J. Chem. Soc., Faraday Trans. 2, 1983, **79**, 1331–1340

Computer Simulation of the Dynamics of Optically Active Molecules in the Liquid State

BY MYRON W. EVANS

Edward Davies Chemical Laboratories, University College of Wales, Aberystwyth SY23 1NE

Received 5th November, 1982

The technique of computer simulation is used to produce detailed information on the molecular dynamics of *R*- and *S*-1,1-chlorofluoroethane and the racemic mixture. A critically important difference in the dynamical behaviour of the two enantiomers is revealed using a rotating frame of reference. This is the source of observable differences in laboratory frame auto-correlation functions of the racemic mixture and therefore in measurable liquid-phase spectra. Therefore, by measuring the spectrum of either enantiomer, followed by that of their racemic mixture, information is provided directly on the statistical correlation between a molecule's rotation and centre-of-mass translation. We believe this to be a new explanation for a well known phenomenon of the molecular liquid and solid states of matter.

The computer-simulation method has now been developed to a degree at which we may begin to explore the details of molecular dynamics and interaction of optically active (or chiral) molecules in the liquid state. These molecules have no centre of symmetry and exist as two distinct enantiomers. Many of the equilibrium physical properties of each enantiomer (mirror-image molecules) are identical, but the molecular-dynamical nature of each species, measured through correlation functions, remains unexplored.

Berne and Pecora[1] have mentioned that the general symmetry rules of parity, time-reversal *etc.* governing the existence of the correlation function $\langle A(t)B(0)\rangle$, where A and B are different dynamical variables, do not apply in an isolated enantiomer. This implies, in principle, the existence of correlation functions which would otherwise vanish by symmetry in liquids whose constituent molecules are not chiral. There exist field-induced phenomena, such as the Pockels effect,[2] which depend on the chirality of the liquid under investigation, and the existence of new cross correlations implies new transport phenomena, some of which are listed by Berne and Pecora.

For these reasons and others, the simulation of the molecular dynamics of chiral liquids is full of interest. In this first, exploratory, paper we have chosen to study the two (*S* and *R*) enantiomers of 1,1-chlorofluoroethane, using a five-site model of the intermolecular pair potential. We adhere to our general programme[3–14] of simulation using transferable parameters taken from the literature. These are the Lennard-Jones ε/k and σ parameters for each atom–atom interaction and partial charges located on each atom.

1,1-chlorofluorethane (the racemic mixture) is increasingly important as a by-product and intermediate in polymer manufacture *via* high-temperature cracking aided by catalysis. The kinetics and thermodynamics of this vapour-phase process are therefore fairly well known, but there has been no experimental work on the molecular dynamics, transport properties or field-induced phenomena in the liquid state (either the racemic mixture or isolated enantiomers). Our simulation is equivalent, therefore, to a coordinated experimental effort carried out with different techniques[15] at one state point on each enantiomer. The validity of the computer-simulation method could be checked by carrying out spectroscopic measurements of various kinds, but our previous work, involving detailed literature searches[3-14] for liquids such as chloroform (*in toto ca.* 1000 papers) suggests that the computer simulation of molecular dynamics is often more incisive than the totality of the experimental work available at one state point. This does not imply, of course, that the experimental effort should be abandoned, but the opposite: the spectroscopic investigation should be intensified and coordinated, using computer simulation as a method of data analysis. Phenomenological theory may then be used to draw general conclusions and construct general hypotheses about the nature of the liquid state. The recent work of Grigolini *et al.*,[16] based on data from computer simulation, suggests that this is fundamentally non-linear. The classical work of Langevin, for example, is in this context a linear approximation[15] and fails qualitatively to explain some fundamental features of simulation. Prominent among these is the mutual interaction of molecular rotation and centre-of-mass translation.[3, 14] In chiral liquids this may be observable[1] through correlation functions of the type $\langle \boldsymbol{v}(t)\boldsymbol{J}^T(0)\rangle$ constructed in the laboratory frame, where $\boldsymbol{v}$ is the centre-of-mass velocity and $\boldsymbol{J}$ the molecular angular momentum. In an optically inactive liquid $\langle \boldsymbol{v}(t)\boldsymbol{J}^T(0)\rangle = 0$ in the laboratory frame, but some of its off-diagonal elements exist for $t > 0$ in a rotating frame of reference,[17] for example the frame of the principal molecular moments of inertia. All these rotating-frame elements exist, in principle, in an enantiomer, and some are not the same in the other enantiomer of a racemic pair because of the mirror-image symmetry.

