edited by P. J. Dobson, J. B. Pendry, and C. J. Humphreys, IOP Conference Series No. 41 (Institute of Physics, Bristol, 1978), pp. 205–217.

[2] L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971).

[3] L. R. Bedell and H. E. Farnsworth, Surf. Sci. 41, 165 (1974).

[4] J. Rundgren and G. Malmström, Phys. Rev. Lett. 38, 836 (1977).

[5] J. B. Pendry, *Low Energy Electron Diffraction* (Academic, London, 1974).

[6] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[7] J. Neve, J. Rundgren, and P. Westrin, J. Phys. C 15, 4391 (1982).

[8] J. M. Cowley, *Diffraction Physics* (North-Holland, Amsterdam, 1981).

[9] E. Zanazzi and F. Jona, Surf. Sci. 62, 61 (1977); J. B. Pendry, J. Phys. C 13, 937 (1980).

[10] J. Philip and J. Rundgren, in *Proceedings of the Conference on Determination of Surface Structure by LEED*, edited by P. M. Marcus (Plenum, New York, 1982), p. 16.

[11] D. L. Adams, H. B. Nielsen, and M. A. van Hove, Phys. Rev. B 20, 4789 (1979).

[12] Y. Gauthier, R. Baudoing, and L. Clarke, J. Phys. C 15, 3231 (1982).

New Phenomenon of the Molecular Liquid State: Interaction of Molecular Rotation and Translation

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The technique of computer simulation is used to reveal a new and unsuspected phenomenon of the molecular liquid state which is observable by several different spectroscopic techniques. The phenomenon is explained in terms of the effect of a molecule's rotation on its own translation (or vice versa). This is directly measurable in optically active molecules, and exists for all molecules in the liquid state.

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The technique of computer simulation has been developed to the point where the molecular dynamics of optically active molecules in the liquid state can be studied in detail for the first time. These molecules have no center of inversion and exist as C_s mirror-image pairs, known as enantiomers. An equimolar mixture of these enantiomers is a racemic mixture.

In this Letter I report the first computer simulation of two enantiomer liquids and of their 50/50 racemic mixture. A new, unexpected, and generally valid spectroscopic phenomenon is revealed by these computations, and can be explained precisely in terms of rotation/translation coupling on a fundamental, molecular scale.

The algorithm was based on a listing from Collaborative Computational Project 5 (CCP5) of the Science and Engineering Research Council (U.K.), extensively modified by Ferrario *et al.*[1-5] The *R* and *S* enantiomers of 1,1-chlorofluoroethane (Fig. 1) were modeled with a 5×5 site-site potential consisting of atom-atom Lennard-Jones terms and partial charges located at the atomic sites. The Lennard-Jones parameters were

$$(\epsilon/k)(\mathrm{Cl\text{-}Cl}) = 127.9\ \mathrm{K};\ \sigma(\mathrm{Cl\text{-}Cl}) = 3.6\ \text{Å}; \qquad (1)$$

$$(\epsilon/k)(\mathrm{C\text{-}C}) = 35.8\ \mathrm{K};\ \sigma(\mathrm{C\text{-}C}) = 3.4\ \text{Å}; \qquad (2)$$

$$(\epsilon/k)(\mathrm{H\text{-}H}) = 10.0\ \mathrm{K};\ \sigma(\mathrm{H\text{-}H}) = 2.8\ \text{Å}; \qquad (3)$$

$$(\epsilon/k)(\mathrm{F\text{-}F}) = 54.9\ \mathrm{K};\ \sigma(\mathrm{F\text{-}F}) = 2.7\ \text{Å}; \qquad (4)$$

$$(\epsilon/k)(\mathrm{CH_3\text{-}CH_3}) = 158.6\ \mathrm{K};\quad \sigma(\mathrm{CH_3\text{-}CH_3}) = 3.5\ \text{Å}. \qquad (5)$$

Partial charges were used as given by Nafie, Polavarapu, and Diem.[6]

At 293 K, with an estimated liquid density of 1.1 g mol^{-1}, 108 molecules of each enantiomer were used in two separate molecular-dynamics runs. Data from these runs were used to evaluate a wide range of time correlation functions in both the laboratory and rotating frames of reference,[7] the latter defined for convenience as that of the principal molecular moments of inertia.

