Molecular handedness and chiral strength determined by matter-wave circular dichroism

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The goal of this study is to determine the strength of the dominant helical potential field, i.e., the chiral strength, of mirror-image molecules with a method which we call electron and positron circular dichroism, a matter-wave phenomenon postulated by many [P. S. Farago, J. Phys. B **13**, L567 (1980); B. Ritchie, Phys. Rev. A **20**, 1915 (1979); R. A. Harris and L. Stodolsky, J. Chem. Phys. **70**, 2789 (1978); P. K. Kabir, G. Karl, and E. Obryk, Phys. Rev. D **10**, 1471 (1974); V. G. Baryshevskii, Yad. Fiz. **4**, 72 (1966) [Sov. J. Nucl. Phys. **4**, 51 (1967)]]. Of five liquid chiral molecules, two were found to be left handed, and one was right handed and two poorly defined. The chiral strength varies between 48.9×10^{-4} and 6.1×10^{-4} eV.

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If β^- radioactive nuclides are dissolved in undiluted liquid enantiomers, their Čerenkov pulse-height spectra of S is shifted with respect to that of R [1]. Thus the naturally left-handed helical β particles interact differently with the two mirror-image molecules. Therefore, the stopping power of the enantiomers are different for the helical β^- particles [2]. This observation enabled us to determine the strength of the helical potential field of enantiomers and to relate handedness at the molecular level to handedness at the elementary particle level. The significance of this study is apparent not only in physics, but also both in chemistry and in biology since the strength and sense of the helical potential field could be factors in recognition, polarization, and catalytic processes, as well as in electron transport via chiral molecules [3].

An electron circular dichroism (ECD) spectrum is the difference of the β^- Čerenkov pulse-height spectra measured in the R and S enantiomers (R-S). With respect to details and methods we refer to earlier papers [1,2]; only essential features necessary to understand the phenomenon are discussed here.

The ECD spectra of five different liquid, nondiluted enantiomeric pairs (Aldrich, Norse) are shown in Fig. 1. The spectrum of 2-phenyl-butyric acid (PBA) is more than 3σ; diethyl-tartrate (DET), 2σ; and α-pinene (PIN), 1σ significance. The others, 2-butanol (BUT) and N,N-dimethyl-1-phenethylamine (DPE) are at the brink of significance; nevertheless, they are well defined. PBA, DET, and BUT have Z-type curves, indicating that the pulse-height spectra of β^- particles were shifted to higher energies when measured in the S enantiomers. For PIN and DPE, which exhibit S-type ECD curves, the converse is observed; pulse-height spectra of β^- particles are displaced toward higher energies in the R enantiomer.

All five enantiomeric pairs were also probed with naturally right-handed β^+ particles emitted by ^{22}Na (ICN Ra-

diochemicals); three of them yielded positron circular dichroism (PCD) spectra (Fig. 2). The spectrum of PBA is 2σ; that of DET, 1σ significance; the spectrum of PIN is almost masked by the high standard deviation. For DPE and BUT, the large standard deviation blurred the PCD spectra beyond description as either an S or Z type. Two factors are responsible for the smaller σ values of ^{22}Na spectra: positron formation and annihilation accompanied by γ-ray production and γ irradiation from ^{22}Na. The concomitantly produced nonpolarized Compton electrons thus may interfere with the PCD spectrum and result in a mixed spectrum with high standard deviations. The PBA spectrum contains an extra peak at channel No. 300, which corresponds to the energy of Compton electrons produced by ^{22}Na γ rays. We cannot explain the extra peak in the PCD spectrum of DET.

