J. Chem. Soc., Faraday Trans. 2, 1983, 79, 1811–1815

Enantiomers and Racemic Mixtures

The Correlation between Rotation and Translation

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Received 9th May, 1983

An explanation for the racemic modification is put forward using computer simulation to quantify the statistical correlation between a molecule's centre-of-mass translational velocity and its own angular momentum when immersed in an ensemble of like or mirror-image enantiomers. It is illustrated with bromochlorofluoromethane and *t*-1,2-dimethylcyclopropane.

The statistical correlation between the centre-of-mass linear velocity ($\boldsymbol{v}$) of a diffusing molecule and its own angular momentum ($\boldsymbol{J}$) about this centre of mass may be quantified in a moving frame of reference through a time-correlation matrix such as $\langle \boldsymbol{v}(t)\boldsymbol{J}^{\mathrm{T}}(0)\rangle_{\mathrm{m}}$. Here $\langle\ \rangle_{\mathrm{m}}$ denotes running-time or ensemble averaging in this frame, usually that of the principal moments of inertia. We have indicated recently[2,3] that moving-frame correlations such as these are responsible for the racemic modification of the molecular dynamics of a pair of enantiomers, and therefore of physical constants such as the melting point. The properties of a pair of enantiomers appear to be identical in the laboratory frame of reference, but in the moving frame some elements of $\langle \boldsymbol{v}(t)\boldsymbol{J}^{\mathrm{T}}(0)\rangle_{\mathrm{m}}$ are antisymmetric in time dependence. These same elements vanish for all t in the racemic mixture, catalysing observable physical differences in the laboratory frame of reference when the two enantiomers are mixed. These results were obtained for the 1-fluoro-1-chloroethanes by computer simulation.[2,3] In this paper we extend the analysis to two chiral systems of different molecular symmetry, the bromochlorofluoromethanes and *t*-1,2-dimethylcyclopropanes. The first system is the simplest type of chiral tetrahedral molecule[4] and the second consists of 'propeller'-shaped molecules of higher chiral symmetry.[5] The bromochlorofluoromethanes typify the basic 'building block' from which more complicated chiral structures such as the canadines or 2-hydroxypropanoic acids (lactic acids) may be constructed. In the propeller-like canadines the racemic modification of the melting point is 42 °C (the mixture melting at the higher temperature), in the lactic acids it is 35 °C (the mixture melting at the lower temperature). Classical phenomenological theory cannot explain these differences because each enantiomer seems to behave identically in the laboratory frame and therefore has to be described by the same set of theoretical parameters. In contrast, there is no difference in the melting point between enantiomers and racemic mixture in the *t*-1,2-cyclopropanedicarboxylic acids, which have the same basic symmetry as the *t*-1,2-dimethylcyclopropanes.

ALGORITHM AND METHOD

The equations of motion for 108 enantiomers of type *R* or *S* were integrated with an algorithm developed by Ferrario *et al.*[6] from the CCP5 listing TETRAH.

