

COMPUTER SIMULATION OF ROTOTRANSFORMATION IN OPTICALLY ACTIVE MOLECULES - Part 3,  
THE TRANS 1,2 DIMETHYL CYCLOPROPANES

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ABSTRACT

The molecular dynamics of the trans 1,2 dimethyl cyclopropanes in the R, S and racemic modifications have been simulated with a computer in the liquid state at 293 K, 1 bar and 13 kbar. Using a simplified representation of the intermolecular pair potential we have obtained the following indications.

- i) The overall pattern of the molecular dynamics is changed (greatly) by the application of hydrostatic pressure.
- ii) There is an intrinsic difference in the molecular dynamical properties of the two enantiomers and racemic mixture. This shows up in a moving frame of reference.
- iii) These differences are due to the statistical correlation between single molecule rotation and translation.
- iv) The symmetry-group properties of the trans 1,2 dimethyl cyclopropanes are such that these differences are not carried through into the laboratory frame, unlike, for example, the 1,1 fluorochloroethanes [6-8] or lactic acids [3], whose molecular symmetry-groups are different, having less overall symmetry.

INTRODUCTION

The dynamics of molecules in the liquid and related condensed states of matter involve rotation and translation (if we ignore intramolecular vibration for the sake of argument). There is a statistical correlation between a molecule's centre of mass translation and its own rotation in the laboratory frame of reference. This cannot be measured, however, through the straightforward correlation function  $\langle \underline{v}(t) \cdot \underline{J}(0) \rangle$  where  $\underline{v}$  is the centre of mass velocity and  $\underline{J}$  the molecular angular momentum. The reason is that  $\underline{v}$  responds differently from  $\underline{J}$  under parity inversion in the laboratory frame [1]. The correlation between these vectors is revealed in a moving frame of reference, as shown by

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Ryckaert et al. [2]. Taking this frame, for convenience, as that of the principal molecular moments of inertia, then the off-diagonal elements of  $\langle \underline{v}(t) \underline{J}^T(0) \rangle_m$  exist, in general, for  $t > 0$ . Here  $\langle \rangle_m$  denotes an average over  $\underline{v}$  and  $\underline{J}$ , both defined with reference to the moving frame.

This is true for any molecular liquid, but correlations of this type are particularly important in molecules which do not have a centre of inversion-symmetry. These exist as separable enantiomers (denoted R or S type) whose physical properties are traditionally said to be identical except in their response to circularly polarised radiation fields (or other symmetry-breaking, externally applied, directional variable [4,5]. We have shown by computer simulation recently [6-10] that elements of the correlation matrix  $\langle \underline{v}(t) \underline{J}^T(0) \rangle_m$  for an R enantiomer differ from those in the S enantiomer. This is the first observation of an intrinsic difference in the physical properties of two enantiomers. There are at least two fundamental consequences of this observation.

i) It explains why the physical, and in particular dynamical, properties of a racemic modification may be different from those of either enantiomer in the laboratory frame of reference [3].

ii) The comparison of the dynamical (e.g. spectral [1]) properties of an enantiomer with those of its racemic modification may be used as a direct measure of the statistical correlation between molecular rotation and translation [6-10].

It is clear from the examples available in the literature [11] that the physical properties of a racemic modification may be i) very different; ii) only slightly different from their enantiomeric counterparts in the laboratory frame. Equilibrium properties such as boiling point, freezing point, density and refractive index are sometimes known, but the dynamical properties of simple optically active molecules have never been studied experimentally in any detail.

The racemic modification of 2 hydroxy propanoic acid (lactic acid), for example, melts at 291 K, while the enantiomers remain solids to 326 K. The spectral details in the racemate are clearly going to be different from those in either enantiomer at a normal room temperature, say, of 293 K. Such spectra are, of course, manifestations of the molecular dynamics. Our reported computer simulations [8,9] of 1,1  $C_2H_4FCI$  and 1,1  $C_2H_4FI$  (fluoro chloro and fluoro iodo ethane respectively) illustrate the sensitivity of the molecular dynamics in the racemic modification to the structure of the molecules in each enantiomer. The molecular dynamics of the racemic modification of 1,1  $C_2H_4FCI$  are markedly different in the laboratory frame from those in either enantiomer at the same input density and using, in the computer simulation [8], the same 5 x 5 site-site pair potential. In 1,1  $C_2H_4FI$ , in contrast [9], the difference is much less marked for the same algorithm, and with the same type of 5 x 5 site-site potential.

Motivated by these results, we have measured and reported the far infrared and inverse Raman spectra of natural products such as (+) 3 methyl cyclohexanone; (+) 3 methyl cyclopentanone; d and l 2 amino butanol; and the three racemic modifications [9]. In these systems, there are slight racemic modifications of the densities and refractive indices recorded in the literature at ambient temperature. Similar slight changes were observed spectrally [9]. These findings were supplemented and corroborated with an approximate 6 x 6 site-site computer simulation of (+) 3 methyl cyclohexanone and its racemic mixture [12].

