

COMPUTER SIMULATION INVERSE RAMAN AND FAR INFRA-RED STUDY OF ROTOTRANSLATIONAL CORRELATION IN OPTICALLY ACTIVE MOLECULES: PART 2; 1,1 FLUOROiodoETHANE, 3 METHYL CYCLOPENTANONE AND 3 METHYLCYCLOHEXANONE

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ABSTRACT

Computer simulation is used to investigate the statistical correlation between the molecular centre of mass velocity (\underline{v}) and molecular angular momentum (\underline{J}) of the optically active molecule 1,1 fluoriodoethane in the liquid state. Of the nine elements of the moving frame correlation matrix $\langle \underline{v}(t) \underline{J}^T(0) \rangle_m$, the diagonal elements vanish by symmetry for all t . The other elements exist, in principle, for $t > 0$, but the (1,3) and (3,1) elements are small in magnitude, and therefore buried in the computer noise, for both the R and S enantiomers and their racemic mixture. The molecular dynamical nature of the two enantiomers is therefore almost identical in the laboratory and any moving frame of reference. This implies that the laboratory frame autocorrelations of each enantiomer are similar to those in the racemic mixture in marked contrast to 1,1 fluorochloroethane [12] where differences in the structure of the (1,3) and (3,1) elements for each enantiomer lead to large and observable differences between laboratory frame autocorrelations in either enantiomer and their racemic mixture. These differences are direct measures of rotation/translation correlation on a fundamental single molecule level.

The simulation is supported by measurements in the far infra-red on the (+) enantiomers and racemic mixtures of 3 methyl cyclohexanone and 3 methyl cyclopentanone in the liquid state at 293K.

INTRODUCTION

The motion of molecules in the liquid state involves combination of rotation and centre of mass translation. The frequent disturbances caused by the interaction of molecular force fields do not remove the statistical correlation between the two type of motion. Recently, this correlation has been quantified [1] using a frame of reference that moves with the molecule. For convenience, this can be the principal

moment of inertia frame. In this frame of reference there exists, for $t > 0$, element of the matrix $\langle \underline{v}(t) \underline{J}^T(0) \rangle_m$, for example, where \underline{v} is the centre of mass linear velocity and \underline{J} the molecular angular momentum. Both vectors are defined in the moving frame of reference.

In the laboratory frame $\langle \underline{v}(t) \underline{J}^T(0) \rangle_1$ vanishes for all t , because of the different parity symmetry of \underline{v} and \underline{J} [2]. It is therefore an interesting challenge to devise a method of measuring directly in the laboratory the statistical correlation between molecular rotation and translation. The classical, phenomenological, theory of molecular diffusion does not consider this type of correlation [3]:- rotational diffusion and translational diffusion are considered separately. This is a major weakness of the phenomenological approach which can now be remedied by the numerical method of computer simulation [4-12].

Even when we have this powerful new technique at our disposal we still have the problem of observing these subtle and basic effects directly in the laboratory frame. They have an indirect effect on autocorrelation functions such as $\langle \underline{v}(t) \cdot \underline{v}(0) \rangle_1$ or $\langle \underline{J}(t) \cdot \underline{J}(0) \rangle_1$ because, clearly these a.c.f.'s are concerned with rototranslational molecular motion. However, cross-correlations such as $\langle \underline{v}(t) \cdot \underline{J}(0) \rangle_1$ always vanish in the laboratory frame because the parity of \underline{v} is opposite to that of \underline{J} . (It should be noted carefully that $\langle \underline{v}(t) \cdot \underline{J}(0) \rangle_1 = 0$ does not imply the absence of correlation between rotation and translation. For example $\langle \underline{v}^2(t) \underline{J}^2(0) \rangle_1 \neq 0$.)

If a molecule does not have a centre of symmetry it can exist as two enantiomers, which are separate liquids whose physical properties are traditionally said to be identical except in their response to circularly polarised radiation fields. A 50/50 mixture of two enantiomers is known as a racemic mixture. Properties of a racemic mixture, such as the freezing point, density and refractive index, can be quite different from their equivalents in either enantiomer. The molecules of enantiomer A are exact mirror images of those of enantiomer B.

Nature often operates through the subtle laws governing the production and reactions of enantiomers. The action of one enantiomer may be wholly different, in the natural state, to that of its mirror image. When we consider that many molecules are diastereomers, with more than one centre of optical activity, the range of possibilities opens out infinitely.

The dynamics and interactions of simple liquid enantiomers (e.g. methane derivatives) have never been studied, except by the most indirect of methods. The reason for this is the simple one that they are difficult to synthesize, except when a natural product happens to be available as an intermediate. When this is the case, an NMR and infra-red spectrum of a liquid enantiomer usually becomes available [13] but is rarely analysed for the information it contains about molecular motion.