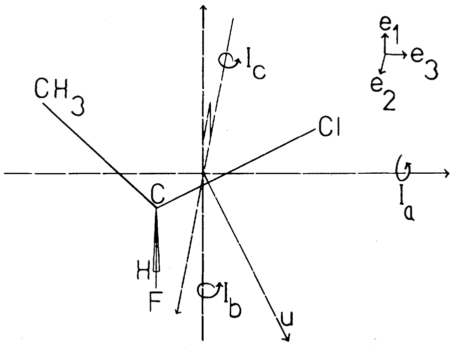

FIG. 1. The S enantiomer of 1,1-fluorochloroethane. The x, y, and z axes label the principal-moment-of-inertia frame, intersecting at the center of mass. The principal moments of inertia are I_a, I_b, and I_c. The direction of the resultant molecular dipole moment is labeled u. Inset: The frame of the unit vectors $\vec{e}_1$, $\vec{e}_2$, and $\vec{e}_3$ (see text). The R enantiomer is obtained by holding a mirror to the plane of the paper, i.e., by interchanging the positions of H and F.

The racemic mixture was simulated at the same density with the same pair potential (consisting of the 25 site-site terms) by use of 54 molecules of type R and 54 of type S. Autocorrelation and cross-correlation functions (ACF's and CCF's) were constructed of three unit vectors $\vec{e}_1$, $\vec{e}_2$, and $\vec{e}_3$ in the principal moment of inertia axes; their time derivatives $\dot{\vec{e}}_1$, $\dot{\vec{e}}_2$, and $\dot{\vec{e}}_3$; the center-of-mass velocity, $\vec{v}$; the resultant molecular angular velocity, $\vec{\omega}$; and the molecular angular momentum, J. Correlation functions among the last three vectors were computed in both frames of reference.

The most important result of this simulation is exemplified in Fig. 2 in terms of the laboratory-frame ACF's $\langle\dot{\vec{e}}_1(t)\cdot\dot{\vec{e}}_1(0)\rangle/\langle\dot{\vec{e}}_1^{\,2}\rangle$ and $\langle\vec{e}_1(t)\cdot\vec{e}_1(0)\rangle$ (P_1- and P_2-rank Legendre polynomials). These functions are the same, within the noise generated by the computer technique itself, for the R and S enantiomers, but *strikingly different for the racemic mixture.* I have verified that the same pattern is exhibited for the other vectors mentioned above.

This is an original, general, and unexpected result, and should be observable straightforwardly with spectroscopies such as[8] far-infrared absorption, dielectric dispersion, spontaneous and stimulated Raman scattering, infrared absorption, Rayleigh scattering, inelastic neutron scattering, tracer diffusion, and related techniques designed to look at band shapes and transport properties of the liquid state. It would be interesting to synthesize both R and S 1,1-fluorochloroethane and to test the molecular simulation directly.

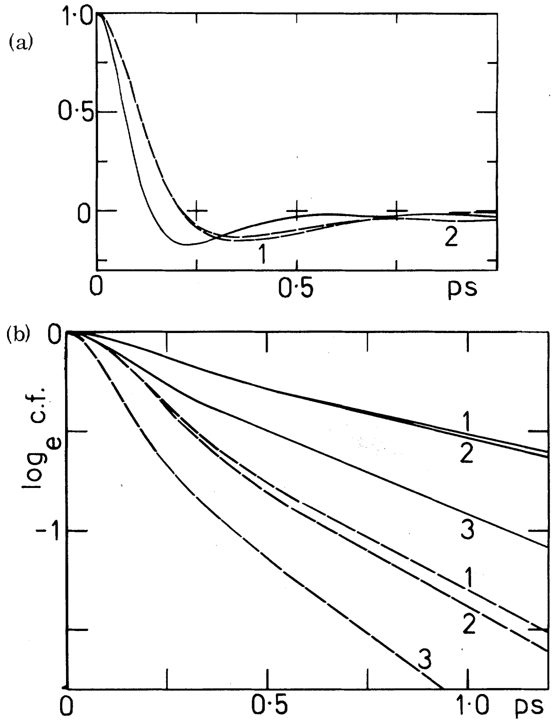

FIG. 2. (a) Dashed lines: (1), $\langle\dot{\vec{e}}_1(t)\cdot\dot{\vec{e}}_1(0)\rangle/\langle\dot{e}_1^{\,2}\rangle$, S enantiomer, laboratory frame; and (2), same as (1), R enantiomer. Solid line, same as for (1), racemic mixture. Note that the Fourier transforms of these functions give far-infrared spectra (Ref. 9). The far-infrared spectrum of the racemic mixture peaks at roughly *twice* the frequency of either enantiomer, whose spectra are identical within the computer-generated noise. (b) P_1 (first rank) (Refs. 8 and 9) and P_2 orientational ACF's of $\vec{e}_1$, laboratory frame. Solid lines: (1), R enantiomer; (2), S enantiomer; (3) racemic mixture (P_1). Dashed lines: (1), S enantiomer; (2), R enantiomer; (3), racemic mixture (P_2). The P_1 functions can be related (Ref. 8) to infrared band shapes and dielectric loss curves, and the P_2 to Raman and Rayleigh spectra. The dielectric relaxation time from (b) *is much shorter* for the racemic mixture than for either enantiomer liquid.