In order to build on this base in a methodical fashion we have chosen to study the optically active trans 1,2 dimethyl cyclopropanes (enantiomers and racemic mixture) by computer simulation. These systems have been chosen because of their following advantages.

i) The 1, 3 dialkylcyclopropanes have been investigated by circular dichroism and show an interesting chiroptical dichotomy [13] with their 2,2 dimethyl relatives. It is clear from this that the element of chirality resides in the asymmetric disposition of the exocyclic methyl groups, and the nature of the observable dichroism is based on combinations of such elements. In other words the R enantiomer is a propeller whose pitch is opposite in sense to that of the S enantiomer. A medium made up of molecular propellers<sup>4,5</sup> should be suitable for the observation of rotation/translation coupling.

ii) The R and S enantiomers have both been synthesized recently [14,15,16] using a chiral platino complex [16]. The liquids are therefore available for spectral study using the wide range of available techniques [17 - 20].

iii) The molecular dynamics in the liquids can be approximated by a properly chosen pair potential, because the molecules of trans 1,2 dimethylcyclopropane are almost non-dipolar and also weakly quadrupolar. The site-site components of the pair potential can therefore be assigned with Lennard-Jones atom-atom terms, the longrange electrostatic terms being almost negligible, in comparison. This is much more convenient than in the lactic acids, which are hydrogen-bonded.

iv) Both the enantiomers and the racemic mixture boil at 1 bar at 301 - 302K. This means that the nature of the intermolecular forces in each case is similar - there is no intrinsic difference between site-site terms, which are therefore transferable between a molecule of enantiomer R<sup>+</sup> interacting with one of enantiomer R<sup>-</sup> or, alternatively, one of enantiomer S. The low boiling point also means that a simulation carried out at 293K can be repeated over a very wide range of liquid density. We find in the computer simulation that the application of approx. 13 kbar of pressure halves the molar volume at 293K, the sample remaining liquid in the enantiomeric and racemic modifications.

v) Unlike the 3 methyl cyclohexanones [9,12] (one enantiomer of which happening to be available as a natural product) the trans 1,2 dimethylcyclopropanes are rigid [21], and just within reach of a realistic and economically viable site-site computer simulation.

As with all optically active liquids at present, there are very few data, if any, available on the molecular dynamical properties of the liquid trans 1,2 dimethyl cyclopropanes. This is the case because both enantiomers have been synthesized only very recently [16]. It seems clear, therefore, that computer simulation is a powerful and independent source of information in this field, and can now provide molecular dynamical explanations for phenomena first observed in the 19th century [3].

#### THE ALGORITHM

This was developed by Ferrario et al. [22] and designed for any molecular geometry. An enantiomer is simulated with 108 molecules, with the usual periodic boundary conditions and conventions of the computer simulation method. A racemic mixture is simulated with 54 molecules of type R and 54 of type S, keeping to the same pair-potential. That is, the atom-atom terms between any two molecules are treated identically (with Lorentz-Berthelot combining rules) but the disposition of the atoms within a molecule of type R is different to that of type S, one molecule being the other's mirror image [6-10]. The input molar volume of each enantiomer and their racemic mixture is kept the same [8,9,12]. The runs are therefore carried out at the same temperature and at constant density.

For purely economic reasons, we are constrained to five, or at most six, sites per molecule. Therefore, in order to represent the trans 1,2 dimethylcyclopropanes several approximations were made to the true geometry [21]. These consisted of treating the methyl group as an entity [23], i.e. as one site, and similarly with the CH and CH<sub>2</sub> groups of the cyclopropane ring. The Lennard-Jones parameters of each of the five sites defined in this way were adjusted to approximately the correct pressure at 293K for the literature density at one bar. These parameters, together with the position of the sites with respect to the centre of mass in each enantiomer, are listed in the table.

The intermolecular pair potential is therefore built up of 25 site-site terms, with no partial charges.

TABLE 1

Lennard-Jones Parameters and Site Positions ( $\text{\AA}$ ) with Respect to the Centre of Mass:  
R and S 1,2 Dimethyl Cyclopropane

Site	$\epsilon/k$ /K	$\sigma$ /Å	R			S		
			$x(\underline{e}_3)$	$y(\underline{e}_1)$	$z(\underline{e}_2)$	$x(\underline{e}_3)$	$y(\underline{e}_1)$	$z(\underline{e}_2)$
CH <sub>3</sub>	158.6	3.3	0.32	1.59	1.25	-0.32	1.59	1.25
CH	35.8	3.4	0.32	0.70	0	-0.32	0.70	0
CH <sub>2</sub>	35.8	3.4	1.09	-0.63	0	-1.09	-0.63	0
CH	35.8	3.4	-0.45	-0.63	0	0.45	-0.63	0
CH <sub>3</sub>	158.6	3.3	-1.22	-1.08	-1.25	1.22	-1.08	-1.25

The CH and CH<sub>2</sub> sites were approximated with carbon Lennard-Jones parameters. Given sufficient computational power, the inter-molecular pair potential can be built up from two sets of Lennard-Jones parameters - those for carbon and those for hydrogen.