With the advent of computer simulation, these difficulties can be circumvented. It turns out that a detailed study of the molecular dynamics of simple enantiomers and their racemic mixtures provides us with precise, experimentally measurable, information on the statistical correlation of rotation with translation in a given molecule. The computer can be used to look at a very simple enantiomer (a methane derivative) and in equal detail at its enantiomeric twin and racemic mixture. The central and major advantage of such a study is the possibility of working with two liquids, A and B, whose laboratory frame properties, for example, spectral bandshapes, are identical, but whose equimolar mixture behaves differently.

In the first of a series of papers on this subject, we investigated the dynamics and interactions in (R) and (S) 1 fluoro 1 chloro ethane, and also the racemic mixture [14]. A critical difference was discovered in the dynamical behaviour of the two enantiomers. The (1,3) and (3,1) elements of the moving frame 3×3 matrix $\langle \underline{v}(t) \underline{J}^T(o) \rangle_m$ were found to be equal in magnitude but opposite in sign in either enantiomer. The other seven elements were similar. Both elements vanish in the racemic mixture for all t. On the other hand, laboratory frame autocorrelation functions such as those of \underline{v} , \underline{J} , angular velocity $\underline{\omega}$, orientation and rotational velocity were always identical in both enantiomers, within the computer noise. Crucially, all these laboratory frame a.c.f.'s were substantially different in the racemic mixture. The only obvious difference in the dynamical behaviour of the two components, A and B of this mixture is that in the (1,3) and (3,1) elements described above. It follows that the difference in the laboratory frame spectra of enantiomers and their racemic mixture is a direct measure of the statistical correlation between molecular rotation and centre of mass translation. This is our central hypothesis.

It is important to realize that the effects observed in the moving frame through the elements of $\langle \underline{v}(t) \underline{J}^T(o) \rangle_m$ also exist in the laboratory frame but become observable only through the differences in the spectra of an enantiomer and racemic mixture. These differences manifest themselves for example in a frequency shift of the far infra-red peak absorption, or dielectric loss, and also by the development of anisotropy in the diffusion of the molecules of the racemic mixture where no such anisotropy had previously been observable in either enantiomer [14].

The findings provide a challenge to the phenomenological theory, which ignores this type of statistical correlation, and also that of direct, spectral observation and corroboration of the detailed predictions of the computer simulation. Unfortunately 1,1 chloro fluoroethane has been synthesized only as a racemic mixture, and the enantiomers do not seem to have been isolated in the laboratory. Until such a synthesis is made it is reasonable to attempt to substantiate the findings for

1 fluoro 1 chloro ethane by a computer simulation of a closely related molecule 1 fluoro 1 iodo ethane, and to compare carefully the results of the two simulations in both the moving and laboratory frames of reference. This paper therefore deals with the computer simulation of the enantiomers of 1,1 fluoro 1 iodo ethane and its racemic mixture.

Computer Simulation Algorithm and Method

This is based on a 5 x 5 site-site approximation to the interaction potential between two molecules of 1,1 fluoro iodo ethane. The Lennard-Jones parameters for each moiety were taken from the literature, and partial charges used to model the electrodynamic interactions [15]. The Lennard-Jones parameters are:

$$\begin{aligned}
 \text{i) } \sigma(\text{I} - \text{I}) &= 4.30\text{\AA}; & \epsilon/k(\text{I} - \text{I}) &= 315.0\text{K} \quad [16] \\
 \sigma(\text{C} - \text{C}) &= 3.40\text{\AA}; & \epsilon/k(\text{C} - \text{C}) &= 35.8\text{K} \quad [17] \\
 \sigma(\text{H} - \text{H}) &= 2.8\text{\AA}; & \epsilon/k(\text{H} - \text{H}) &= 10.0\text{K} \quad [4] \\
 \sigma(\text{F} - \text{F}) &= 2.7\text{\AA}; & \epsilon/k(\text{F} - \text{F}) &= 54.9\text{K} \quad [14] \\
 \sigma(\text{CH}_3 - \text{CH}_3) &= 3.5\text{\AA}; & \epsilon/k(\text{CH}_3 - \text{CH}_3) &= 158.6\text{K} \quad [18].
 \end{aligned}$$

Therefore the interaction between one pair of molecules is modelled with 25 atom-atom terms each made up of a sum of Lennard-Jones and charge-charge atom-atom interactions. The usual methods of molecular dynamics computer simulation are employed to solve the equations of motion for 108 of these molecules. The difference between the runs for the R and S enantiomer is that in the positions of the five atoms with respect to the centre of mass of each of the 108 molecules, as tabulated below.

