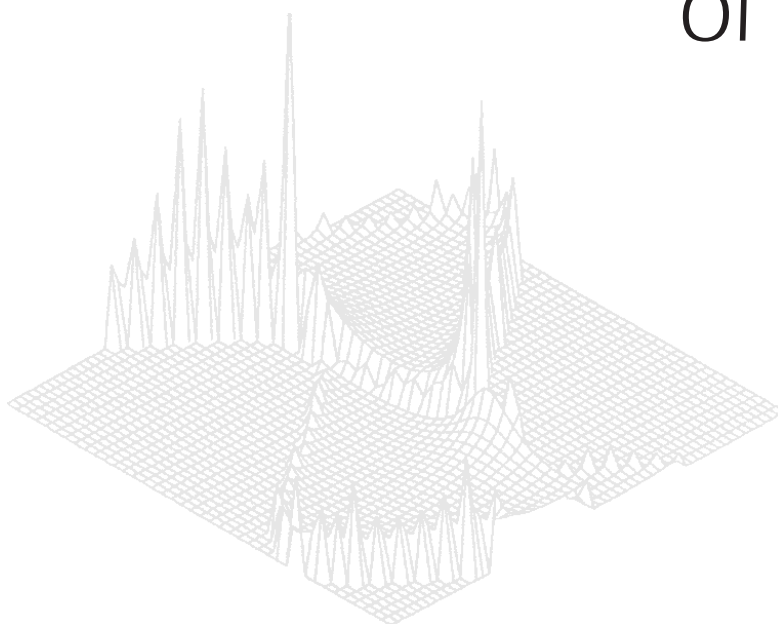

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Electron Dichroism: Interaction of Spin-polarised Electrons with Chiral Molecules*

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Abstract

This paper discusses a problem which would be worth studying with (e, 2e) experiments, a technique which has been so successfully used by Erich Weigold: Can spin-polarised electrons distinguish between left- and right-handed molecules? This has been a matter of long-standing discussion and speculation and of controversial experiments. The results presented here show that the attenuation of electron beams passing through chiral molecules is clearly spin-dependent. This is analogous to the circular dichroism of light and is therefore called electron dichroism. The size of the effect agrees with what has been predicted by theoretical estimates.

1. Introduction

Working in the field of electron scattering in the 1970s, you could not help hitting upon a name in the literature you had not heard before. Judging from the great number of fine papers that person had an enormous productivity, so I really wondered why he could appear like a supernova on the skies of atomic physics while I had not even noticed his name before. It took me a while to find the solution to this enigma of the person whose name sounded so German: Erich Weigold. The solution was that he had previously worked in nuclear physics, where he had a remarkable record, and had then switched to atomic physics where he started from scratch. He applied the experimental techniques he had used in nuclear physics so successfully to (e, 2e) experiments that in a few years everybody knew his name.

This personal history indicates that Erich Weigold always likes to start something new. And so it happened that he became interested in polarised electrons. They had appeared as a novel and valuable tool in various fields of physics, so he felt that they might also be useful to him. That is how we came together and—small wonder—a few years later he had the best (e, 2e) results with polarised electrons. The only chance of telling him something new is to present results on a topic on which he has yet to lay his hands.

* Dedicated to Professor Erich Weigold on the occasion of his sixtieth birthday.

2. How do Electrons interact with Chiral Molecules?

A problem that has intrigued scientists, not only physicists, for a long time is: how do electrons interact with chiral molecules, i.e. molecules possessing a handedness (Kessler 1985)? A chiral molecule is not identical to its mirror image, just as a right hand is not identical to its mirror image, which is a left hand. It turns out that we frequently find such chiral molecules in living organisms; amino acids and sugars are examples. We all have learned as young students that there are L-sugars and D-sugars which turn the linear polarisation of light to the left or to the right. One also knows that circularly polarised light is differently attenuated by chiral molecules, depending on the sense of rotation of the light. This is called circular dichroism.