SUMMARY OF DATA ON LIQUID 1-CHLORO-1-FLUOROETHANE

In order to emphasize the incisiveness of the computer-simulation method we provide a short summary of the literature on the racemic mixture. The enantiomers do not seem to have been isolated.

Durig *et al.*[18] have recorded the infrared and Raman spectra of the racemic mixture at room temperature and assigned the features in terms of C_s symmetry. According to Durig *et al.* non-bonded interactions are important in determining the magnitude of the torsional barriers in the molecule. Thomas *et al.*[19] have measured the microwave spectrum, quadrupole coupling and barrier to internal rotation in the molecule. In the present paper we remove the internal-rotation complication by regarding the $-CH_3$ group as a single site, using for this purpose the successful Lennard-Jones parameter of Lassier and Brot.[20] Thomas *et al.* point out that the molecule has no plane of symmetry, implying that dipole-moment components exist in all the axes of the principal moment-of-inertia system (see fig. 1). A rough analysis of the probable direction of the dipole moment indicates, however, that $\mu_B \gg \mu_A > \mu_C$ in the standard notation, *i.e.* the dipole-moment direction almost coincides with the B axis of the principal moment of inertia frame illustrated in fig. 1. In the computer simulation we define three unit vectors, $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ and $\boldsymbol{e}_3$, in these axes and, according to Thomas *et al.*, $\boldsymbol{e}_1$ is the dipole unit vector to a good approximation. Thomas *et al.*[19] have also measured the three rotational constants for both the ^{35}Cl and ^{37}Cl isotopes. Using these data we obtain the three principal moments of inertia as: $I_A = 93.1 \times 10^{-40}$ g cm^2, $I_B = 178.2 \times 10^{-40}$ g cm^2 and $I_C = 254.3 \times 10^{-40}$ g cm^2.

These experimental values were used as a check for the three principal moments of inertia calculated using Hirschfelder's method from literature geometrical data taking $-CH$ as an 'atom'. We used this method to define the directions of the