TABLE 1
Atom Coordinates Relative to Centre of Mass (\AA)

Atom	Enantiomer R			Atom	Enantiomer S		
	$x(\underline{e}_3)$	$y(\underline{e}_1)$	$z(\underline{e}_2)$		$x(\underline{e}_3)$	$y(\underline{e}_1)$	$z(\underline{e}_2)$
I	0.57	0.33	-0.12	I	0.57	0.33	0.12
C	-1.18	-0.90	-0.12	C	-1.18	-0.90	0.12
H	-1.18	-1.53	-1.02	H	-1.18	-1.53	1.02
F	-1.18	-1.70	1.03	F	-1.18	-1.70	-1.03
CH ₃	-2.31	0.16	-0.12	CH ₃	-2.31	0.16	0.12

The unit vectors \underline{e}_1 , \underline{e}_2 and \underline{e}_3 of this table are defined (fig. (1)) with respect to the frame of the principal moments of inertia, whose three axes intersect at the centre of mass. For convenience, this is also our rotating frame of

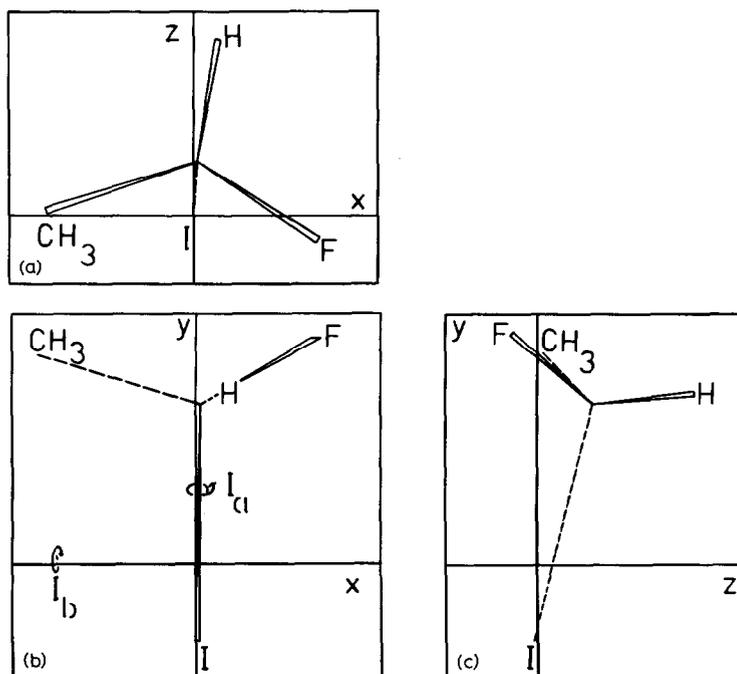


Figure (1)

Principal moment of inertia frame for 1,1 C_2H_4FI .

The three axes intersect at the centre of mass. The inset shows the frame of the three unit vectors \underline{e}_1 , \underline{e}_2 and \underline{e}_3 .

reference. In the simulation run for the racemic mixture 54 molecules are of type R and 54 of type S.

The three runs were carried out independently at an input temperature of 293K and an estimated liquid density of 1.9 gm/ml (the real 1,1 fluoroiodoethane molecules has not been synthesised yet in any form). The samples were melted and equilibrated from a face centred cubic array. Thereafter about 1000 time steps of 0.005 ps each were run to generate dynamical information on the vectors governing the molecular motion. These were \underline{v} ; \underline{J} ; $\underline{\omega}$; force (\underline{F}); torque (\underline{T}_q); orientation, \underline{e}_1 , \underline{e}_2 and \underline{e}_3 ; and rotational velocity $\dot{\underline{e}}_1$, $\dot{\underline{e}}_2$ and $\dot{\underline{e}}_3$. The first five vectors were generated in both the usual (laboratory) frame of reference and in the moving frame. The trajectories of these vectors over 1000 time steps for each of the 108 molecules were stored on disk. Auto and cross-correlation functions were computed with separate sub-routines.

RESULTS AND DISCUSSION

The heavy iodine atom means that 1,1 C₂H₄FI (unlike its chloride counterpart) is an offset rotor. Its diffusion in the liquid state is more anisotropic than 1,1C₂H₄FCl and the role of rotation-translation coupling wholly different.

