

Molecular Dynamics of Optically Active Molecules in the Liquid State: Direct Observation of Rotation/Translation Coupling

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By simulating, on a computer, the molecular dynamics of (*R*)- and (*S*)-1,1-chlorofluoroethane enantiomer liquids, together with the racemic mixture, a major new spectroscopic property of the molecular liquid state is revealed directly (in the laboratory frame) to be a consequence of rotation/translation coupling.

The classical theory of molecular diffusion in liquids¹ ignores the effect of a molecule's rotation on the translation of its own centre of mass (and *vice-versa*). The reason for this is not clear, and the basic mechanism has remained clouded in uncertainty up to the recent development of the rotating frame trap of computer simulation by Ryckaert *et al.*² In this communication we develop a new method for observing this basic phenomenon directly by spectroscopy.

The molecular dynamics of the two enantiomers, (*R*) and (*S*), of 1,1-chlorofluoroethane have been simulated using 108 molecules interacting pair-wise with a site-site potential. By using 54 molecules of each enantiomer, the racemic mixture can be studied in the same way. The data generated by the three separate runs may be averaged into the relevant auto- and cross-correlation functions necessary for the direct spectral observation of rotation/translation coupling.

Both the (*R*) and (*S*) enantiomers were modelled with the same 5 × 5 atom-atom Lennard-Jones parameters: $\epsilon/k(\text{Cl-Cl}) = 127.9 \text{ K}$, $\sigma(\text{Cl-Cl}) = 3.6 \text{ \AA}$; $\epsilon/k(\text{C-C}) = 35.8 \text{ K}$, $\sigma(\text{C-C}) = 3.4 \text{ \AA}$; $\epsilon/k(\text{H-H}) = 10.0 \text{ K}$, $\sigma(\text{H-H}) = 2.8 \text{ \AA}$;

$\epsilon/k(\text{F-F}) = 54.9 \text{ K}$, $\sigma(\text{F-F}) = 2.7 \text{ \AA}$; $\epsilon/k(\text{CH}_3\text{-CH}_3) = 158.6 \text{ K}$, $\sigma(\text{CH}_3\text{-CH}_3) = 3.5 \text{ \AA}$. Electrostatic interactions were modelled in both cases in terms of the partial charges and reported by Nafie *et al.*³ The three runs were carried out at the same density (1.1 g mol^{-1}) and temperature (293 K) using the same number of time-steps throughout.

The important result of this simulation is exemplified in Figure 1 in terms of the laboratory frame autocorrelation functions (a.c.f.): $\langle \dot{e}_1(t) \cdot \dot{e}_1(0) \rangle / \langle \dot{e}_1^2 \rangle$. Here e_1 is a unit vector in the I_{33} axis of either enantiomer. The Fourier transform of this type of a.c.f. is a far i.r. spectrum,¹ a sensitive source of information on molecular dynamics. The a.c.f. of each enantiomer is the same, as expected, *but that of the racemic mixture differs greatly*. From Figure 1 the far i.r. spectrum of the racemic mixture would peak at *almost twice* the frequency of either enantiomer. The same pattern emerges for the other vectors controlling the molecule's dynamics, such as e_2 and e_3 , the other two unit vectors in the principal moment of inertia frame; the molecular angular velocity (ω) and momentum (J), and the centre of mass translational velocity (v). By look-

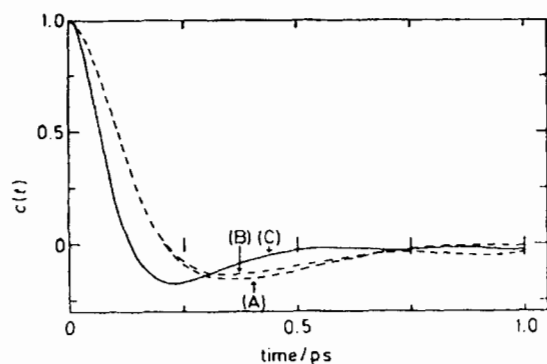


Figure 1. $\langle \dot{e}_1(t) \cdot \dot{e}_1(0) \rangle / \langle \dot{e}_1^2 \rangle$: laboratory frame. (A) (*S*) enantiomer, (B) (*R*) enantiomer, (C) racemic mixture.

ing at $\langle e_1(t) \cdot e_1(0) \rangle$, for example, it is possible to say that the dielectric relaxation time of the racemic mixture is approximately half that of either enantiomer.

The effect of mixing the (*R*) and (*S*) enantiomers on the liquid state molecular dynamics is therefore very pronounced.

The usual statement that enantiomers have identical physical properties, (except in their response to circularly polarised irradiation) is true in some cases in the laboratory frame of reference. By constructing the rotating (moment of inertia) frame² cross-correlation matrix $\langle v(t) \cdot J^T(0) \rangle$ a critical difference in the behaviour of the two enantiomers can be observed.

The (3,1) and (1,3) elements of this matrix are equal in magnitude but opposite in sign. For example, the (1, 3) element of the (*R*) enantiomer has a time dependence which is the exact mirror image of that of the (*S*) enantiomer. In the racemic mixture both the (1, 3) and (3, 1) elements vanish for all t . The time dependence of the other seven elements, on the other hand is identical in all three cases. These results will be reported in detail elsewhere. In dynamical terms this is the only way of explaining why the spectrum of a 50/50 A/B mixture should be strikingly different from that of A and B when the latter spectra are identical.

The new spectral phenomenon illustrated in Figure 1 is therefore the first *direct* observation of the effects of rotation/translation coupling carried through into the laboratory frame. Therefore it would be interesting to synthesize (*R*)- and (*S*)-1,1-chlorofluoroethane liquids (they have not yet been isolated) and test the computer simulation directly.

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