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Computer Simulation of the Statistical Correlation between Rotation and Translation in 3-Methylcyclohexanone

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Computer simulation is used to investigate rotation/translation coupling in the (+) enantiomer and racemic mixture of 3-methylcyclohexanone. A rough model of the intermolecular pair potential suffices to corroborate recent spectral results on the nature of the liquid-state molecular dynamics of 3-methylcyclohexanone.

We have indicated recently[1–4] that an experimental insight into the nature of rotation/translation coupling in molecules may be obtained by comparing a spectrum of an enantiomer with that of its racemic mixture. Essentially the reason for this is that the only perceptible statistical dynamic difference between two enantiomers is found in a moving-frame matrix such as $\langle \boldsymbol{v}(t)\boldsymbol{J}^{\mathrm{T}}(0)\rangle_m$, where $\boldsymbol{v}$ is the molecular centre-of-mass velocity and $\boldsymbol{J}$ is the transposed molecular angular momentum vector. For the two enantiomers specific elements of this matrix may differ in sign. In the racemic mixture these same elements might cancel by symmetry, leading to observable differences in the laboratory frame of reference. These manifest themselves in auto-correlation functions of dynamical vectors associated with a molecule's motion (rotation and translation) and therefore, by Fourier transformation, in the frequency dependence of spectra of various kinds.[5]

We have reported separately far-infrared and inverse Raman data on (+) 3-methylcyclohexanone and its racemic modification.[6] Slight differences were found in both types of spectra, indicating that the elements of $\langle \boldsymbol{v}(t)\boldsymbol{J}^{\mathrm{T}}(0)\rangle_m$ for this molecule differ, in turn, only slightly. In this paper we aim to corroborate this finding by attempting a computer simulation of 3-methylcyclohexanone in its enantiomeric and racemic modifications. The methods are those developed previously for 1,1-C_2H_4FCl and 1,1-C_2H_4FI, where the rotation/translation effect is large and small, respectively.[3,6]

It is clear from the literature that the racemic modification of some enantiomers may differ considerably in physical characteristics, and that of others only very slightly. Two examples from the thousands available in the literature are the lactic acids and the subject of this paper, 3-methylcyclohexanone. Racemic lactic acid melts at 291 K, the enantiomers at ~26 K. The characteristics of all three 3-methylcyclohexanones are, on the other hand, very similar (the densities at 293 K being the same to two decimal places). Even when the densities are identical, however (as in the input to our simulation[1–3] of 1,1-C_2H_4FCl), the molecular-dynamical properties of the racemate may differ considerably from those in either enantiomer. Clearly, therefore, the well known racemic modification of the physical properties of enantiomers can now be traced, according to our central hypothesis, to the effects of a molecule's rotation on its centre-of-mass translation and *vice versa*. Small changes in molecular characteristics may have a very large effect on the statistical correlation between molecular rotation and translation and therefore

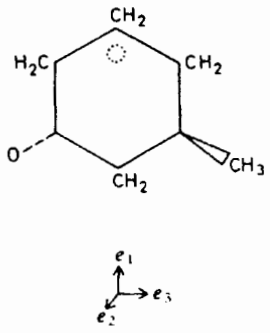

Fig. 1. Illustration of the moment-of-inertia frame for 3-methylcyclohexanone, simplified six-site representation. Inset: frame of e_1, e_2 and e_3.

on the physical properties of the racemic modification. The aim of what follows is to illustrate and explain this theory for a specific optically active molecule using a combination of spectroscopy and computer simulation.

THE ALGORITHM

Fig. 1 illustrates our simple six-site representation of 3-methylcyclohexanone. This is a first approximation to the true geometry necessitated purely by limitations on available computer power (CDC 7600). The pair potential is therefore made up of 36 atom–atom Lennard-Jones interactions with parameters as follows:[7–9] (i) $\varepsilon/k(CH_3) = 158.6$ K, $\sigma(CH_3) = 4.0$ Å; (ii) $\varepsilon/k(CH) = 75.4$ K, $\sigma(CH) = 3.7$ Å; (iii) $\varepsilon/k(C) = 35.8$ K, $\sigma(C) = 3.4$ Å; (iv) $\varepsilon/k(O) = 58.4$ K, $\sigma(O) = 2.8$ Å; (v) $\varepsilon/k[(CH_2)_3] = 158.6$ K, $\sigma[(CH_2)_3] = 4.0$ Å; (vi) $\varepsilon/k(CH_2) = 75.4$ K, $\sigma(CH_2) = 3.7$ Å.

The positions of these species with respect to the centre of mass of the molecule, taken in the first approximation as a rigid framework, are recorded in table 1 for the two enantiomers (1 and 2).