The (1,3) and (3,1) elements of the rotating frame matrix $\langle \underline{v}(t) \underline{J}^T(o) \rangle$ are vanishingly small in 1,1 C₂H₄FI in both enantiomers and the racemic mixture. This is in marked contrast to 1,1 C₂H₄FCl, where these elements are critically important in determining the nature of the t/r correlation [14]. The dynamical difference between S, 1,1 C₂H₄FI and R, 1,1 C₂H₄FI is therefore small, as measured by the

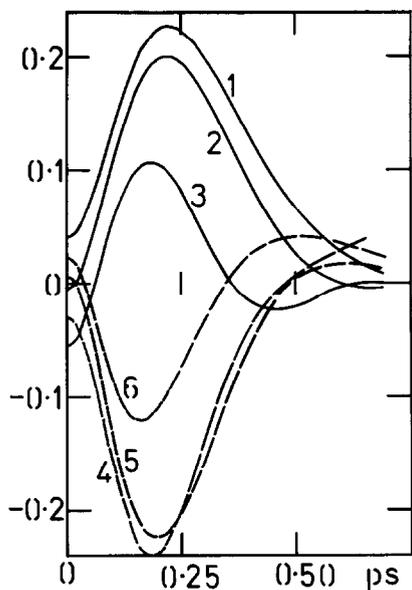


Figure (2)

(1,2) and (2,1) elements of the moving frame matrix $\langle \underline{v}(t) \underline{J}^T(o) \rangle$. $((1,2) \equiv \langle \underline{v}_1(t) \underline{J}_2(o) \rangle / (\langle \underline{v}_1^2 \rangle \langle \underline{J}_2^2 \rangle))$

- (1) R enantiomer, (1,2) element;
- (2) S enantiomer, (1,2) element;
- (3) racemic mixture, (1,2) element;
- - - (4) R enantiomer, (2,1) element;
- - - (5) S enantiomer, (2,1) element;
- - - (6) racemic mixture, (2,1) element;

Ordinate: correlation function; Abscissa: time/ps.

elements of $\langle v(t) \underline{J}^T(o) \rangle_m$. The difference in the elements (1,3) and (3,1), in particular, is much smaller than in the chloride derivative (1,1 C_2H_4FC1) between one enantiomer and the other. Accordingly, by our reasoning of the introduction to this paper, we may expect that the difference in the laboratory frame a.c.f.'s between enantiomer and racemic mixture should be correspondingly smaller than in 1,1 C_2H_4FC1 and we shall see presently that this is, indeed, the case.

The (1,2), (2,1), (2,3) and (3,2) elements of each enantiomer are similar and are illustrated in figs. (2) and (3) together with those for the racemic mixture. There is an interesting difference in the nature of the rotation/translation correlation between the enantiomers and racemic mixture. The (1,2) and (2,1) elements are halved, approximately, in intensity in the racemic mixture, and the (2,3) and (3,2) elements change over in sign. The (2,3) element, for example, is positive in each enantiomer but negative in the racemic mixture (with approximately the same intensity). (The diagonal elements of $\langle v(t) \underline{J}^T(o) \rangle_m$ vanish by symmetry in all three cases for both enantiomers and racemic mixture.)

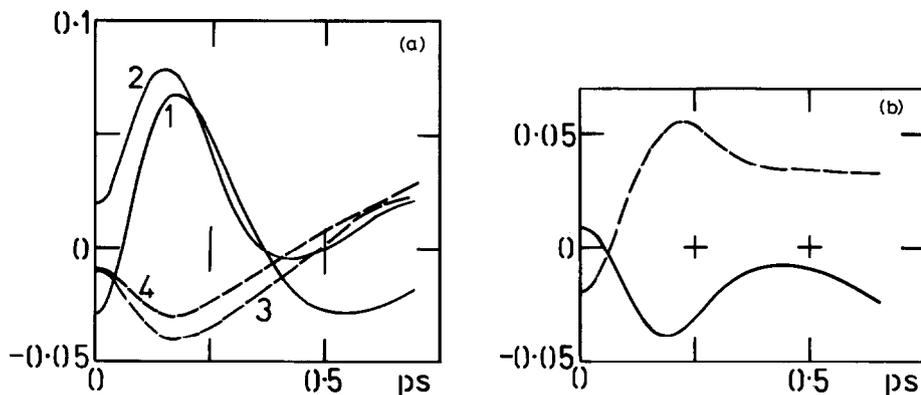


Figure (3)

(a) (2,3) and (3,2) elements of the moving frame matrix

- (1) S enantiomer, (2,3) element;
- (2) R enantiomer, (2,3) element;
- - - (3) S enantiomer, (3,2) element;
- - - (4) R enantiomer, (3,2) element.

(b) Racemic mixture

- - - (3,2) element; — (2,3) element.

Note the change of sign.

Ordinate: correlation function; Abscissa: time/ps.