Contrary to the situation with light, one does not know how the transmission of electrons is affected by chiral molecules. This has been discussed for a long time since it might shed light on an enigma that has puzzled scientists since the time of Louis Pasteur: Why has Nature a preference for a certain handedness in certain molecules in living organisms? One finds, e.g. only L-amino acids in natural proteins and only D-sugars in carbohydrates and nucleic acids. One cannot see a reason, however, why there should have been a preference for one handedness when life originated. The only plausible explanation for the dissymmetry found in Nature is that it has developed during evolution; e.g. the right-handed amino acids may have been preferably destroyed by some mechanism. But by which mechanism? This has been a matter of long-standing discussion and speculation. A plausible mechanism was suggested by Ulbricht and Vester (1962): It is conceivable that longitudinally polarised electrons from radioactive β -emitters have preferably degraded one of the enantiomers (that is what the right- and left-handed variants are called). A small imbalance produced in this way somewhere may then have been further augmented by chemical mechanisms, so that today's dissymmetry of living organisms has developed.

Many experiments have been performed to find a more solid basis for this vague hypothesis. Racemic mixtures, which contain equal numbers of L- and

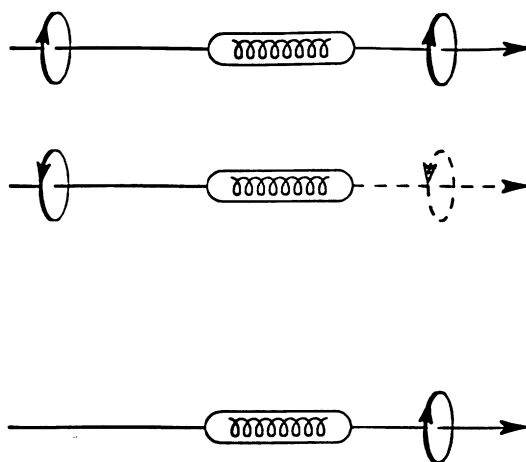


Fig. 1. Attenuation of electron beams by a chiral target.

D-enantiomers, were irradiated with polarised electrons in order to find out whether the degradation depends on the handedness of the molecule. I do not know any other field in physics where the results were so controversial: small positive results were always counterbalanced by negative ones.

A more general question was raised by Peter Farago (1980, 1981) in Edinburgh who asked: is it possible at all to see a difference in the interaction of polarised electrons with chiral molecules? Let us discuss the following process (Fig. 1): A longitudinally polarised electron beam passes through a chiral target, where it is attenuated by a certain amount. If a beam of the opposite helicity passes through the same target, symmetry does not forbid that it becomes attenuated by a different amount. If you add up the two processes, you obtain the third process shown in the figure. On the left-hand side you have an unpolarised beam, since a mixture of two beams of equal intensities but opposite helicities results in an unpolarised beam. The outgoing beam, however, is polarised because the two component beams of opposite helicities have different intensities, so that in the resulting beam the two spin states are not equally populated.

The figure also illustrates the direct analogy with optical circular dichroism. You have just to interpret it as circularly polarised light, right- and left-handed, which is attenuated by a different amount. Because of this analogy we call this process with electrons ‘electron dichroism’.

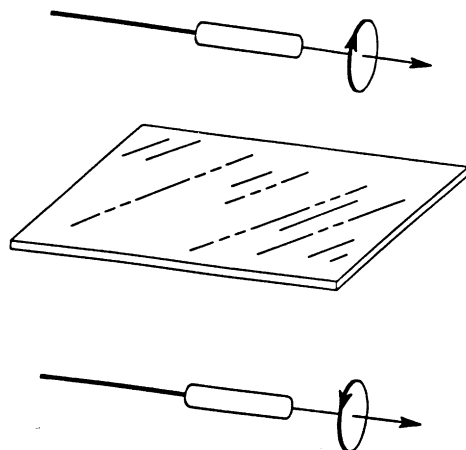


Fig. 2. A conceivable violation of parity conservation with a non-chiral target.

Fig. 2 explains why this cannot happen with a non-chiral target. If it did happen, as indicated there, with a target possessing reflection symmetry we could look at this experiment in a mirror and we would see the same incident beam and the same target as in the lab, but a right-handed beam emerging in the mirror while a left-handed beam emerges in the lab. This violates parity conservation, because one and the same initial state (same beam, same target) must not yield different results in the lab and in the mirror. Needless to say, parity-violating interactions are completely negligible in the processes discussed here.