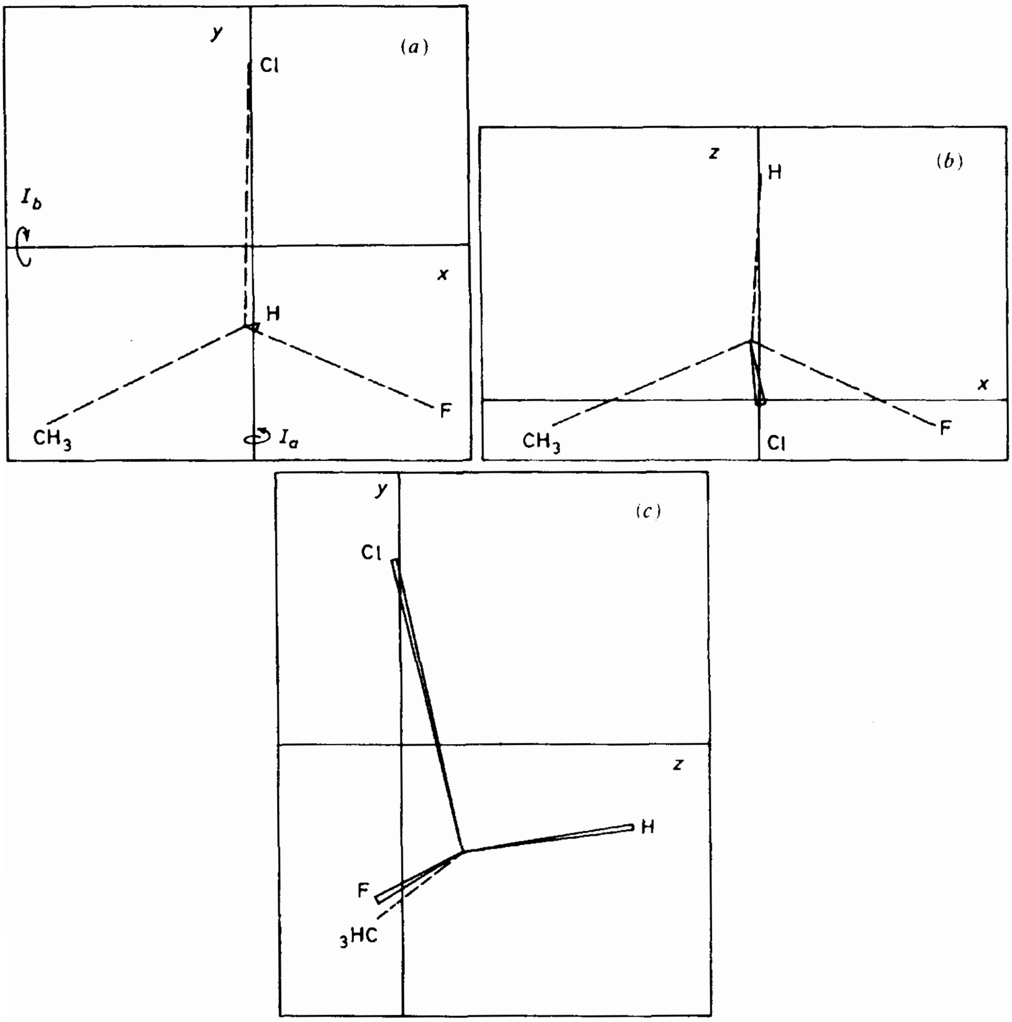

Fig. 1. Projections of the R-1,1-C_2H_4FCl molecule in the principal moment-of-inertia frame. The x, y and z directions define the axes of $\boldsymbol{e}_3$, $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$, respectively, intersecting at the centre of mass.

three principal moment-of-inertia axes illustrated in fig. 1 and intersecting at the centre of mass. Using literature bond lengths and angles this method gave $I_A = 90.1 \times 10^{-40}$ g cm^2, $I_B = 167.4 \times 10^{-40}$ g cm^2 and $I_C = 247.3 \times 10^{-40}$ g cm^2. The atomic coordinates in Å relative to the centre of mass for the two enantiomers are recorded in table 1.

Nafie *et al.*[21] have recently initialised the study of vibrational optical activity (v.o.a.) in perturbed degenerate modes using model calculations based on a fixed partial-charge model for the 1-substituted halogenoethanes including 1-chloro-1-fluoroethane. This is a new phenomenon based on the chiral perturbation of symmetric chemical groups (in this case CH_3) containing degenerate pairs of modes. This perturbation gives rise to a couplet signal having equal and opposite v.o.a.

Table 1. Coordinates relative to centre of mass (Å)

enantiomer 1				enantiomer 2			
atom	$x(\boldsymbol{e}_3)$	$y(\boldsymbol{e}_1)$	$z(\boldsymbol{e}_2)$	atom	$x(\boldsymbol{e}_3)$	$y(\boldsymbol{e}_1)$	$z(\boldsymbol{e}_2)$
Cl	0.00	1.22	−0.025	Cl	0.00	1.22	0.025
C	−0.05	−0.51	0.40	C	−0.05	−0.51	−0.40
H	0.01	−0.53	1.49	H	0.01	−0.53	−1.49
F	1.12	−1.05	−0.16	F	1.12	−1.05	0.16
CH_3	−1.34	−1.15	−0.16	CH_3	−1.34	−1.15	0.16

intensity for the two modes. This complements the phenomenon of Raman optical activity. Calculations were carried out by these authors using perturbations of charge or polarizability, mass, geometry and potential energy. The fixed partial-charge parameters of Nafie *et al.* can be used directly in the molecular-dynamics simulation to deal with the intermolecular electrodynamics in a simple manner.

Finally, Sugie *et al.*[22] have determined the dipole moment of 1-chloro-1-fluoroethane in the vapour-phase racemic mixture from the $J = 1 \rightarrow 0$ transition of the microwave spectrum and have analysed the Stark effects.

Sugie *et al.* report a resultant dipole moment of 2.068 D for the vapour-phase racemic mixture, with components in the principal moment of inertia frame of $\mu_A = 0.954$ D, $\mu_B = 1.836$ D and $\mu_C = 0.013$ D. These experimental results contradict the assertion made by Thomas *et al.*[19] that $\mu_B \gg \mu_A = \mu_C$. It seems more likely, from a study of fig. 1 for example, that Sugie *et al.* are accurate in their assessment.