With the parameters of table 1, molecular dynamics simulation runs were carried out at 293K, with an external pressure of 1 bar and of ca 13 kbar for both the enantiomers and the racemic modification. The data generated with these runs were stored on disk and used to construct, by running-time averaging [1], auto and cross correlation functions in both the laboratory and moving frames of reference. The vectors used in these calculations were  $\underline{v}$ , the molecular centre of mass velocity;  $\underline{\omega}$ , the molecular angular velocity;  $\underline{J}$ , the molecular angular momentum; the molecular force  $\underline{F}$  and torque  $\underline{T}_q$ ; the orientational unit vectors  $\underline{e}_1$ ,  $\underline{e}_2$  and  $\underline{e}_3$  in the principal moment of inertia frame (fig. (1)); their time derivatives  $\dot{\underline{e}}_1$ ,  $\dot{\underline{e}}_2$  and  $\dot{\underline{e}}_3$ . The vectors  $\underline{v}$  and  $\underline{J}$  were transformed from the laboratory to the principal moment of inertia frame of reference and in this frame the elements of the correlation matrix  $\langle \underline{v}(t) \underline{J}^T(o) \rangle_m$  were computed for both enantiomers and their racemic modification.

Some equilibrium properties are available from the simulation runs, and are listed in table 2.

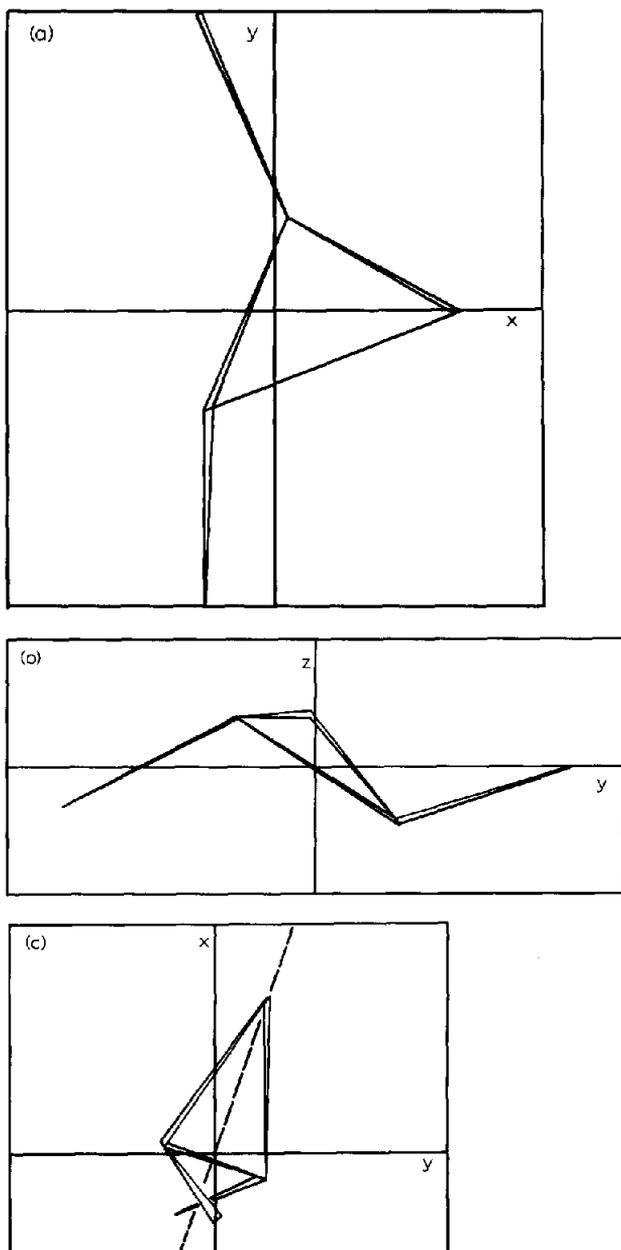


Fig. 1. The moving frame of reference for R trans 1,2 dimethylcyclopropane three projections. The S enantiomer is obtained by holding a mirror e.g. in the Zy plane. The dashed line is in the plane of twist pseudo-symmetry.

TABLE 2  
Equilibrium Properties from the M.D. Runs

Property (output)	1 bar			"13 k bar"		
	(R)	(S)	(RS)	(R)	(S)	(RS)
Rot. temp/K	296.7	300.3	299.5	297.4	291.6	298.8
Transl. temp/K	291.2	293.5	294.7	291.9	292.7	286.7
Total Energy/ kJ mole <sup>-1</sup>	-8.05	-8.1	-8.2	-19.9	-19.7	-19.7
Mean Press./ kbar (output)	-0.3 ±0.4	-0.3 ±0.4	-0.1 ±0.2	12.8 ± 1.0	13.1 ± 1.0	13.2 ± 1.0

## RESULTS AND DISCUSSION

The autocorrelation functions in the laboratory frame for both the R and S enantiomers should be identical, and this serves to check the level of "computer noise" in the simulation. Figure (2) is an illustration of this check for the angular velocity autocorrelation function of the R and S enantiomers under 13 kbar of pressure. The curves are identical within the computer noise.

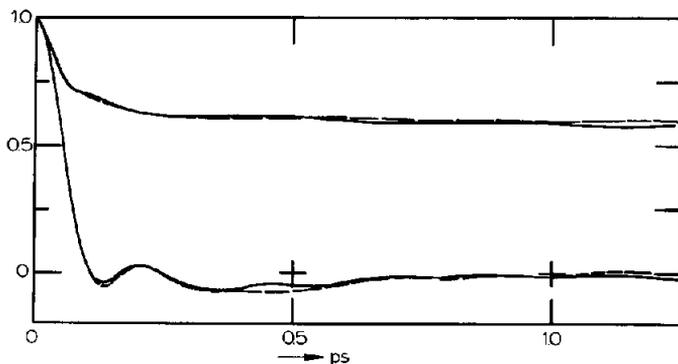


Fig. 2. Angular velocity autocorrelation functions in the laboratory frame under about 13 kbar of hydrostatic pressure.