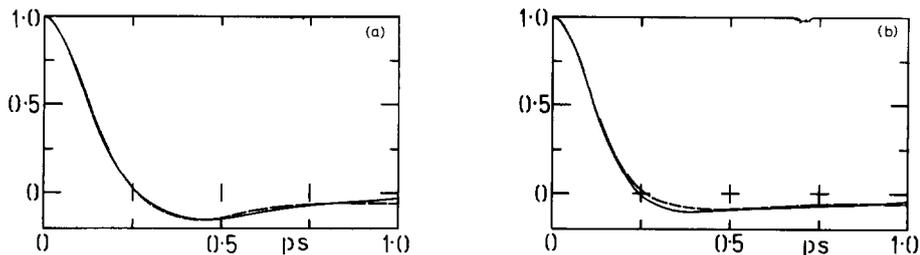


Figure (4)

(a) Rotational velocity autocorrelation function, lab. frame

$$\langle \dot{e}_1(t) \cdot \dot{e}_1(0) \rangle / \langle \dot{e}_1^2 \rangle$$

— S enantiomer; - - - racemic mixture.

(b) As for (a), $\langle \dot{e}_3(t) \cdot \dot{e}_3(0) \rangle / \langle \dot{e}_3^2 \rangle$

Ordinate: correlation function; Abcissa: time/ps.

The way in which these moving frame differences are carried through into the laboratory frame may be discerned with a range of lab. frame autocorrelation functions. Among the most sensitive are the three rotational velocity a.c.f.'s (of \dot{e}_1 , \dot{e}_2 and \dot{e}_3). A Fourier transform of a suitable combination of these provides a far infra-red spectrum [3], a sensitive measure of molecular dynamics in the liquid state. These are illustrated in figs 4(a) and 4(b) for the S enantiomer and the racemic mixture. These a.c.f.'s are anisotropic in the laboratory frame but the differences between component and mixture are small, very much smaller than in 1,1 C₂H₄FCl [14]. According to our central hypothesis, this finding can be explained by the fact that the dynamical difference (in $\langle \underline{v}(t) \underline{J}^T(0) \rangle_m$) are small between the R and S enantiomers of C₂H₄FI. There is, on the other hand, a distinct and measurable dynamical difference between $\langle \underline{v}(t) \underline{J}^T(0) \rangle_m$ for R and S C₂H₄FCl, and there are also big laboratory frame differences [14] in the rotational velocity autocorrelation functions.

This pattern is repeated in the other vectors of interest, such as \underline{e}_1 , \underline{e}_2 and \underline{e}_3 (fig. (5)) and $\underline{\omega}$ (fig. (6)).

The translational part of the overall molecular motion may be viewed through $\langle \underline{v}(t) \cdot \underline{v}(0) \rangle / \langle v^2 \rangle$ (fig. (7)), and significantly, there is a small but real difference between the S enantiomer and racemic mixture. This implies, simply, that we must consider rotation and translation, as our central hypothesis demands.

Finally, the reasoning extends to a.c.f.'s of force (\underline{F}) and torque (\underline{T}_q) in the laboratory frame, and to their second moments, such as:

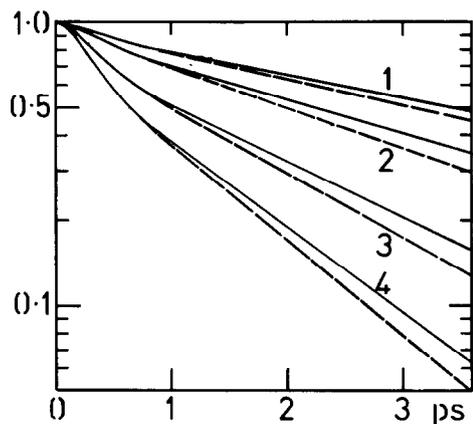


Figure (5)

Oriental autocorrelation functions of the unit vectors \underline{e}_1 and \underline{e}_3 , lab. frame

— S enantiomer (1) $P_1(\underline{e}_3)$; (2) $P_1(\underline{e}_1)$; (3) $P_2(\underline{e}_3)$; (4) $P_2(\underline{e}_1)$.

- - - racemic mixture.

Ordinate: correlation function; Abscissa: time/ps.

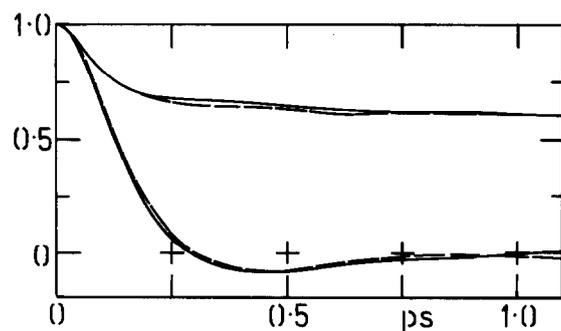


Figure (6)

Angular velocity autocorrelation functions, lab. frame.