DESCRIPTION OF ALGORITHM

This was developed by Ferrario and Evans[3] for molecules of any symmetry interacting *via* atom–atom sites. The interaction between a pair of 1-chloro-1-fluoroethane molecules is modelled therefore by 25 atom–atom terms with the following Lennard-Jones parameters ($\varepsilon/\boldsymbol{k}$ in K, σ in Å): (1) $\varepsilon/\boldsymbol{k}(\text{Cl—Cl})^{20} = 127.9$, $\sigma(\text{Cl—Cl}) = 3.6$; (2) $\varepsilon/\boldsymbol{k}(\text{C—C})^{20} = 35.8$, $\sigma(\text{C—C}) = 3.4$; (3) $\varepsilon/\boldsymbol{k}(\text{H—H})^{3} = 10.0$, $\sigma(\text{H—H}) = 2.8$; (4) $\varepsilon/\boldsymbol{k}(\text{F—F})^{23} = 54.9$, $\sigma(\text{F—F}) = 2.7$; (5) $\varepsilon/\boldsymbol{k}(\text{CH}_3\text{—CH}_3)^{20} = 158.6$, $\sigma(\text{CH}_3\text{—CH}_3) = 3.5$. Cross terms are evaluated with the Lorentz–Berthelot rules, *e.g.* $\varepsilon/\boldsymbol{k}(\text{H—Cl}) = \{[\varepsilon/\boldsymbol{k}(\text{H—H})][\varepsilon/\boldsymbol{k}(\text{Cl—Cl})]\}^{1/2}$ and $\sigma(\text{H—Cl}) = \frac{1}{2}[\sigma(\text{H—H}) + \sigma(\text{Cl—Cl})]$.

Electrodynamic interactions between a pair of molecules are simulated with the fixed partial-charge parameters of Nafie *et al.*[21]

The simulation was carried out at 293 K. The density of 1-chloro-1-fluoroethane in the liquid state at this temperature seems to be unknown. Therefore we adopted the following estimate. The densities of molecules closely related to 1-chloro-1-fluoroethane are roughly the same at 293 K. For example, that of 1-chloro-2-fluoroethane is 1.1747 g cm^{-3}, that of 1,1-dichloroethane is 1.1575 g cm^{-3} and that of 1,1-difluoroethane is 0.95 g cm^{-3} (saturated pressure). The density of 1,1-dichloro-1-fluoroethane at 283 K is 1.25 g cm^{-3}, and by extrapolation close to that of the others at 293 K. It is unlikely, therefore, that the density of a racemic mixture of 1-chloro-1-fluoroethane is much different from 1.1 g cm^{-3} at 283 K. This provides a molar volume of 75.1 cm^3, which was used as the input molar volume for the computer simulation.

108 molecules of each enantiomer were arranged initially on a face-centred cubic lattice, which was melted using *ca.* 2000 time steps of 0.005 ps each to conserve the equilibrium total energy to within *ca.* ±0.1%. At equilibrium the relevant dynamical data were loaded on to a disc and stored prior to use in sub-routines designed to calculate a wide variety of correlation functions (the time domain equivalent of spectra of various types) using running-time averaging. Auto- and cross-correlation functions can be computed among vectors such as: (i) $\boldsymbol{v}$, the molecular centre-of-mass velocity; (ii) $\boldsymbol{J}$, the molecular angular momentum; (iii) $\boldsymbol{\omega}$, the molecular angular velocity; (iv) the orientation vectors $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ and $\boldsymbol{e}_3$ defined in fig. 1 (both first- and second-rank Legendre a.c.f.); (v) the rotational velocities $\dot{\boldsymbol{e}}_1$, $\dot{\boldsymbol{e}}_2$ and $\dot{\boldsymbol{e}}_3$ for far-infrared spectra.[15]

Correlation functions among (i) to (iii) can be computed either in the static (laboratory) frame, the rotating frame of fig. 1 or any other frame, for each enantiomer. A.c.f. of type (iv) and (v) can be related[3-15] to infrared, dielectric, Raman, Rayleigh and far-infrared spectra. Those of type (i), (iii) and (iv) can be related to various n.m.r. data. Incoherent neutron scattering data provide insights in principle, but rarely in practice, to rototranslational interaction.

We remark at this point that the normal racemic mixture is a 50% solution of the one enantiomer in the other. Components of this solution are chemically identical but physically different, and use may be made of this fact to study the role of cross-correlations without changing the environment around any given molecule. It is possible to use the computer to simulate not only the molecular dynamics of the normal racemic mixture, but also the different concentrations of one enantiomer in the other. Any convenient correlation function sensitive to the nature of these solutions could then be used to monitor the role of multi-molecular cross-correlations in the chiral liquid. For example, if there are two enantiomers of type 1 in a bath of 106 enantiomers of type 2, one would look for statistical correlations between the two type 1 molecules. Since all 108 molecules are chemically identical, the same model pair potential is effective throughout, reducing the programming effort and computer time in the simulation of the dilute solution.

Combining this method with the suggestions of Nafie *et al.*,[21] the experimental techniques of vibrational optical activity or Raman optical activity could be used to investigate the role of vibration/rotation coupling, supplementing the technique[15] of isotopic dilution.