When a process is compatible with symmetry principles, then it is by no means granted that it will actually occur. There must be a suitable interaction to

bring forth the process. When we have a different transmission of electrons with different spin orientations, this must, of course, be produced by an interaction that depends on the spin. Since spin-dependent interactions, like the spin-orbit interaction, are small one cannot expect a large effect. How large the effect is, if it exists at all, can only be found by experiment, since theory in this field is still in its infancy.

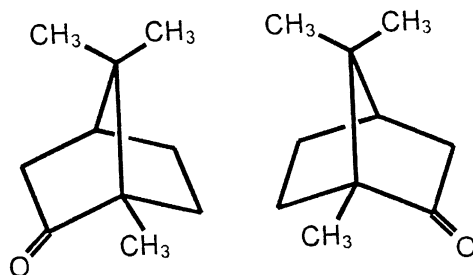


Fig. 3. Camphor enantiomers.

3. Experimental Verification of Electron Dichroism

A first attempt was made by Campbell and Farago (1987) with camphor (Fig. 3) which can be handled conveniently: both enantiomers are inexpensive and can be easily evaporated to fill a target cell with the necessary vapour pressure. Longitudinally polarised electrons of 5 eV were sent through vapour of one handedness and a comparison was made between the transmitted intensity $I(P)$ for polarisation parallel to the beam axis and the intensity $I(-P)$ for polarisation antiparallel to the beam axis. Campbell and Farago determined the so-called transmission asymmetry:

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

The values they claimed to have seen were about 3×10^{-3} and had different signs for right- and left-handed camphor. This seemed to be the verification of electron dichroism. But the result was very surprising, because it was 10 times larger than could be anticipated even from the most optimistic theoretical estimates.

This called for further experiments, which were started a few years ago by T. Gay's group (Trantham *et al.* 1995) in the United States and by my group. First we repeated the camphor experiments with considerably increased sensitivity and accuracy. This turned out to be necessary because neither Gay's group nor mine could find any positive result. The measured transmission asymmetry was zero and remained zero, even when we lowered the detection limit far below 10^{-4} . We made our measurements not only at 5 eV for comparison with the Edinburgh data, but in small steps from less than 1 eV up to 10 eV. As shown in Fig. 4, at none of the energies could a statistically significant nonzero value be found. So both Gay's and our conclusion was that the Edinburgh data, which in this

figure would be located well off the page, are artefacts. We discussed this with our friends in Edinburgh and they agreed. Obviously such measurements are quite troublesome.

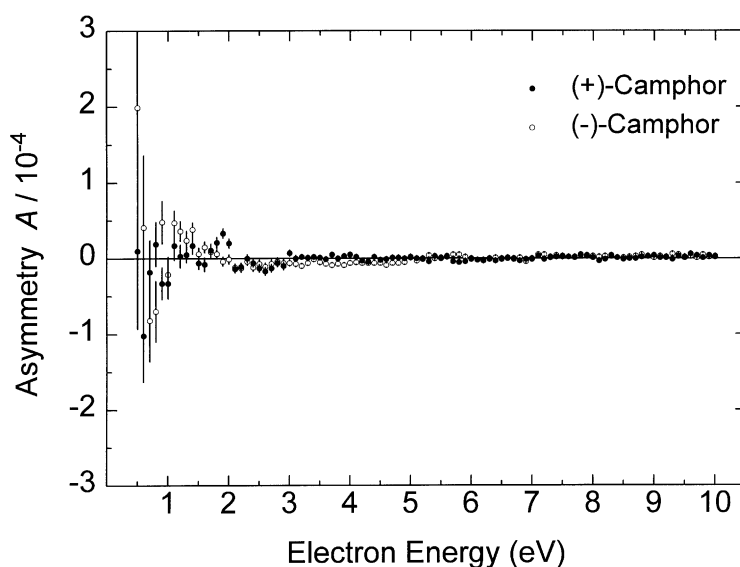


Fig. 4. Transmission asymmetry for the camphor enantiomers.