Three observations may be drawn from the comparison of Figs. 1 and 2. First, the amplitudes of the PCD spectra are somewhat smaller than that of the ECD spectra for the same compound, which reflects the smaller helicity of the β^+ particles from ^{22}Na (0.690 mean) than those of β^- particles from ^{32}P (0.906 mean). Thus, a positive correlation between the degree of polarization (v/c) of the particle and the amplitude exists. The second observation is that the S- or Z-type spectrum characterizes a compound whether it was probed with left-handed β^- or with right-handed β^+ particles. One may be tempted by the following interpretation: the β^- and β^+ particles are opposite with respect to their spin (σ) momentum (p) coupling $\vec{\sigma}\vec{p}$, $\vec{\sigma}\vec{p}$, but as a consequence of their opposite charge, they are identical with respect to their magnetic-moment–momentum coupling. Therefore, the shape of the ECD and PCD spectra should depend on the sense and strength of the helical potential field of the molecular species and on the direction of the magnetic moment of the moving particle but not on either its charge or spin alone. This conclusion is, however, tentative because the PCD spectra have a more complex structure with addi-

tional peaks of unknown origin.

Third, all ECD and PCD spectra sum to zero over the broad energy band of polarized $\beta^{\pm}$ particles. Therefore, a sum rule analogous to the Kuhn-Condon Rule, which governs optical rotation of chiral molecules [4], is valid for matter-wave circular dichroism. Unlike optical circular dichroism, the ECD and PCD are remarkably simple,

an observation which indicates that the helical $\beta^{\pm}$ particles react to the dominant potential field of the enantiomers. The existence of a dominant helicity is apparent in large chiral molecules; hexahelicene or more interestingly, the right-handed polypeptide α helix and the DNA double helix.

Two null tests preclude the possibility that the ECD and PCD spectra result from an unknown parameter rather than depend on the helicity of the media and the impinging β particles. In the first, the two enantiomers
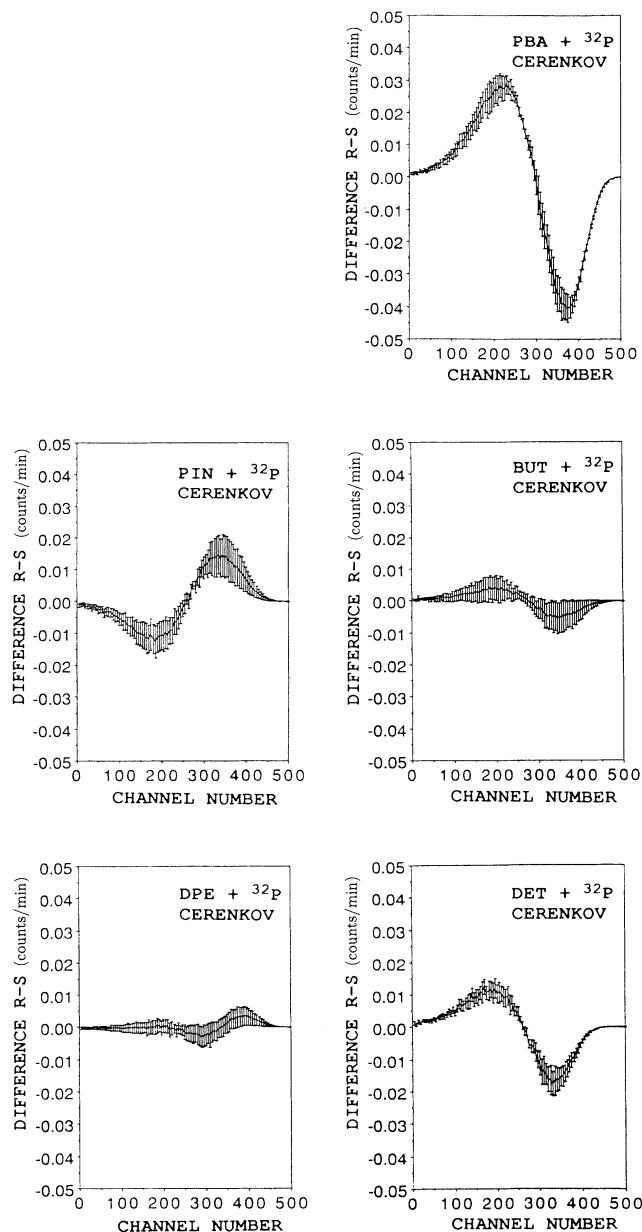