A more interesting possibility, and a more straightforward proposition spectroscopically, is to look at a spectrum, such as that in the far-infrared, of each enantiomer and compare the results with the spectrum of the racemic mixture. If there is any difference it would provide the first direct evidence of the existence of a rototranslational correlation function. We aim to probe this hypothesis further in this paper by computing $\langle \boldsymbol{e}_1(t)\cdot\boldsymbol{e}_1(0)\rangle$, $\langle \boldsymbol{e}_2(t)\cdot\boldsymbol{e}_2(0)\rangle$ and $\langle \boldsymbol{e}_3(t)\cdot\boldsymbol{e}_3(0)\rangle$.

RESULTS AND DISCUSSION

In fig. 2 we exemplify the result that the auto-correlation functions of a range of vectors are identical, in the laboratory frame, for each enantiomer but distinctly different in the racemic mixture. Fig. 2 illustrates this result for the three orientational auto-correlation functions mentioned above. In each case the correlation time is shorter in the racemic mixture than in either enantiomer. The obvious question is why should a 50/50 mixture of A, with isotropic rotational correlation time τ_A, and B, with an isotropic rotational correlation time $\tau_B = \tau_A$, behave in this way. We shall suggest eventually that the only possible explanation is the statistical

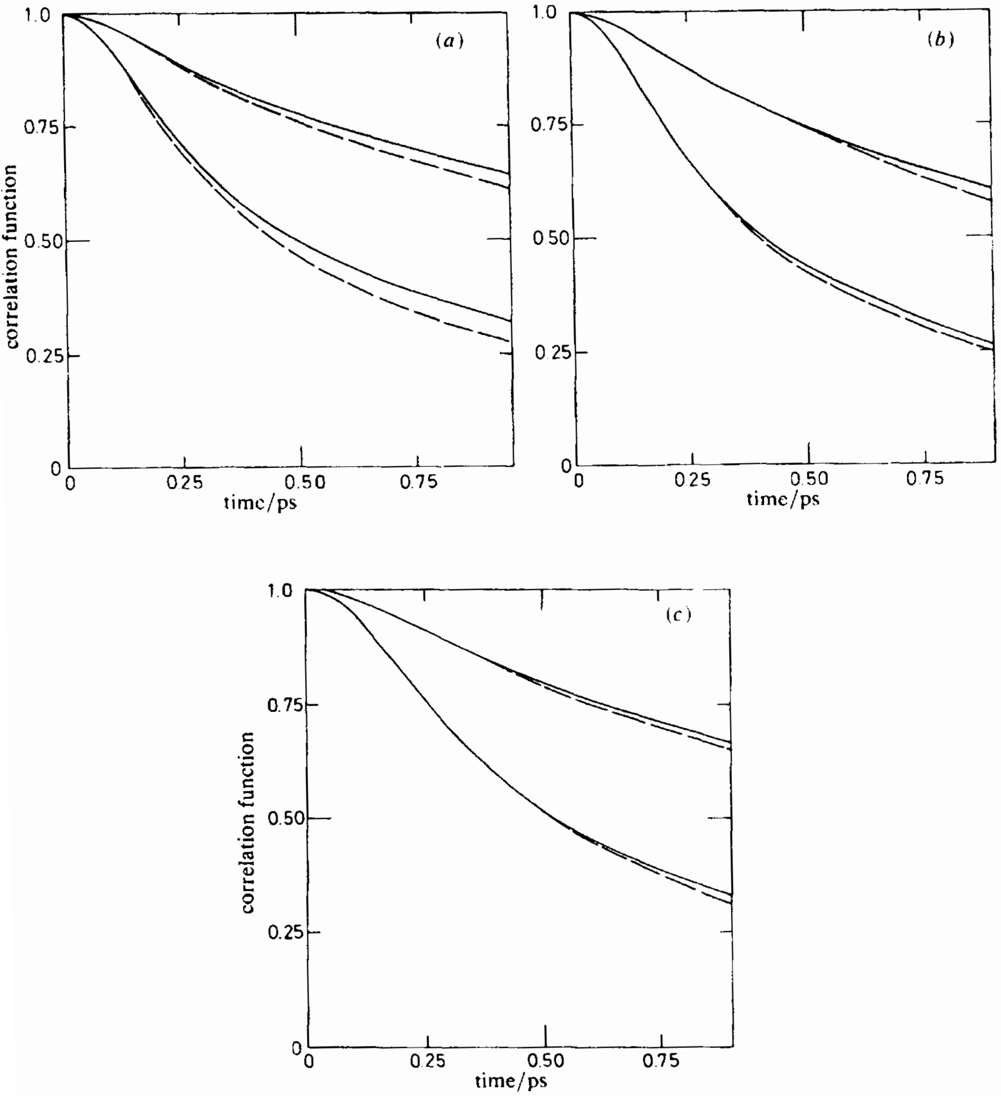

Fig. 2. Orientational auto-correlation functions in the laboratory frame of reference. (*a*) (——) enantiomer, (- - -) racemic mixture; top: first-rank a.c.f., $\langle \boldsymbol{e}_3(t)\cdot\boldsymbol{e}_3(0)\rangle$; bottom: second-rank a.c.f., $\frac{1}{2}\langle 3[\boldsymbol{e}_3(t)\cdot\boldsymbol{e}_3(0)]^2-1\rangle$. (*b*) As for (*a*), $\boldsymbol{e}_2$ vector. (*c*) As for (*a*), $\boldsymbol{e}_1$ vector.

correlation of molecular rotation with centre-of-mass translation. It is not possible to explain this result with the classical Debye theory of isotropic rotational diffusion,[15] or with any other theory of purely rotational diffusion. Similar results for $\boldsymbol{\omega}$, $\boldsymbol{J}$ and torque ($\boldsymbol{T}_q$) were obtained in terms of a.c.f., *e.g.