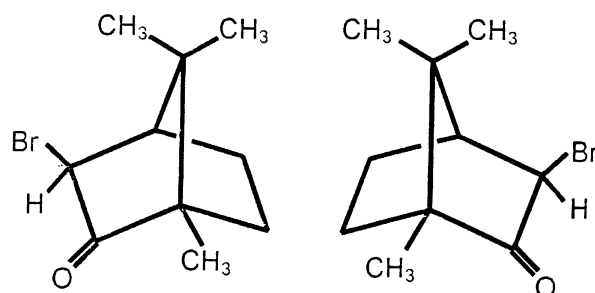


Fig. 5. The (+)-bromocamphor (right) and (–)-bromocamphor (left) molecules.

If we assume that the effect, if it exists, is caused by the spin–orbit interaction which increases dramatically with the atomic number Z , then the chances should be much better with chiral molecules containing heavy atoms with high Z . Unfortunately, there are not too many such molecules; besides they are hard to evaporate and have to be brought to high temperatures to obtain the necessary vapour pressure. When doing this, the molecules have to remain stable. So it was quite a problem to find suitable target molecules. But finally we succeeded in detecting electron dichroism in bromocamphor, which is very similar to camphor, but contains a bromine atom with atomic number 35 (Fig. 5).

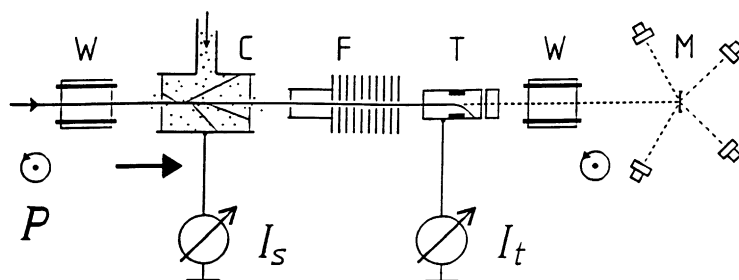


Fig. 6. Schematic diagram of our apparatus for the verification of electron dichroism: W, Wien filter; C, gas cell; F, filter lens; T, transport optics/Faraday cup; and M, Mott analyser.

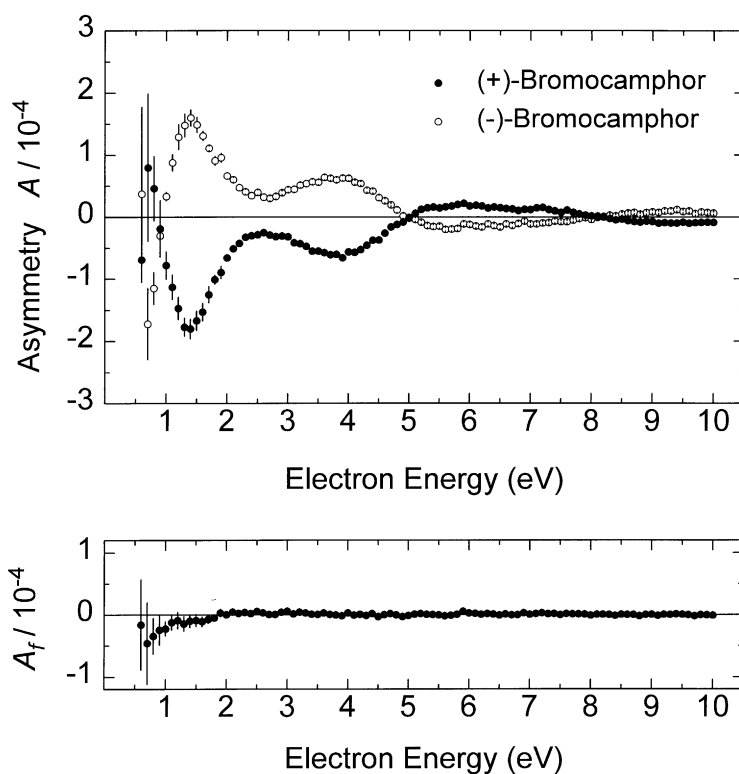


Fig. 7. Above: the transmission asymmetry for bromocamphor. Below: the instrumental asymmetry.