— S enantiomer; - - - racemic mixture.

Bottom $\langle \underline{\omega}(t) \cdot \underline{\omega}(0) \rangle / \langle \omega^2 \rangle$.

Top $\langle \underline{\omega}(t) \cdot \underline{\omega}(t) \underline{\omega}(0) \cdot \underline{\omega}(0) \rangle / \langle \omega^4 \rangle$.

Ordinate: correlation function; Abscissa: time/ps.

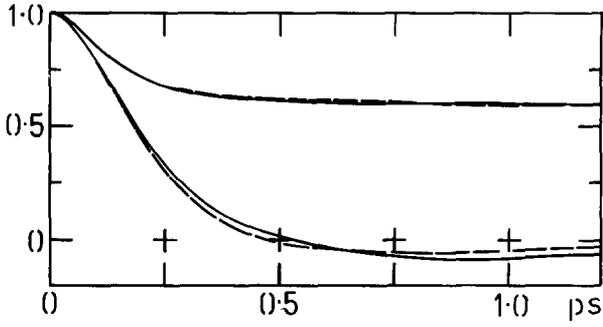


Figure (7)

As for Fig. (6), centre of mass linear velocity.

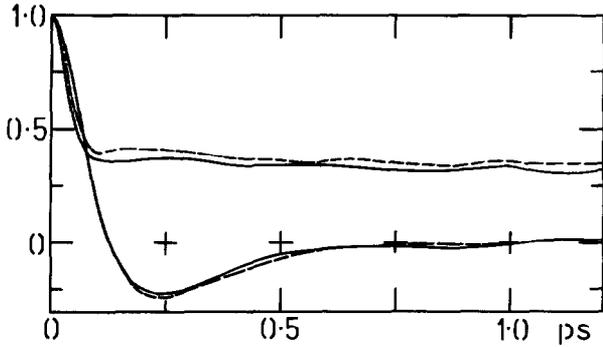


Figure (8)

As for Fig. (6), force.

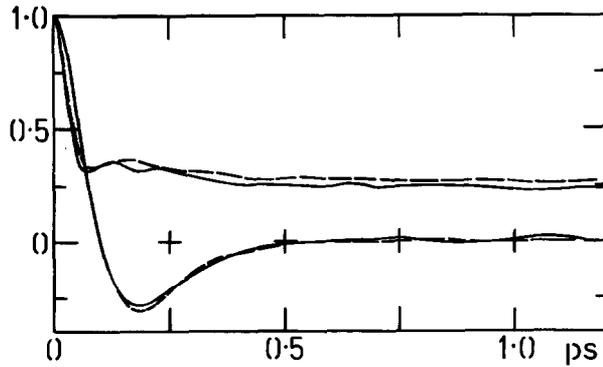


Figure (9)

As for Fig. (6), torque.

$\langle \underline{F}(t) \cdot \underline{F}(t) \underline{F}(o) \cdot \underline{F}(o) \rangle / \langle F^4(o) \rangle_{\ell}$ (fig. (8) and fig. (9)). Again these laboratory frame differences are much smaller than in 1,1 C_2H_4FCI [14].

In summary, therefore, the molecular dynamical differences between the S and R enantiomers of 1,1 fluoriodoethane, as represented by the (1,3) and (3,1) elements of $\langle v(t) J^T(o) \rangle_m$ are insignificant. They are so small that they are buried in the noise of our simulation run. Our central hypothesis is supported by the fact that the finite laboratory frame differences (in a range of a.c.f.'s) between an enantiomer and racemic mixture of 1,1 C_2H_4FI are also small.

The Hypothesis

The difference between an auto-correlation function of a molecular dynamical vector in a liquid enantiomer and its racemic mixture is a directly observable measure of some critical elements of the moving frame statistical correlation between molecular rotation and translation.