FIG. 1. Čerenkov ECD spectra of liquid enantiomers. Abscissa, channel number; ordinate, counts per minute normalized to 10. All spectra are computer generated and represent the average of four independent R and S spectra subtracted from each other (R-S) in all combinations (16 subtractions). The vertical bars represent standard deviations. The purities of compounds were guaranteed by the manufacturer to be 99+%. Purity was reevaluated by the authors with absorption spectroscopy and gas chromatography.
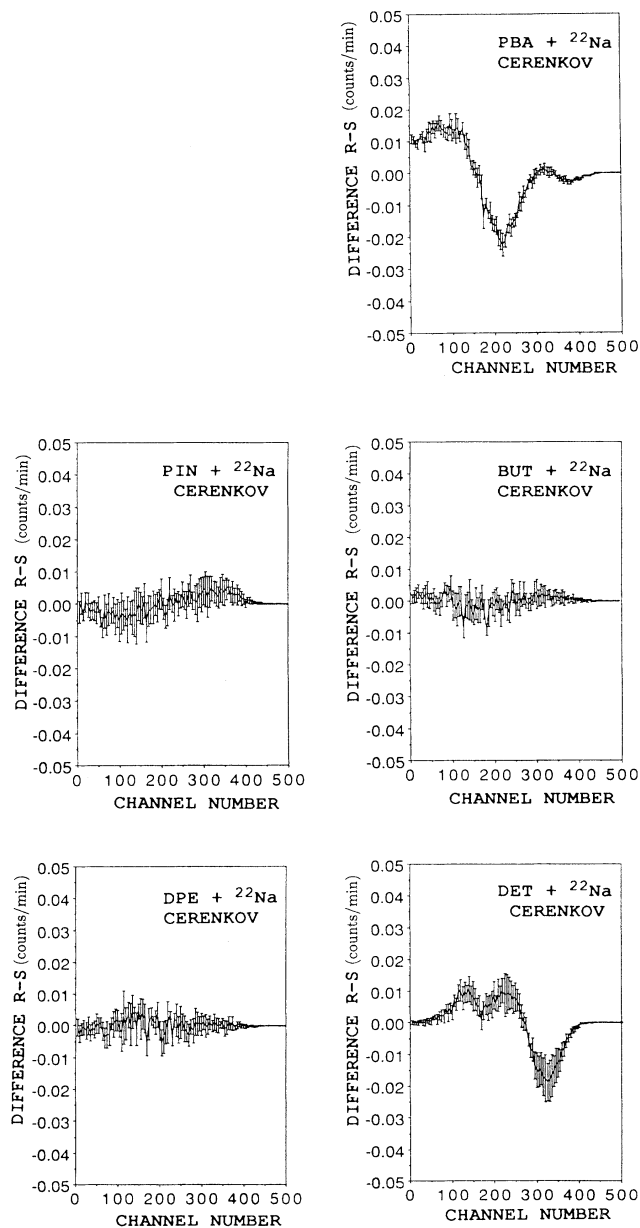
FIG. 2. Čerenkov PCD spectra of liquid enantiomers. Abscissa, channel number, ordinate, counts per minute normalized to 10. All spectra are computer generated and represent the average of four independent R and S spectra subtracted from each other (R-S) in all combinations (16 subtractions). The vertical bars represent standard deviations.

were probed with nonpolarized Compton electrons. These were produced by γ irradiation from ^{137}Cs pellets (New England Nuclear) placed inside a lead and copper shield and positioned above the surface of the enantiomers in the experimental vial. For all enantiomers, the nonpolarized electrons resulted in overlapping pulseheight spectra; their differential spectrum approximates a straight line.

In the second null test optically inactive racemic mixtures (M) were irradiated with both β^- and β^+ particles. The racemic mixtures were freshly prepared, vortexed, and the pulse-height spectra measured immediately because racemic mixtures often crystallize a few days after preparation. For both β^+ and β^- particles the M-PBA and M-DET pulse-height spectra were never in the median between the R and S spectra, but were always closer to the S spectra than to the R. A more precise location of the M spectra generated with β^+ particles could not be defined due to the intrinsically high standard deviations discussed before. Therefore the following refers only to the ECD spectra. The S-M ECD differential spectrum with DET approaches a straight line, which indicates that the M spectra almost overlaps with the S. The location of the M-PBA spectra shows more variation than that of DET; however, all 30 of the measured M-PBA spectra were located between the median and S. The ECD for PIN were less well defined, althought characteristic, than those for PBA and DET. The M spectra for BUT and DPE did not differ significantly from those of the enantiomers. Therefore, the Bethe equations [5] were solved for PBA, DET, and PIN only (Table I).