* $\langle\boldsymbol{\omega}(t)\cdot\boldsymbol{\omega}(0)\rangle/\langle\boldsymbol{\omega}^2\rangle$, and their second moments, such as $\langle\boldsymbol{\omega}(t)\cdot\boldsymbol{\omega}(t)\boldsymbol{\omega}(0)\cdot\boldsymbol{\omega}(0)\rangle/\langle\omega^4\rangle$. Again the results for the $\boldsymbol{R}$ and $\boldsymbol{S}$ enantiomers are always identical in the laboratory frame of reference, but different from their equivalents in the racemic mixture. A.c.f. involving the molecular centre-of-mass velocity ($\boldsymbol{v}$) behave similarly.

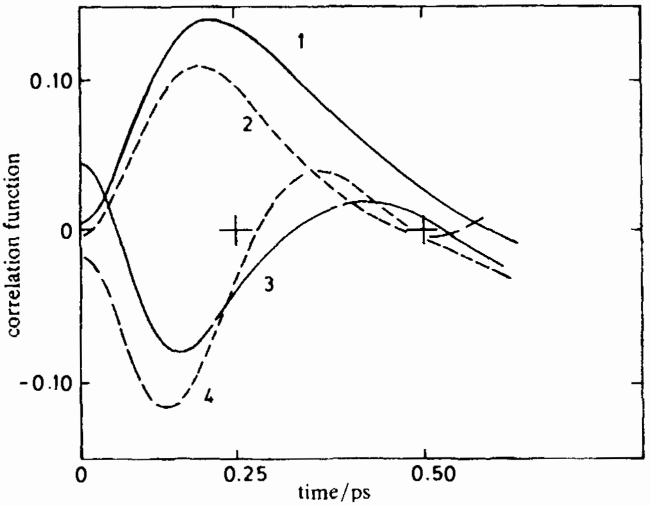

Fig. 3. Elements of the rotating-frame matrix: $\langle \boldsymbol{v}(t)\boldsymbol{J}^T(0)\rangle$. (1), (1, 2) $\equiv \langle v_1(t)J_2(0)\rangle / \langle v_1^2\rangle^{1/2}\langle J_2^2\rangle^{1/2}$, enantiomer; (2), (1, 2), racemic mixture; (3), (2, 1), enantiomer; (4), (2, 1), racemic mixture.

ROTATION–TRANSLATION COUPLING

We must look for a dynamical property (*i.e.* correlation function) which is different for the *R* and *S* enantiomers, otherwise there would be no way of telling the A and B components apart in dynamical terms and therefore no way of explaining why a mixture of identical components should behave at all differently. At first sight this seems impossible because any organic chemistry textbook will assert that the physical properties of enantiomers are identical except to circularly polarized radiation fields.

This may be true for time-dependent properties in the laboratory frame, but is not true in a rotating frame of reference, where the statistical correlation of rotation and centre-of-mass translation may be observed[3-14] on a single-molecule level by constructing a correlation matrix such as $\langle \boldsymbol{v}(t)\boldsymbol{J}^T(0)\rangle$. In fig. 3–5 we illustrate the off-diagonal elements of this matrix for the *R* and *S* enantiomers and racemic mixture. The diagonal elements vanish by symmetry for all t. The noise level in the functions may be judged by the general symmetry constraint that they should all vanish at $t = 0$. (This level is determined purely by artificial restrictions on computer time and power.) The elements are reliable to *ca.* 0.4 ps when the noise level masks the time dependence of the correlation function under investigation.