———— R enantiomer ; - - - S enantiomer

Lower curves :  $\langle \underline{w}(t) \cdot \underline{w}(0) \rangle / \langle w^2 \rangle$

Upper curves :  $\langle \underline{w}(t) \cdot \underline{w}(t) \underline{w}(0) \cdot \underline{w}(0) \rangle / \langle w^4 \rangle$

Ordinate : C.f.'s ; Abscissa : time/ps.

## MOLECULAR DYNAMICS SIMULATION AT HIGH PRESSURE

By halving the atmospheric molar volume at 293K, we have obtained a variety of data for each enantiomer and their racemic mixture at output pressures listed in table 2. The laboratory frame autocorrelation functions of the other vectors are also identical for the R and S enantiomers. The overall molecular diffusion at this density is anisotropic (fig. (3)), and the oscillatory negative tails of autocorrelation functions such as those of  $\underline{w}$  or  $\underline{v}$  (fig. (4)) typify high density molecular dynamics [1]. We note that second moments such as  $\langle \underline{w}(t) \cdot \underline{w}(t) \underline{w}(0) \cdot \underline{w}(0) \rangle / \langle \underline{w} \rangle^4$  or  $\langle \underline{v}(t) \cdot \underline{v}(t) \underline{v}(0) \cdot \underline{v}(0) \rangle / \langle \underline{v} \rangle^4$  go swiftly to their Gaussian limits - which is an independent check on the validity of the algorithm for both enantiomers. This is the case also for the deeply oscillatory force autocorrelation function of fig. (5). Finally, the orientational laboratory frame a.c.f.'s of fig. (6) show, apart from the Verlet parameter, that the sample is still liquid, because their decay is virtually exponential with correlation times in the intermediate range. Again, each orientational a.c.f. is identical for the (R) and (S) enantiomer, so that the "noise level" in the algorithm is satisfactorily small.

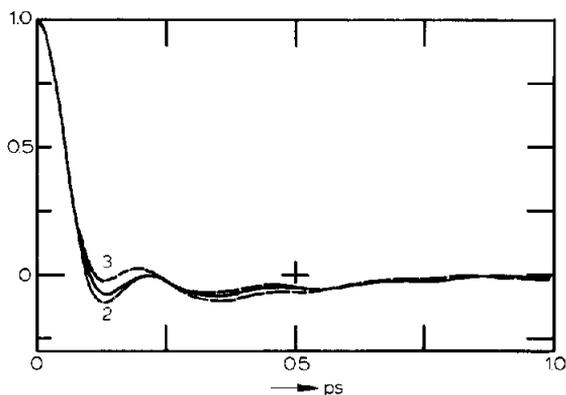


Fig. 3. Rotational velocity a.c.f.'s, R enantiomer

$$\begin{aligned}
 \text{---} & \quad \langle \dot{e}_1(t) \cdot \dot{e}_1(0) \rangle / \langle \dot{e}_1^2 \rangle ; \\
 \text{---} (2) & \quad \langle \dot{e}_2(t) \cdot \dot{e}_2(0) \rangle / \langle \dot{e}_2^2 \rangle ; \\
 (3) & \quad \langle \dot{e}_3(t) \cdot \dot{e}_3(0) \rangle / \langle \dot{e}_3^2 \rangle .
 \end{aligned}$$

Ordinate: C.f.'s ; Abscissa: time/ps/

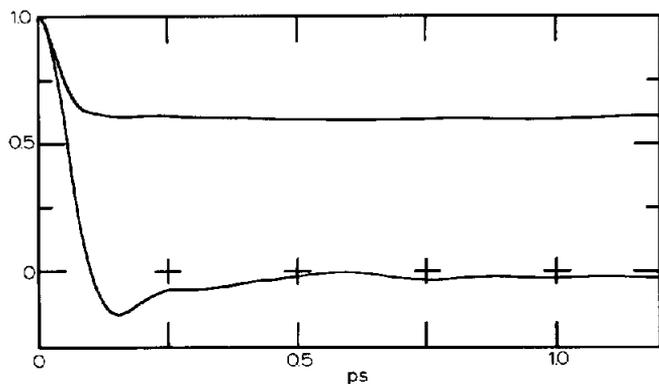


Fig. 4. Linear, centre of mass, velocity a.c.f.'s, R enantiomer  
 Linear, centre of mass, velocity a.c.f.'s, R enantiomer

—, Lower,  $\langle \underline{v}(t) \cdot \underline{v}(0) \rangle / \langle v^2 \rangle$

Upper,  $\langle \underline{v}(t) \cdot \underline{v}(t) \underline{v}(0) \cdot \underline{v}(0) \rangle / \langle v^4 \rangle$ .

Ordinate: C.F.'s; Abscissa : time/ps.