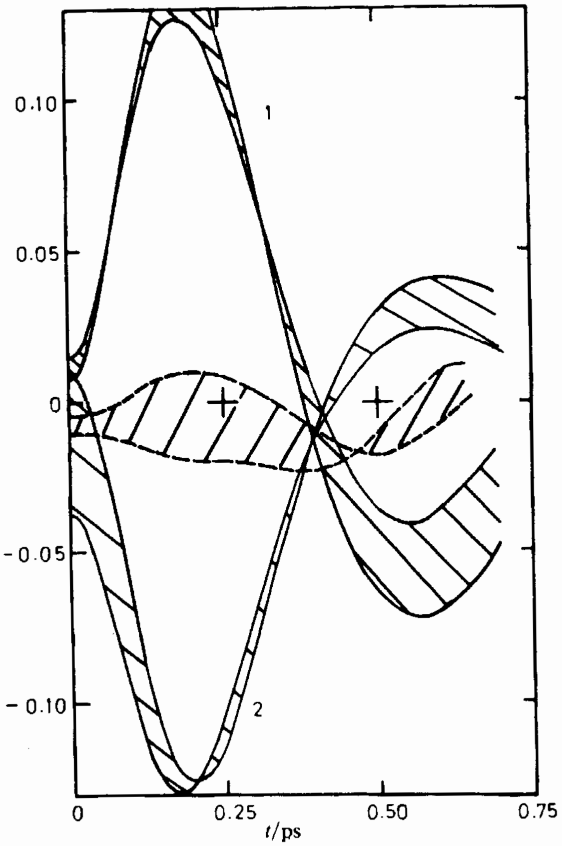

Fig. 1. Computer simulation of CHBrClF at 293 K, 1 bar showing some antisymmetric off-diagonal elements of $\langle \boldsymbol{v}(t)\boldsymbol{J}^{\mathrm{T}}(0)\rangle_{\mathrm{m}}$. (1) (1, 3) element, *R* enantiomer, $[(1,3)\equiv \langle v_1(t)J_3(0)\rangle/(\langle v_1^2\rangle^{1/2}\langle J_3^2\rangle^{1/2})]$; (2) (1, 3) element, *S* enantiomer; (– – –) (1, 3) element, racemic modification. Hatched areas represent 'noise-level' in the running-time averaging.

The racemic mixture was simulated with 54 molecules of type *R* mixed with 54 of type *S*. The system was equilibrated over *ca.* 2000 time steps of 0.05 ps each and time-correlation functions computed with running-time averaging in both frames of reference (laboratory and principal moments of inertia) from vectors such as $\boldsymbol{v}$, $\boldsymbol{\omega}$, $\boldsymbol{J}$ (the molecular angular momentum), $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ and $\boldsymbol{e}_3$ (unit vectors in the three principal moment of inertia axes), and their time derivatives $\dot{\boldsymbol{e}}_1$, $\dot{\boldsymbol{e}}_2$ and $\dot{\boldsymbol{e}}_3$. The latter may be related by Fourier transformation to far-infrared spectra,[7] which are especially sensitive to the short-time (sub-picosecond) details of molecular rototranslation in the laboratory frame.

RESULTS AND DISCUSSION

In both systems some of the moving-frame cross-correlation functions mirror each other in time dependence (fig. 1 and 2) in the two enantiomers and disappear in the racemic mixture. Some of the normalised elements of $\langle \boldsymbol{v}(t)\boldsymbol{J}^{\mathrm{T}}(0)\rangle$ are positive (+), some are negative (−) and some are vanishingly small (θ). The overall

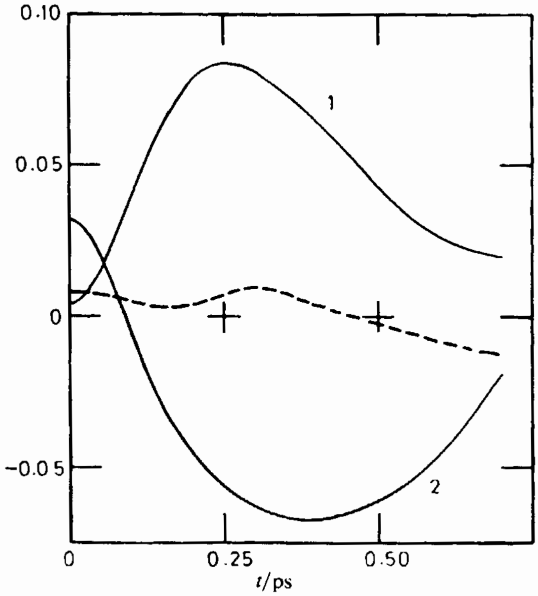

Fig. 2. Simulation of *t*-1,2-dimethylcyclopropane at 293 K, 1 bar. (1) (2, 1) element, *S* enantiomer; (2) (2, 1) element, *R* enantiomer; (– – –) racemic mixture.

symmetry (based on empirical molecular-dynamics results) of the correlation matrix in both enantiomers and racemic mixture is summarised below.

In these matrices the (1, 1) element, for example, would be

$$(1, 1) \equiv \frac{\langle v_1(t) J_1(0)\rangle}{\langle v_1^2\rangle^{1/2}\langle J_1^2\rangle^{1/2}}.$$

The (1, 2) element is

$$(1, 2) \equiv \frac{\langle v_1(t) J_2(0)\rangle}{\langle v_1^2\rangle^{1/2}\langle J_2^2\rangle^{1/2}} \quad etc.$$