The classical theory of molecular diffusion ignores the effect of a molecule's rotation on its own translation and vice versa.[9] This effect can be observed for example through the elements of the rotating-frame correlation matrix[7] $\langle\vec{v}(t)\vec{J}^T(0)\rangle$. In Fig. 3 I illustrate that the (1,3) and (3,1) elements (see Fig. 1) of this matrix are equal but *opposite in sign* for the R and S enantiomers and vanish for all t in the racemic mixture. The (2,1), (1,2), (3,2), (2,3), and diagonal elements remain the *same* in *both* the

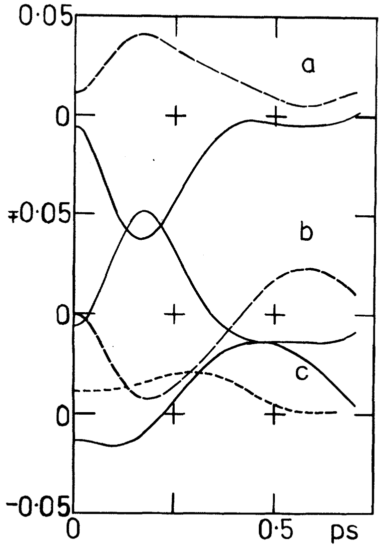

FIG. 3. The critical (3, 1) and (1, 3) elements of $\langle \vec{v}(t)\vec{J}^T(0)\rangle$ in the rotating frame. (a) Dashed line, $(3,1) \equiv \langle v_3(t)J_1(0)\rangle / \langle v_3^2\rangle^{1/2}\langle J_1^2\rangle^{1/2}$ for the *R* enantiomer; solid line, (1, 3) for the *R* enantiomer. (b) Dashed line, (3, 1) for the *S* enantiomer; solid line, (1, 3) for the *S* enantiomer. N. B. These are opposite in sign to those of (a). (c) Dashed line, (3, 1) for the racemic mixture; solid line, (1, 3) for the racemic mixture. Note that (i) the noise level may be judged from the fact that all these should vanish by symmetry at $t = 0$; (ii) the functions are reliable out to about 0.3 ps and thereafter become too noisy for comment; (iii) (c) is all noise, i.e., both elements have vanished; (iv) the noise is caused purely by restrictions on computer time, and can be cut out by long enough runs. The noise level here is much higher, relatively, than for the ACF's of Fig. 2.

enantiomer liquids *and* racemic mixture. In the racemic mixture, therefore, *two elements of the matrix* $\langle \vec{v}(t)\vec{J}^T(0)\rangle$ *vanish,* the rest remaining the same as those in either enantiomer.

This property is responsible for the *laboratory-frame* differences illustrated in Fig. 2, which are therefore *directly observable* spectroscopic manifestations of molecular-scale rotation-translation coupling. There seems to be no other way of explaining why the rototranslational spectrum of a mixture of 50% enantiomer *A* in 50% enantiomer *B* should be *different* from that of either component when the spectra of each pure component are *identical.* (This applies also for laboratory-frame ACF's such as those of $\vec{v}$, $\vec{\omega}$, and $\vec{J}$ or of molecular force and torque.)

Finally, I mention that rotation-translation coupling is present in *all molecular liquids,* optically active or not, but can be seen *directly* in the former, as I have shown.

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[1] M. Ferrario and M. W. Evans, to be published.

[2] M. Ferrario and M. W. Evans, Adv. Mol. Relaxation Int. Proc. 23, 69, 113 (1982).

[3] G. J. Evans and M. W. Evans, to be published.

[4] B. Janik, J. Sciesinski, M. W. Evans, E. Kluk, and T. Grochulski, Chem. Phys. 70, 77 (1982).

[5] M. W. Evans, J. Chem. Phys. 76, 5473, 5480 (1982), and to be published.

[6] L. A. Nafie, P. L. Polavarapu, and M. Diem, J. Chem. Phys. 73, 3530 (1980).

[7] J.-P. Ryckaert, A. Bellemans, and G. Ciccotti, Mol. Phys. 44, 979 (1981).

[8] M. W. Evans, G. J. Evans, W. T. Coffey, and P. Grigolini, *Molecular Dynamics* (Wiley/Interscience, New York, 1982), Chap. 6.

[9] Ref. 8, Chaps. 1, 2, and 5.