Experimental Notes - Inverse Raman Spectroscopy

Unlike normal Raman spectroscopy, where monochromatic light at one fixed wavelength is incident on the Raman sample and the scattered Raman restriction is analysed into its different wavelength components, in Inverse Raman spectroscopy two monochromatic beams are incident coaxially, and the frequency difference between them is varied by scanning the frequency of the lower frequency laser through the resonance condition

$$\nu_h - \nu_L = \nu_{vi} b$$

where $\nu_{vi} b$ is one of the Raman active transitions in the molecules under study. The name Inverse Raman was given to this technique after it was first observed [20,21] because at this precise resonance condition the interaction of the two laser beams in the Raman medium produces a decrease in the intensity of the higher frequency beam, ν_h . Since the signal intensity depends on the product of the powers of the two lasers employed it is advantageous to use pulsed lasers exhibiting high peak powers but relatively low average powers (to avoid excessive sample heating effects) [22]. The experimental apparatus employed in this study of Inverse Raman spectra using picosecond lasers has been fully described in [23]. A mode-locked Spectra Physics Model 171-06 argon ion laser, producing $\sim 1W$ average power at 514.5nm in mode-locked continuous train of pulses, each pulse being of duration $\sim 200ps$ with a repetition rate of ~ 82 MHz, is employed to pump synchronously two dye lasers A and B. Both were employed as mode-locked synchronously pumped lasers. Dye laser A was operated with Rhodamine 6G dye at a fixed wavelength (614.7nm) and served as a probe laser. Dye laser B, scannable in the range 620 - 680nm was operated with DCM dye serving as a pump laser. The Inverse Raman spectra were measured using a standard phase-sensitive

method with the amplitude modulation of pump beam at 10 MHz. The spectral resolution of the system was about 1 cm^{-1} . The average power of the pump laser was $\sim 20 \text{ mW}$ and the power of the probe beam at the detector $\sim 1 \text{ mW}$. The length of the Raman cell was 2.5mm. An optogalvanic detector was used for calibration purposes.

Two peaks of the inverse Raman spectron of liquid (+) 3 methyl cyclo hexanone and the racemic mixture were scanned at 293K and the experiment repeated six times. The frequencies of these peaks were 643 cm^{-1} and 749 cm^{-1} . The half-width to peak height ratios (x_1 and x_2) of these two peaks were measured and compared. For the racemic mixture the ratio x_1/x_2 was 1.045 ± 0.033 (r.m.s. deviation from the mean). The same ratio for the (+) enantiomer was 0.964 ± 0.024 . There is therefore, a small but statistically significant difference between simple observables such as x_1/x_2 between enantiomer and racemic mixture under the same conditions. In the three lactic acids for example (R and S enantiomers and racemic mixture) this small change would be amplified very greatly, since the enantiomers melt at 323K and are therefore solids at room temperature, and the racemic mixture melts at 291K, and is therefore a liquid at a normal room-temperature of 293K. The only dynamical explanation for this effect is rotation/translation correlation, such as that in $\text{C}_2\text{H}_4\text{FCl}$, whose mass distribution (atom for atom) about the optically active centre is very similar to that of $\text{C}_2\text{H}_4(\text{OH})\text{COOH}$, lactic acid.

Far Infra-red Power Absorption

All the above information has been obtained by computer simulation. In order to support our hypothesis with spectral data we have chosen, in this explanatory stage of our work, to measure the far infra-red power absorption [3] of available, simple, enantiomers. The only liquids readily available seem to be (+) 3 methyl cyclohexanone and (+) 3 methyl cyclopentanone, with their racemic mixtures.

The far infra-red power absorption of these liquids are illustrated in figs (10) and (11). These spectra were obtained by interferometry [3] and checked with laser spectroscopy at spot frequencies. The ordinate (neper cm^{-1}) is significant in these spectra [3]. There are small, but real differences between the (+) enantiomers and racemic mixtures which cannot be explained on the basis of density differences or beam polarisation effects. These differences are accentuated in the (+) 3 methyl cyclopentanone, whose rotation of polarised light is ten times that of (+) 3 methyl cyclohexanone. Both these liquids have a broad liquid range, and the differences between enantiomer and racemic mixture would be accentuated at lower temperatures. The (-) enantiomers are not

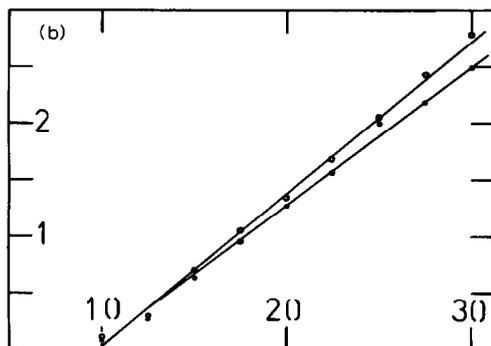
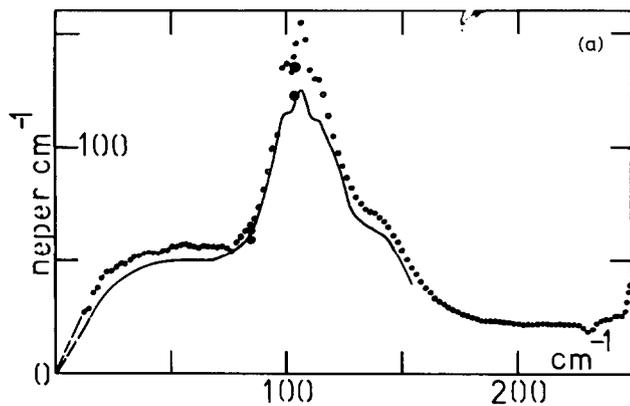