Before presenting the results, we refer to Fig. 6 which illustrates the experiment from the PhD thesis of Stefan Mayer (Mayer *et al.* 1996). An electron beam of 40% longitudinal polarisation from a GaAs source passes through a gas cell containing the chiral molecules of one handedness, where it is attenuated by a factor of 10 or so. The transmitted beam can either be sent into the Mott detector for polarisation analysis or, in another mode of operation, the electrons

can be caught in a Faraday cup where the current I_t that is transmitted through the gas cell is measured with an electrometer amplifier. Its output is digitised and fed into a computer which calculates the asymmetry according to equation (1). We also measure the scattered current I_s in the cell which is not transmitted through the gas. These two currents are proportional to the incident current, so that we could eliminate spurious asymmetries caused by fluctuations of the incident current by normalising the transmitted current to I_s . This reduced the spurious asymmetries to 10^{-3} which was tested with non-chiral molecules or the empty gas cell. The remaining spurious asymmetries were much more troublesome. They were caused by minute changes in the position or the angular spread of the incident beam when it was switched between positive and negative polarisation. The reduction of these instrumental asymmetries took us many months and was very troublesome. But finally we were rewarded by results of the kind shown in Fig. 7. The upper part presents the asymmetry in units of 10^{-4} versus the electron energy between 1 and 10 eV in steps of 100 meV.

The measured asymmetries differ significantly from zero and have opposite signs for the right- and left-handed molecules, as required by symmetry. In a separate study we have searched for the cross-section resonances of our molecules and it turns out that they occur near those energies where we found the maxima of the asymmetry. It is well known that such resonances occur when an electron attaches itself to the molecule forming a short-lived compound state. The electron thus interacts with the molecule for a longer time so that one has also a longer interaction time of the spin-orbit coupling, which obviously results in a larger asymmetry.

If the measurements had no systematic errors, the sum of the two curves should be zero. This is, however, not quite the case as shown by the lower diagram in Fig. 7 which gives the sum of the data. The deviation of this curve from zero is caused by instrumental asymmetries which, at energies above 1.5 eV, are, however, only 10^{-5} or less.

We have not only measured the transmission asymmetries in this type of experiment, but have also carried out the experiment where an unpolarised electron beam passes through a chiral target and the polarisation of the outgoing beam is measured (see the lowest diagram in Fig. 1). The polarisations of $(2.30 \pm 0.72) \times 10^{-4}$ for (+)-bromocamphor and $(-1.52 \pm 0.72) \times 10^{-4}$ for (-)-bromocamphor measured at 1.4 eV are in accordance with the results of the transmission-type experiment, but the error bars in the polarisation are five times larger, showing that the polarisation experiment is more difficult.

We have found electron dichroism in other molecules, as well. Fig. 8 shows a few examples measured by Christoph Nolting (see Nolting *et al.* 1997). In each of these molecules there is a heavy atom surrounded by three camphor-like ligands. The atomic numbers of the heavy atoms range from 59 to 70. It is possible to see clear structures in these curves, but we are far from a quantitative understanding of the results. We carried out this series of measurements anticipating that the asymmetries would increase with increasing Z , but this is not really the case, as can be seen.

Fig. 9 presents asymmetries for dibromocamphor which contains two bromine atoms, instead of the one in bromocamphor. The two bromine atoms do not, however, give a larger effect than the molecule with one atom. A comparison with

bromocamphor shows that the maximum is even lower for dibromocamphor. The effect of the second bromine atom is to change the structure of the asymmetry curve and to diminish the effect.