Initially we thought that the unexpected position of the M spectra is due to the physical properties (freezing point, density, etc.) of racemic mixtures, which differ considerably from those of the enantiomers. Density, the relevant parameter, is higher in the racemic mixture than in the enantiomers. However, as the density increases the collisional stopping power of β^- particles should also increase. Thus one could expect the M spectra to be shifted towards the R rather than the S. The most reasonable explanation, however, is that the S enantiomer depolarizes the β^- particles, an effect which is theoretically well established but never observed [3,6]. The S enantiomer must be right handed in order to depolarize the lefthanded β^- particles. Consequently, with respect to ECD and PCD, the S enantiomer and the racemic mixture are similar; for the first β^- particles do not have an average helicity but the molecules do, while in the second case

TABLE I. Mean collisional stopping power (linear energy transfer) of the R and S enantiomers and M racemic mixtures for [32]P β^- particles. Standard deviations are indicated by $\pm$.

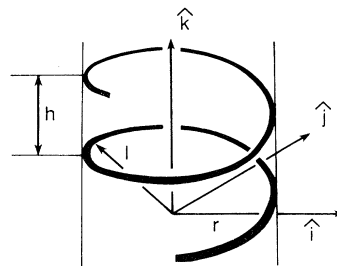| | Collisional stopping power ($\mathrm{eV}\,\mu\mathrm{m}^{-1}$) | | |
Enantiomer	R	M	S
2-phenyl-butyric acid	205.7	201.8	199.7
(PBA)	±1.2	±0.3	±0.1
Diethyl tartrate (DET)	186.7	186.1	185.7
	±0.2	±0.2	±0.3
α-Pinene (PIN)	209.6	210.1	210.5
	±0.2	±1.1	±0.3

FIG. 3. Parameters of a helix (explanation in text).

molecules do not have an average helicity, but the $\beta^\pm$ particles do. Neither permits a chiral discrimination.

We modeled the situation in the following way. Imagine a left-handed solenoid l_1 for the β^- particle with radius r_1 and pitch h_1, then a bigger solenoid l_2 for the molecule with r_2 and h_2, Fig. 3. This bigger solenoid may be either right or left handed. Suppose a current I_1 is moving in the smaller solenoid l_1. Let us now push the smaller solenoid into the bigger right- or left-handed solenoid. Current I_2 will be induced in the l_2 solenoid, which according to Lentz's law will counteract the I_1 current of l_1. The question is thus reduced to the determination of the strength of the interacting force if $l_1 l_2$ are parallel (left-left and right-right) or antiparallel (leftright). Consider one turn only; then the parametric equation of the helices are

$$\mathbf{l}_i^{(\pm)}(s)=\widehat{\mathbf{i}}r_i\cos(s)\pm\widehat{\mathbf{j}}r_i\sin(s)+\widehat{\mathbf{k}}\frac{h_i}{2\pi}s \ ,$$

$$i=1,2 \ , \ 0\le s \le 2\pi \ ,$$

where $\widehat{\mathbf{i}}$, $\widehat{\mathbf{j}}$, and $\widehat{\mathbf{k}}$ are the Cartesian unit vectors, s is the parameter, and $+$ or $-$ indicates the helicity of the coil. The interaction between two helices $l_1^{(\pm)}(s)$ and $l_2^{(\pm)}(t)$ carrying I_1 and I_2 constant currents, respectively, is

$$\mathbf{F}^{(\pm)}=\frac{I_1 I_2}{c^2}\int\int\frac{[d\mathbf{l}_1^{(+)}(s)\cdot d\mathbf{l}_2^{(\pm)}(t)]\mathbf{X}_{1,2}(s,t)}{|\mathbf{X}_{1,2}(s,t)|^3} \ , \quad (1)$$