Figure (10)

a) The far infrared spectra of 3 methyl cyclohexanone

●●●● Results for the racemic mixture

— Results for the enantiomer

Ordinate $\alpha(\bar{\nu})/\text{neper cm}^{-1}$

Abscissae Wavenumber/ cm^{-1}

b) The variation of Transmission at 61 cm^{-1}

● Racemic mixture, ○ enantiomer

Ordinate Volts

Abscissae Pathlength (cms)

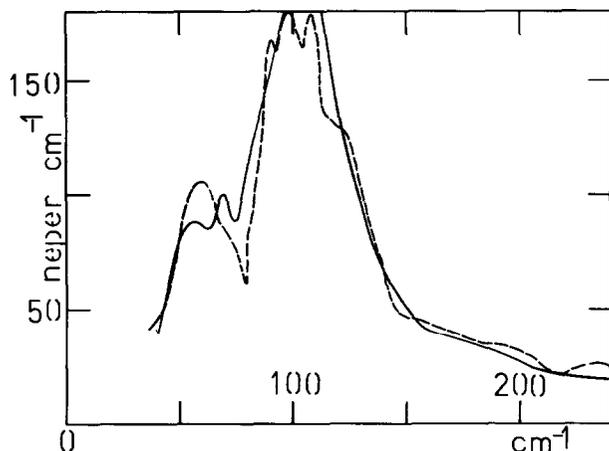


Figure (11)

The far infrared spectra of 3 methyl cyclopentanone.

ooooo The racemic mixture

- - - - The enantiomer

Ordinate $\alpha(\bar{\nu})/\text{neper cm}^{-1}$

Abcissae Wavenumber/ cm^{-1}

available (i.e. are not natural by-products) but are expected to have the same far infra-red spectra in all respects to the (+) enantiomers. The spectral differences in figs. (10) and (11) are therefore attributable to mode-mode correlation, springing from rotation/translation/vibration correlation on the one molecule level. These differences are indirect evidence for our hypothesis, based on computer simulation.

Future Work

(i) The synthesis of R and S 1,1 $\text{C}_2\text{H}_4\text{FCl}$ and $\text{C}_2\text{H}_4\text{FI}$ would be the first stage in a spectral evaluation of the detailed predictions of the computer simulations.

(ii) Future computer simulations of this kind will be concentrated on the two enantiomers of trans, 1,2 dimethylcyclopropane [18] and their racemic mixture. These are propellor shaped molecules with right and left handed pitch. It is significant that the density of the racemic mixture is about half that of each enantiomer at only about five degrees below the boiling point. The latter is the same in the enantiomers and racemic mixture. The intermolecular forces are therefore similar in both cases, because the boiling points are the same, but the

structure and dynamics are very pronouncedly different. Strong rotation/translation correlation is therefore to be expected. Both enantiomers have recently been synthesized [19].

Acknowledgements

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Appendix

The 2 amino 1 butanol molecule is chiral with a degree of flexibility in its mass distribution. The far infra-red spectra of Fig. (1A) illustrate the t/r effect in that the absorption of the racemic mixture is clearly different from that of the enantiomer. The densities of both samples are similar.

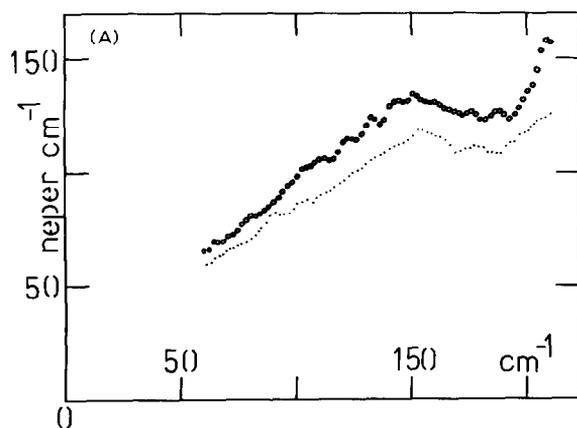


Figure (1A)

The far infrared spectra of 2 amino 1 butanol

ooooo The racemic mixture

..... (+) 2 amino 1 butanol

Ordinate $\alpha(\bar{\nu})/\text{neper cm}^{-1}$

Abcissae Wavenumber/ cm^{-1}