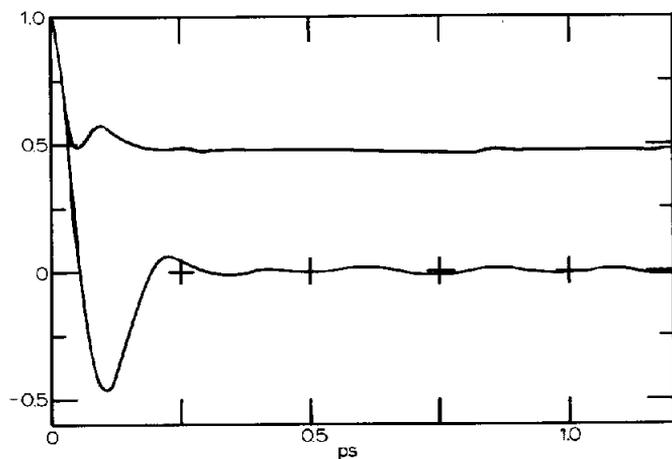


Fig. 5. As fir fug. 4, force a.c.f.'s.

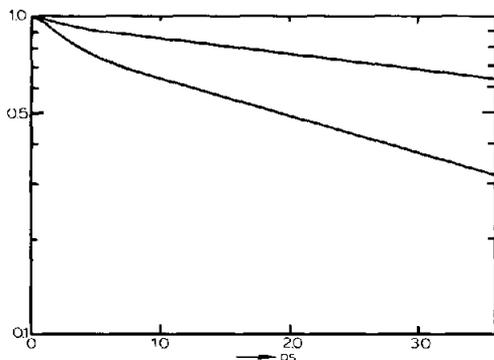


Fig. 6. As for fig. 3., orientational a.c.f.'s, semi-logarithmic scale.

——,  $P_1(\underline{e}_1) \doteq P_1(\underline{e}_2)$  ; (upper)

$P_2(\underline{e}_1) \doteq P_2(\underline{e}_2)$  ; (lower)

Ordinate C.F.'s; Abcissa : time/ps.

#### CORRELATIONS IN THE MOVING FRAME OF REFERENCE

The molecular symmetry of the trans 1,2 dimethyl cyclopropanes is higher than the  $C_s$  symmetry of 1,1  $C_2H_4FCI$  or 1,1  $C_2H_4FI$ . In consequence, only two elements of  $\langle \underline{v}(t) \underline{J}^T(o) \rangle_m$  appear above the computer noise in each enantiomer. These are illustrated in fig. 7(a) for the R enantiomer and fig. 7(b) for the S enantiomer. It is clear that both elements change sign from one enantiomer to the other, but remain equal and opposite in magnitude. The other four off-diagonal elements remain buried in the noise of the simulation run for each enantiomer. In the racemic mixture (fig. 7(c) the elements of figs. 7(a) and 7(b) have vanished into the noise. Fig. (7) therefore quantifies a difference in the molecular dynamics of the two enantiomers and racemic mixture.

These moving frame effects are not, however, carried through into the laboratory frame, because our simulation run on the racemic mixture produces a range of autocorrelation functions virtually identical with those illustrated in figs. (2) and (6) for either enantiomer. These results for the 1,2 dimethyl-cyclopropanes are therefore wholly unlike those previously reported [6 - 8] for the 1,1 fluorochloroethanes. In the latter all six off-diagonal elements of  $\langle \underline{v}(t) \underline{J}^T(o) \rangle_m$  appear in both enantiomers. Two of these elements invert sign from one enantiomer to the other and vanish in the racemic mixture, the other four remaining the same. These effects are carried through into the laboratory frame in a big way [6].