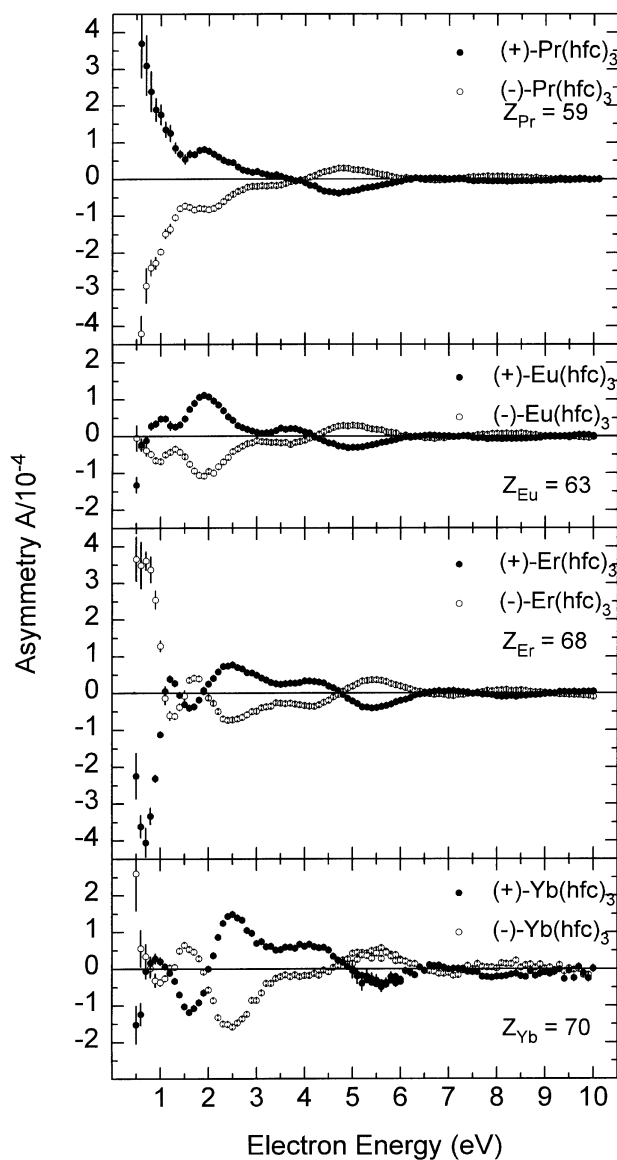


Fig. 8. Transmission asymmetries for chiral molecules containing heavy atoms.

However, the results are not always different from what one might anticipate. Nature likes to fool us a little bit and so I show in Fig. 10 two results which come closer to the Z dependence we had anticipated. These chiral molecules contain one iodine atom with $Z = 53$ and one bromine atom with $Z = 35$ respectively.

And, indeed, we find larger asymmetries in the iodine case. Incidentally, we could obtain in these cases only one of the enantiomers, so that the opposite curves are missing.