Bromochlorofluoromethanes

$$\begin{array}{ccccccccccc} & R & & & & S & & & & RS & \\ 0 & + & + & & 0 & + & - & & 0 & + & 0 \\ - & 0 & + & & - & 0 & + & & - & 0 & + \\ - & + & 0 & & + & + & 0 & & 0 & - & 0 \end{array}$$

t-1,2-*dimethylcyclopropanes*

$$\begin{array}{ccccccccccc} & R & & & & S & & & & RS & \\ 0 & + & 0 & & 0 & - & 0 & & 0 & 0 & 0 \\ - & 0 & 0 & & + & 0 & 0 & & 0 & 0 & 0 \\ 0 & 0 & 0 & & 0 & 0 & 0 & & 0 & 0 & 0 \end{array}$$

Note that none of the diagonal elements exist by basic symmetry results.[1] The effects of the antisymmetry in the moving frame are carried through to the laboratory frame in different ways for these two systems. This is illustrated in fig. 3 and 4

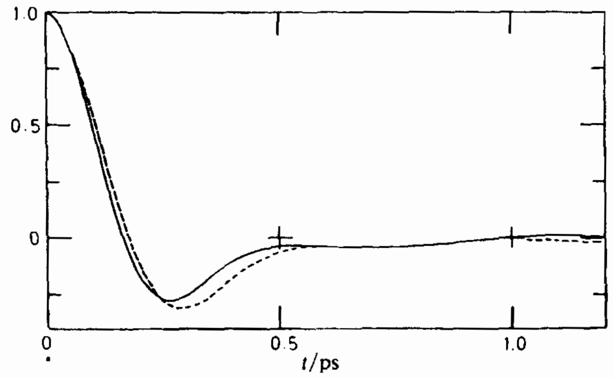

Fig. 3. $\langle \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0)\rangle / \langle \omega^2 \rangle$ (enantiomers) for CHBrClF in the laboratory frame. (– – –) Racemic modification.

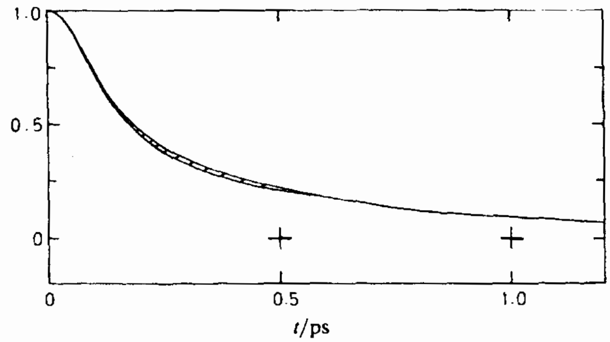

Fig. 4. Plot of $\langle \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0)\rangle / \langle \omega^2 \rangle$ (enantiomers) for *t*-1,2-dimethylcyclopropane in the laboratory frame. (– – –) Racemic modification, as for enantiomers on this scale.

through one of the basically important autocorrelation functions in the laboratory frame, the angular velocity a.c.f. $\langle \boldsymbol{\omega}(t) \cdot \boldsymbol{\omega}(0)\rangle / \langle \omega^2 \rangle$. The racemic modification in the *t*-1,2-dimethylcyclopropanes is much smaller than in the bromochlorofluoromethanes according to the simple site–site model used in our computations. The results of fig. 3 suggest that the modification should be observable straightforwardly in the far-infrared.

There has been very little spectral-bandshape work on the racemic modification, and the new computational results reported here pose a new challenge also to the analytical theory of molecular diffusion.[8] This has to explain why moving frame matrices of different symmetry transform rotation/translation effects into the laboratory frame in different ways for different molecular structures.

The difference in physical properties between enantiomer and racemic mixture is therefore an observable phenomenon whose roots have been traced directly, using computer simulation, to the cross-correlation between v and J. In molecules which are not chiral, this type of cross-correlation is still present, and may be quantified[1,9] by computer simulation through $\langle \boldsymbol{v}(t) \boldsymbol{J}^{\mathrm{T}}(0)\rangle_{\mathrm{m}}$.

We note that symmetry considerations[1] imply that some matrix elements are equal in sign for both enantiomers and that others are different.

The S.E.R.C. and CCP5 are thanked for financial support. Dr M. Ferrario is acknowledged for his role in modifying the program TETRAH.

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[8] For a review see P. Grigolini, *J. Stat. Phys.*, 1982, **27**, 283; see also M. W. Evans, G. J. Evans, W. T. Coffey and P. Grigolini, *Molecular Dynamics* (Wiley–Interscience, New York, 1982), chap. 9 and 10.

[9] See, for example, G. J. Evans and M. W. Evans, *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**, 137; 153.

(PAPER 3/735)