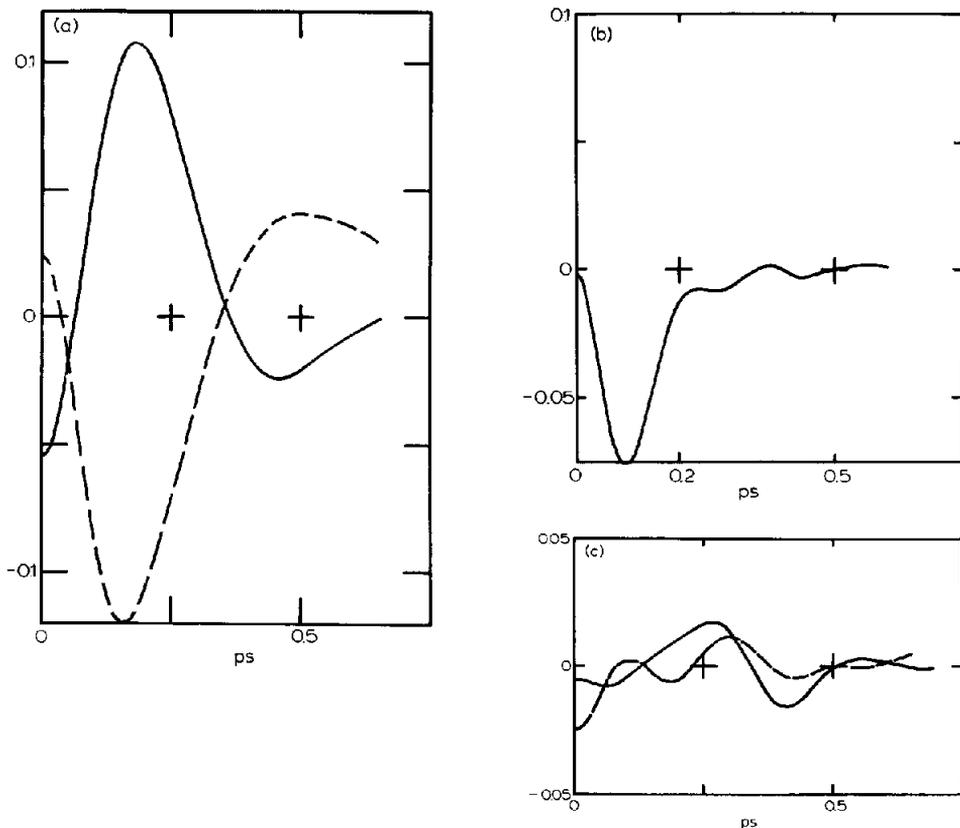


Fig. 7.

- (a) R enantiomer : ——— (1,2)  $\equiv \frac{\langle v_1(t) J_2(o) \rangle}{\langle v_1^2 \rangle^{1/2} \langle J_2^2 \rangle^{1/2}}$   
 - - - - (2,1) ;

(b) S enantiomer, as for (a). Note the changes of sign.

(c) Racemic mixture, noise only. Orindates : normalised c.f.; Abscissae: time/ps

The cases of 1,1  $C_2H_4FI$  and the 3 methylcyclohexanones are intermediate, in the sense that measurable differences in  $\langle \underline{v}(t) \underline{J}^T(o) \rangle_m$  produce small, but real differences in laboratory frame a.c.f.'s such as those of figs. (2) to (6).

It therefore seems clear that the racemic modification of molecular dynamical properties in any frame of reference is a precise function of the symmetry group to which a particular chiral molecule belongs, and within this classification, a sensitive function of the atomic mass distribution with respect

to the molecular centre of mass. There is no molecular symmetry difference between 1,1  $C_2H_4FCI$  and 1,1  $C_2H_4FI$ , but the properties of  $\langle \underline{v}(t) \underline{J}^T(o) \rangle_m$  are different because of the different mass distribution. The 1,2 dimethyl cyclopropanes on the other hand, belong to a different symmetry group, and despite their chirality the characteristics of  $\langle \underline{v}(t) \underline{J}^T(o) \rangle_m$  in these molecules are similar to those of an optically inactive  $C_{3v}$  symmetry molecule such as [24,25]  $CHBr_3$ , or  $CH_3I$ , i.e. only two of its elements are measurably large, and these are equal and opposite in sign. In terms of symmetry, this is also the case for the racemic mixture of fig. 7(c), i.e. no elements of the matrix are discernible above the noise in this case. The magnitudes of the symmetric elements of figs. 7(a) and 7(b) have been reduced to zero, but this produces no change in the laboratory frame a.c.f.'s.

These computations use simplified representations of intermolecular potential energy surfaces, which are assumed to be pairwise additive. The overall pattern of information produced by the same algorithm-structure is, however, strikingly different according to molecular characteristics. It is therefore unlikely that the detailed information typified in figs. (2) to (7) is an artifact of the computer simulation method. It has been known since Pasteur's discovery of chirality in the tartaric acids [3] that the racemic modification is sometimes very large and sometimes very small. We have already mentioned this earlier in the paper. In the particular case of the 1,2 dimethyl cyclopropanes the experimental data are sparse, but it is known that the boiling points of the enantiomers and racemic mixture are identical. The refractive index of the racemic mixture at 293K is 1.3713, and that of the l enantiomer at 289K is 1.3699. The boiling points of racemic mixtures are often similar to those of their components, but this is not the case for the melting points. Unfortunately, very few simple chiral molecules are available whose boiling points and melting points are both known. However, even when the densities of enantiomers and racemic mixture are kept identical, as in all our computer simulations, the racemic modification of the molecular dynamics can vary markedly from one molecular geometry to another.

#### MOLECULAR DYNAMICS AT ATMOSPHERIC PRESSURE

The equivalent laboratory frame auto-correlation functions to those in figs (2) - (7) were produced by using the literature density at 1 bar. These runs produced the output parameters of table (2). The input molar volume at 1 bar is twice that at 13 kbar and this produces great changes in the nature of the molecular dynamics.

These are illustrated in figs (8) to (13), which are the equivalents, respectively, of figs (2) to (7). Again these autocorrelation functions have been checked for both R and S enantiomers. The equivalents in the racemic mixture are again the same, on the scale of figs (8) to (13), as the results for each enantiomer.

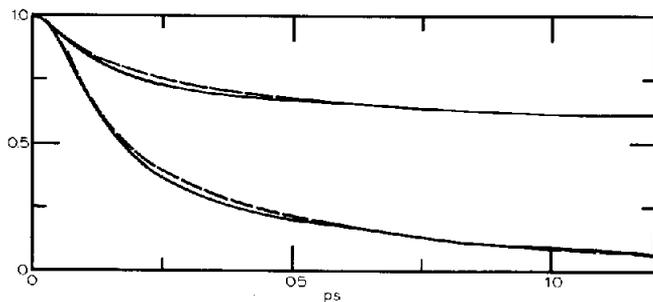


Fig. 8. As for fig. 2., 1 bar, 293K.