All six off-diagonal elements of the rotating frame exist in both *R* and *S* enantiomers. These are illustrated in fig. 3–5. The (1, 2), (2, 1), (3, 2) and (2, 3) elements (fig. 3 and 4) are identical, within the noise level, for both enantiomers. They are similar in the racemic mixture [fig. 3(*b*) and 4(*b*)]. Crucially, the (3, 1) and (1, 3) elements are not (fig. 5). Both (1, 3) and (3, 1) elements are equal in magnitude but opposite in sign for the *R* and *S* enantiomers. This property is therefore a measurable dynamical difference between the *R* enantiomer and the *S* enantiomer.

In the racemic mixture [fig. 5(*b*)] both elements vanish in the computer-generated noise. Therefore, in the racemic mixture only four (off-diagonal) ele-

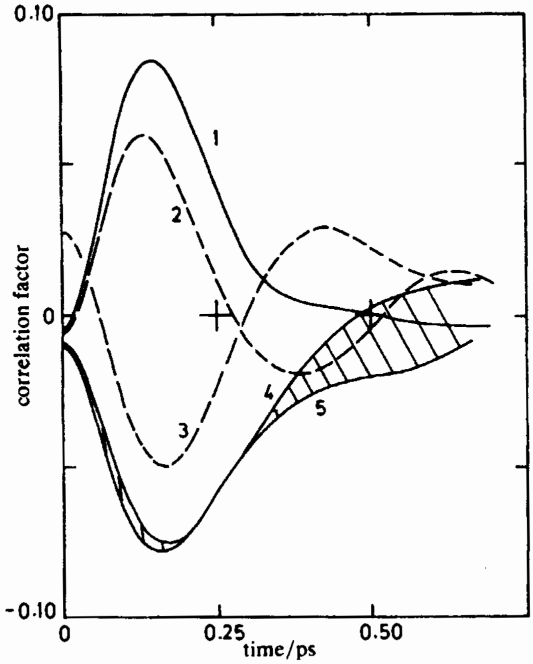

Fig. 4. (1), (2, 3) element, enantiomer; (2), (2, 3) element, racemic mixture; (3), (3, 2) element, racemic mixture; (4) and (5), (3, 2) elements for both enantiomers. The hatched region indicates the noise level in the simulation.

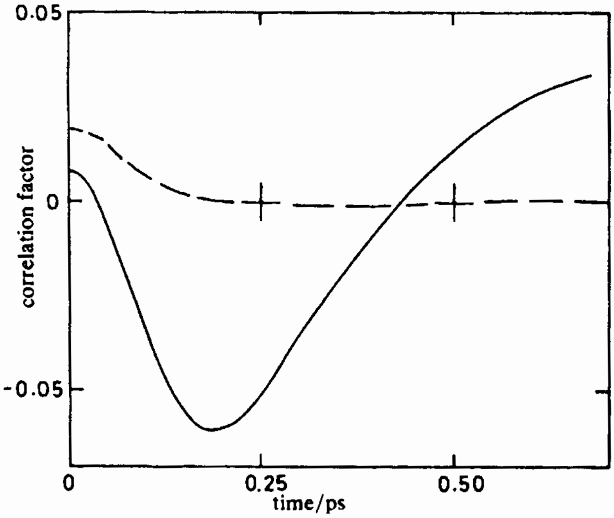

Fig. 5. (——) (3, 1) element, *S* enantiomer; (– – –) racemic mixture. The (3, 1) element of the *R* enantiomer is the mirror image of that of the *S* enantiomer.

ments exist in the rotating-frame matrix $\langle \boldsymbol{v}(t)\boldsymbol{J}^T(0)\rangle$, *i.e.* the (1, 2), (2, 1), (3, 2) and (2, 3) elements.

We therefore arrive at the conclusion that this is the only possible source of the differences in time dependence exemplified in fig. 2 between the laboratory-frame a.c.f. of either enantiomer and the racemic mixture. Therefore the measurement of liquid-phase spectra for enantiomers and their racemic mixture is a direct source of information on the statistical correlation between a molecule's rotation and centre-of-mass translation.

Finally, we point out that the rototranslational effects illustrated here for an optically active molecule exist in all molecules. Laboratory-frame a.c.f. (or spectra) in all molecular liquids are rototranslational in origin (if, for argument's sake, we exclude vibration). Usually, rototranslational effects can be observed only in the rotating-frame trap of computer simulation.[17] However, by using optically active molecules as illustrated, they can be revealed directly in the laboratory frame and therefore measured experimentally.