where $\mathbf{X}_{1,2}=l_1^{(+)}-l_2^{(\pm)}$. The double integral on the right-hand side of Eq. (1) cannot be evaluated analytically; however, it was calculated numerically at different values of r_i and h_i ($i=1,2$). r_1 and h_1 were varied between 0.1 and 1.0 for l_1 while $r_2=1$ and $h_2=1$ (arbitrary units) were kept constant. In another set of calculations the larger coil had two windings with pitch $h_2=2$, i.e., the helix was $2h_1$ long. Results show that the interaction is greatest along the k axis, thus the largest component of the stopping power is along the helix axis. The most important conclusion is that the interaction in all directions (i,j,k) is bigger between two parallel coils than between two antiparallel ones, i.e., $F^{(+)}/F^{(-)}>1$ ($\cong2.6$ in our case). Here $F^{(\pm)}=|\mathbf{F}^{(\pm)}|$.

Therefore, we might conclude that the stopping power of a left-handed molecular helix is bigger for the lefthanded β^- particles than that for a right-handed molecular helix. The dominant helical potential field in R-PBA is left handed, that in S-PBA is right handed, a con-

clusion consistent with the observation and its interpretation that S-PBA depolarizes the left-handed β^- particles and consequently the S pulse-height spectra is closer to that of the racemic mixture. In this simple, classical model we have assumed that the stopping power is proportional to the magnitude of the interaction between two helices. According to quantum mechanics the stopping power is proportional to the scattering cross section of the incident spin-polarized particle on the chiral molecule. The quantum scattering cross section, however, is calculated from the scattering amplitude, which in first order is the matrix element of the interaction. Thus, the "classical" approach is justified, at least at higher collision energies, where one does not expect a rapidly changing cross section.

There is computational evidence though that at low energies and in first order the spin-dependent contribution to the cross section changes sign as the scattering energy varies [7], suggesting that caution must be exercised when interpreting results obtained at fixed collision energies.

Now the question arises, how can the strength of the helical potential field be determined? Apparently it is directly related to the difference between the collisional stopping power of the M racemic mixture and the R enantiomer.

$$\chi_R = \frac{(dE/dx)M - (dE/dx)R}{(n/x)(v/c)_{\text{mean}}} .$$ (2)

We name χ (from Greek, $\chi\epsilon\iota\rho$, for hand) the chiral strength of a molecule, dE/dx is the linear energy transfer of the racemic mixture M and the R enantiomer, (v/c) is the mean helicity of the β^- particles (0.906 for ^{32}P), and (n/x) is the number of molecules over the distance x in μm which was estimated on the basis of molecular size and density, and found to be ~ 881, ~ 776, and

~ 906 in the order of PBA, DET, and PIN. The chiral strength for the three enantiomers are as follows:

$$\chi = \begin{cases} -48.9(\pm 18.8)\times 10^{-4} \text{ eV} , & R\text{-PBA} \\ -8.5(\pm 5.6)\times 10^{-4} \text{ eV} , & R\text{-DET} \\ +6.1(\pm 3.9)\times 10^{-4} \text{ eV} , & R\text{-PIN} . \end{cases}$$

The $+$ sign indicates right handed, the $-$ sign indicates left-handed dominant helical potential field. The chiral strength of PBA is significantly bigger than that of DET or PIN by 1.85σ standard deviation. There is, however, no significant difference between the chiral strengths of DET and PIN. It is not surprising that R enantiomers can have opposite helicities; the Cahn-Ingold-Prelog convention [8], although unambiguous, does not define the sense of optical rotation at any photon energy, nor does it define the sense of the dominant helical potential field.

Although liquid enantiomers were used in this study, the electron circular dichroism method is applicable to other chiral molecules. Finally, although the data were interpreted on the basis of electromagnetic interactions between $\beta^\pm$ particles and chiral molecules, they cannot be excluded a priori that parity-violation effects arising from interference between the weak and electromagnetic amplitudes may also contribute to the observed ECD and PCD spectra.

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