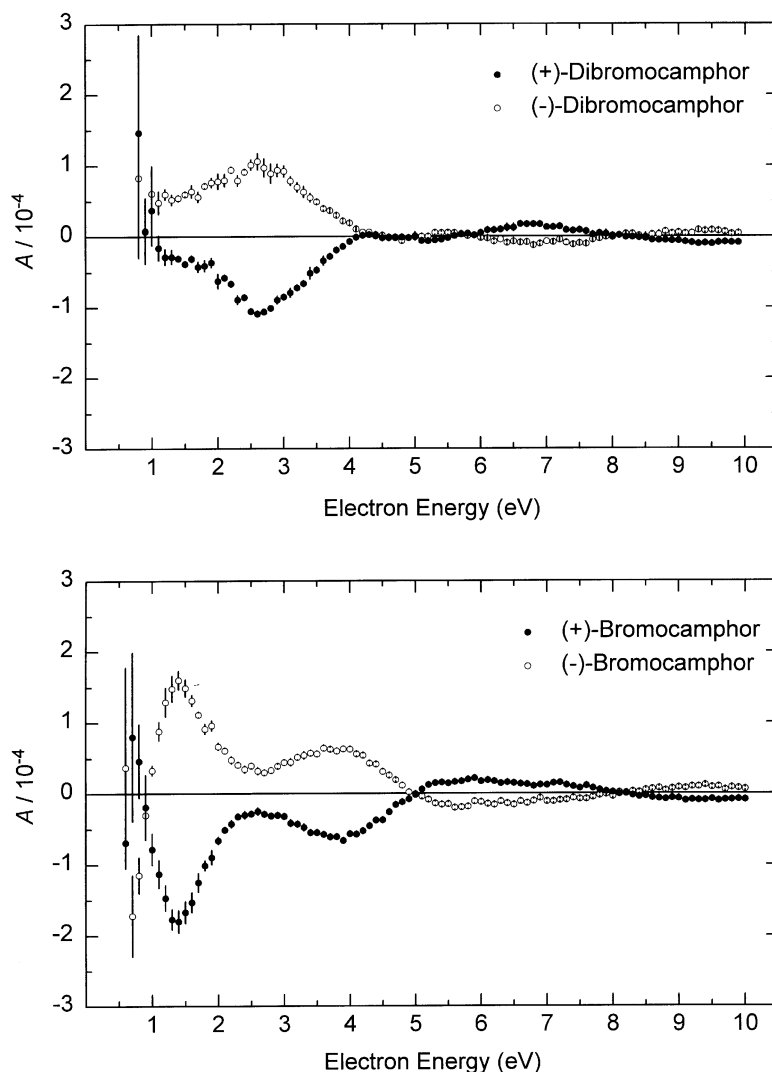


Fig. 9. Comparison of transmission asymmetries for dibromocamphor (above) and bromocamphor (below).

While it must be admitted that, on the whole, we do not understand the details of all these curves, neither do the theoreticians. Even though theoretical groups in Britain and Germany have successfully attacked the problem of electron dichroism (e.g. K. Blum in Münster and D. Thompson in Belfast), the molecules shown here are far too complicated for quantitative calculations. However, for simple model molecules quantitative results have been obtained which agree with the asymmetries of order 10^{-4} found in our experiments (Fandreyer *et al.* 1990).

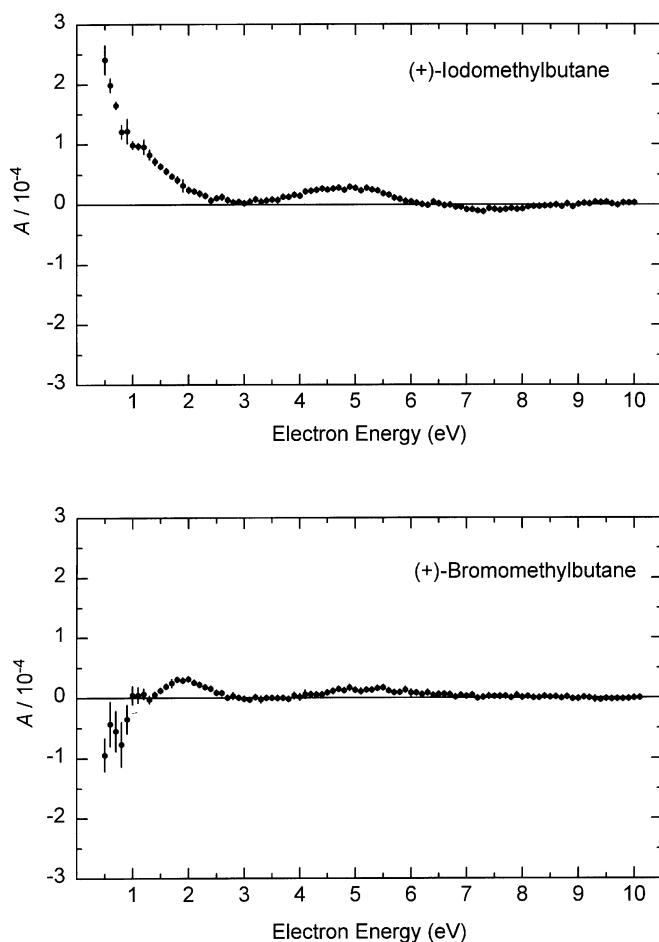


Fig. 10. Transmission asymmetries for (+)-iodomethylbutane (above) and (+)-bromomethylbutane (below).

On the basis of these results one can tackle the question of why Nature is not ambidextrous with much greater optimism. Differences in the transmission of polarised electrons through chiral molecules do in fact exist, so that we now have a better chance of solving the enigma of the dissymmetry in living organisms.

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