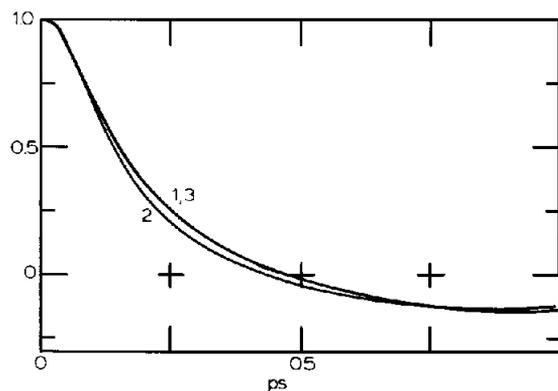


Fig. 9. As for fig. 3., 1 bar, 293K.

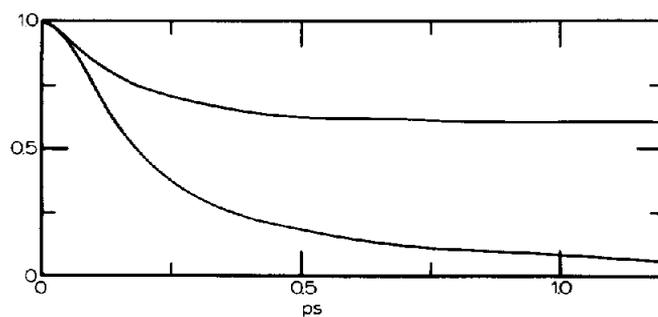


Fig. 10. As for fig. 4., 1 bar, 293K.

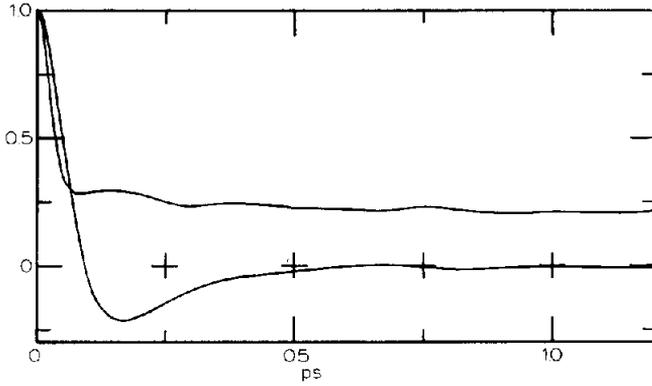


Fig. 11. As for fig. 5., 1bar, 293K.

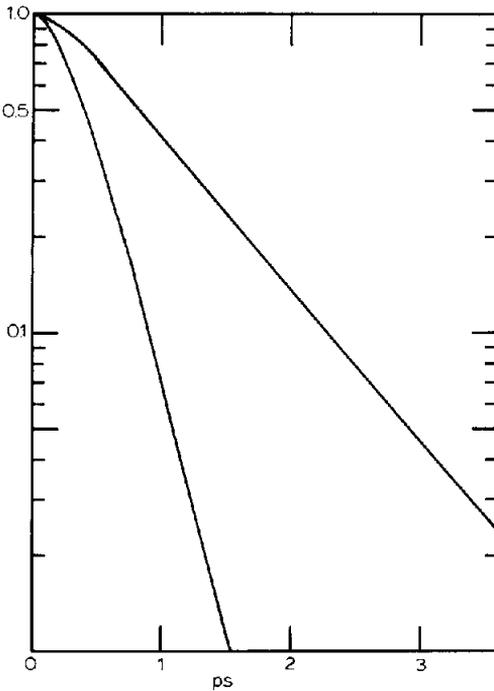


Fig. 12. As for fig. 6., 1bar, 293K.

The molecular dynamics, as manifest in these auto correlation functions, typify those [1] at low densities - the liquids being only 5K or so below their boiling points under atmospheric pressure. The linear and angular velocity auto-correlation functions are thus nearly exponential, except near  $t = 0$ . The rotational velocity a.c.f.'s of fig. (9) show that the overall diffusion is nearly

isotropic in the laboratory frame visible to far infra-red spectroscopy [1], and the fairly deep negative overshoot of these functions reflect the freedom of movement available at this density and temperature. The orientational auto-correlation functions of fig. (12) are exponential (except near the time origin) but with much shorter correlation times than those of fig. (6). The second moment a.c.f.'s of angular velocity (8), linear velocity (fig. 10) and force (fig. 11) take a much longer period of time to reach their Gaussian limits than under 13 kbar and during this period cannot be described by classical Maxwell-Boltzmann statistics. Grigolini et al [26 - 30] have pointed out that this is a sign of non-linearity in the governing diffusion equations of phenomenological theory - a class of Kramers equations [1], or alternatively non-linear generalised Langevin equations [30] such as those of the itinerant oscillator with a cosine potential. A generally valid numerical algorithm is now available to solve these equations for auto-correlation functions.

The moving frame cross-correlation matrix  $\langle \underline{v}(t) \underline{J}^T(0) \rangle_m$  at atmosphere pressure contains in each enantiomer two non-vanishing off-diagonal elements which are illustrated for the R and S type molecules in figs 13(a) and 13(b) respectively.