One of the most striking experimentally observed examples of the racemic modification of molecular-dynamical properties is in the lactic acids. In these cases both enantiomers melt at 326 K, whereas the racemic mixture melts at 291 K. Therefore spectra of the lactic (2-hydroxypropanoic) acids taken at 293 K will show obvious differences due to the different intermolecular forces working in a dynamical context. A computer simulation of the 2-hydroxypropanoic acids should be able to reproduce the different melting points in the enantiomer and racemic mixture and explain these differences in a molecular-dynamical context.

APPENDIX

The racemic modification of far-infrared properties predicted by the computer simulation of this paper has been observed recently by Evans *et al.*[23] using far-infrared interferometric and submillimetre laser spectroscopy. The naturally occurring enantiomers and racemic mixture of 3-methylcyclohexanone, 3-methylcyclopentanone and 2-aminobutanol were measured in the region up to 250 cm^{-1} The racemic modification in this case is small, but measurable, and corroborates the results of the computer simulation.

It is a pleasure to acknowledge the help and advice of the S.E.R.C. CCP5 group, and of Drs M. Ferrario, G. J. Evans, C. J. Reid, J. K. Vij, W. T. Coffey and J. K. Moscicki, and Profs. P. Grigolini and K. Singer. The S.E.R.C. Fellowships and Training Section is thanked for the award of an Advanced Fellowship. This work was carried out on the Aberystwyth UMRCC link with the CDC 7600 and Honeywell 6080 computers. The staffs at both centres are thanked for their support.

[1] B. J. Berne and R. Pecora, *Dynamic Light Scattering with Applications to Physics, Chemistry and Biology* (Wiley-Interscience, New York, 1976).

[2] S. Kielich, in *Dielectric and Related Molecular Processes*, ed. M. Davies (The Chemical Society, London, 1972).

[3] M. W. Evans and M. Ferrario, *Chem Phys.*, 1981, **72**, 141.

[4] M. W. Evans and M. Ferrario, *Chem Phys.*, 1981, **72**, 147.

[5] M. W. Evans and M. Ferrario, *Adv. Mol. Relaxation Processes*, in press; 1982, **23**, 113; 1982, **22**, 245; 1982, **23**, 69.

[6] V. K. Agarwal, G. J. Evans and M. W. Evans, *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**, 137.

[7] G. J. Evans and M. W. Evans, *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**, 153.

[8] M. W. Evans, *Adv. Mol. Relaxation Processes*, in press (methyl iodide).

[9] M. W. Evans and G. J. Evans, *Adv. Mol. Relaxation Processes*, in press (chloroform).

[10] M. W. Evans, *Adv. Mol. Relaxation Processes*, in press (acetonitrile).

[11] G. J. Evans and M. W. Evans, *J. Chem. Soc. Faraday Trans. 2*, in press (t-butyl chloride).

[12] M. W. Evans, to be published.
[13] M. W. Evans, *J. Chem. Soc., Faraday Trans. 2*, in press.
[14] B. Janik, J. Sciesinski, M. W. Evans, E. Kluk and T. Grochulski, *Chem. Phys.*, 1982, **70**, 77.
[15] M. W. Evans, G. J. Evans, W. T. Coffey and P. Grigolini, *Molecular Dynamics and Theory of Broad Band Spectroscopy* (Wiley-Interscience, New York, 1982), chap. 6 and 12.
[16] For a review, see P. Grigolini, *Nuovo Cimento B*, 1981, **63**, 174.
[17] J-P. Ryckaert, A. Bellemans and G. Ciccotti, *Mol. Phys.*, 1981, **44**, 979.
[18] J. R. Durig, C. J. Warren, W. E. Bucy and A. E. Sloan, *Spectrochim. Acta, Part A*, 1976, **32**, 175.
[19] C. H. Thomas, K. D. Nisbet and G. Graner, *J. Chem. Phys.*, 1974, **61**, 5072.
[20] B. Lassier and C. Brot, *J. Chim. Phys.*, 1968, **65**, 1723.
[21] L. A. Nafie, P. L. Polavarapu and M. Diem, *J. Chem. Phys.*, 1980, **73**, 3530.
[22] M. Sugie, H. Takeo and C. Matsmura, *Bull. Chem. Soc. Jpn*, 1978, **51**, 3065.
[23] G. J. Evans and M. W. Evans, *Chem. Phys. Lett.*, 1983, **96**, 416.

(PAPER 2/1861)