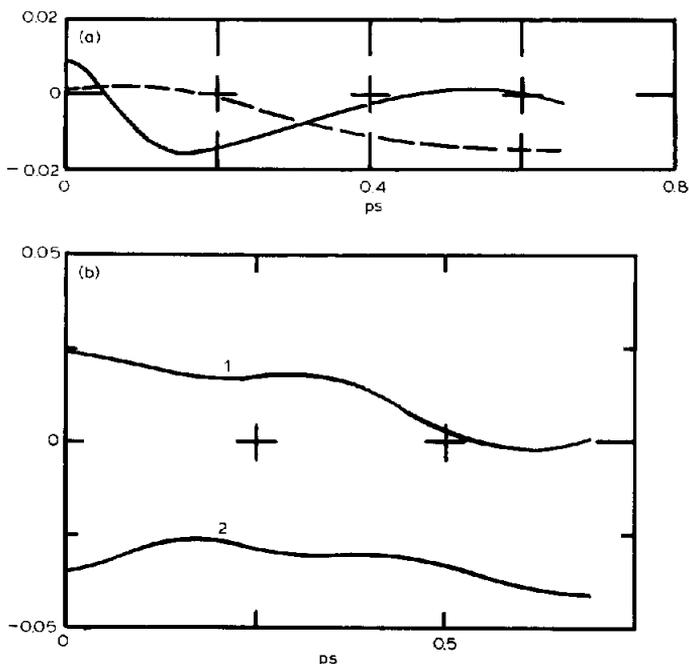


Fig. 13. As for fig. 7., 1bar, 293K. a) S enantiomer; b) racemic mixture.

Again the two non-vanishing elements are equal and opposite in time dependence and invert sign from one enantiomer to the other. At 1 bar they are longer lived and less oscillatory than at 13 k bar. In the racemic mixture (figs (13c)) both "signals" vanish in the "noise".

The overall anti-symmetry of the elements of a cross-correlation matrix such as  $\langle \underline{v}(t) \underline{J}^T(o) \rangle_m$  is therefore maintained. The matrix is an "anti-symmetric" one in both enantiomers (with diagonal, and four of the off-diagonal, elements zero). In enantiomer R the anti-symmetry is exactly opposite in sense to that of the S enantiomer. In the racemic mixture the matrix is symmetric (in fact a null matrix). A tentative symmetry based explanation is appended of why there is no laboratory frame racemic modification of dynamical properties in the symmetry group of the trans 1,2 dimethyl cyclopropanes.

#### SUMMARY OF SALIENT POINTS

i) In the moving frame of reference, defined by the principal moments of inertia, there is an intrinsic difference in molecular dynamical properties of (R) and (S) trans 1,2 dimethyl cyclopropane. This means that the dynamical behaviour of the R enantiomer is different from that of the S enantiomer and also different from that of the racemic modification.

ii) These differences are due to the statistical correlation between each molecule's rotational movement and its own centre of mass translation.

iii) The symmetry group of the trans 1,2 dimethyl cyclopropanes is such that these differences are not carried through into the laboratory frame. In consequence no difference is observable between the lab-frame auto-correlation functions of enantiomer and racemic mixture for a range of relevant vectors associated with the molecular dynamics in the liquid phase.

#### ACKNOWLEDGEMENTS

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#### APPENDIX

We compare in table 3 the symmetry patterns of the moving frame matrix  $\langle \underline{v}(t) \underline{J}^T(o) \rangle$  for three optically active systems simulated recently [6-9]. We note

- i) that the sum of the signs within each matrix is zero;
- ii) that the symmetry of the matrices in the racemic mixtures is higher than that in the corresponding enantiomers;

- iii) that in the trans 1,2 dimethyl cyclopropanes the matrix in the S enantiomer is the transpose of that in the R enantiomer, and that  $\underline{\underline{M}}(R) - \underline{\underline{M}}^T(S) = \underline{\underline{0}}$  where  $\underline{\underline{M}}$  denotes the complete 3 x 3 matrix in each case.

The symbol  $\delta$  in the 1,1 fluoriodethanes means that we expect these elements to exist for  $t > 0$  but have not been able to see them above the noise of the simulation run. The reason for this is that the molecular symmetry-group of 1,1  $C_2H_4FI$  is the same as that of 1,1  $C_2H_4FCl$ , where these elements have been observed [6-8].

TABLE 3

Symmetries of  $\langle \underline{v}(t) \underline{J}^T(0) \rangle_m$

Molecular Liquids	R Enantiomer	S Enantiomer	Racemic Mixture
1,1 $C_2H_4FCl$ (big racemic modification [6-8])	$\begin{bmatrix} 0 & + & - \\ - & 0 & - \\ + & + & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & + & + \\ - & 0 & - \\ - & + & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & + & 0 \\ - & 0 & - \\ 0 & + & 0 \end{bmatrix}$
1,1 $C_2H_4FI$ (Very small modification [9])	$\begin{bmatrix} 0 & + & \delta \\ - & 0 & + \\ \delta & - & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & + & \delta \\ - & 0 & + \\ \delta & - & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & + & 0 \\ - & 0 & - \\ 0 & + & 0 \end{bmatrix}$
trans 1,2 dimethyl cyclopropane (no modification)	$\begin{bmatrix} 0 & + & 0 \\ - & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & - & 0 \\ + & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$

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