Using these data a molecular-dynamics simulation was carried out on enantiomer 1 and the racemic mixture using in each case a total of 108 molecules and our usual methods, which have been reported elsewhere.[10–16]

The data from *ca.* 600 time steps of 0.005 s each were stored on disc and used to compute auto- and cross-correlation functions in the following vectors: (i) $\boldsymbol{v}$, the centre-of-mass linear velocity; (ii) $\boldsymbol{\omega}$, the molecular angular velocity; (iii) $\boldsymbol{J}$, the

Table 1. Atomic positions (Å) in the enantiomers of 3-methylcyclohexanone (simplified representation)

	enantiomer 1			enantiomer 2		
species	$x(e_3)$	$y(e_1)$	$z(e_2)$	$x(e_3)$	$y(e_1)$	$z(e_2)$
CH_3	2·44	1·10	0·34	2·44	1·10	−0·34
CH	1·09	0·35	0·34	1·09	0·35	−0·34
C	−1·43	0·35	0·34	−1·43	0·35	−0·34
O	−1·50	−0·39	1·08	−1·50	−0·39	−1·08
$(CH_2)_3$	−0·17	−0·73	−1·04	−0·17	−0·73	1·04
CH_2	−0·17	0·81	0·93	−0·17	0·81	−0·93

molecular angular momentum; (iv) $\boldsymbol{F}$, the molecular force; (v) $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ and $\boldsymbol{e}_3$, the orientational vectors in the principal moment of inertia frame (fig. 1); (iv) $\dot{\boldsymbol{e}}_1$, $\dot{\boldsymbol{e}}_2$ and $\dot{\boldsymbol{e}}_3$, their time derivatives.

The cross-correlation matrix $\langle \boldsymbol{v}(t)\boldsymbol{J}^{\mathrm{T}}(0)\rangle_m$ was computed in a moving frame of reference defined as that of the principal moments of inertia. In this frame the off-diagonal elements of the matrix exist for $t > 0$ and measure quantitatively the correlation between molecular rotation and centre-of-mass translation.[17]

RESULTS AND DISCUSSION

The differences in the elements of $\langle \boldsymbol{v}(t)\boldsymbol{J}^{\mathrm{T}}(0)\rangle_m$ for the enantiomer and racemic modification have an effect in the laboratory frame of reference, and the magnitude of this effect is illustrated through auto-correlation functions such as that of $\boldsymbol{v}$ [fig. 2(*a*)]. In this frame both enantiomers produce the same auto-correlation function, which is, however, different from that in the racemic modification. The differences in fig. 2(*a*) are therefore directly observable manifestations of the nature of the moving-frame matrix $\langle \boldsymbol{v}(t)\boldsymbol{J}^{\mathrm{T}}(0)\rangle_m$. Fig. 2(*a*), 3(*a*) and 3(*b*) illustrate the same effect for $\boldsymbol{J}$, $\boldsymbol{\omega}$ and $\boldsymbol{F}$, respectively, in the laboratory frame.

The a.c.f. associated with combinations of $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ and $\boldsymbol{e}_3$ or with $\dot{\boldsymbol{e}}_1$, $\dot{\boldsymbol{e}}_2$ and $\dot{\boldsymbol{e}}_3$ are observable[5] from spectra such as dielectric and far-infrared absorption. Fig. 4(*a*) shows the a.c.f. of $\dot{\boldsymbol{e}}_1$, $\dot{\boldsymbol{e}}_2$ and $\dot{\boldsymbol{e}}_3$ (the rotational velocities) for enantiomer 1 (or 2) and fig. 4(*b*) shows them for the racemic modification. The differences in the isotropy of the overall molecular diffusion as illustrated in fig. 4(*a*) and (*b*) are again due to the correlation between rotation and translation. It follows that any phenomenological approach that does not take this correlation into account cannot describe these differences.[5]

Finally, in the laboratory frame, fig. 5 notes the differences between enantiomer and racemate for $\boldsymbol{e}_1$, $\boldsymbol{e}_2$ and $\boldsymbol{e}_3$, the orientational unit vectors of fig. 1. Dielectric

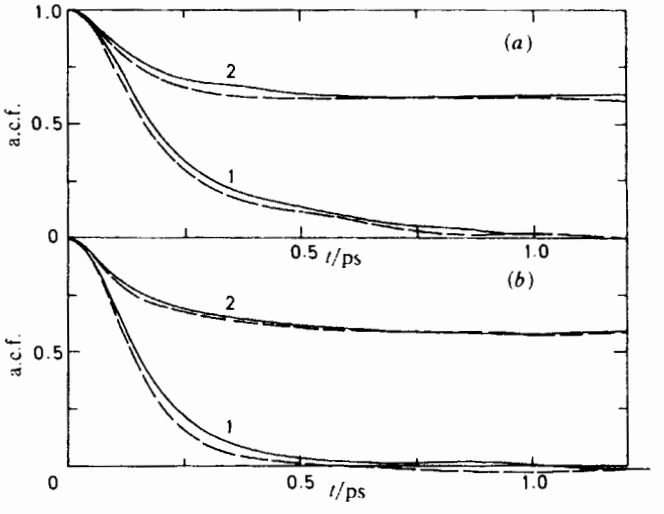

Fig. 2. (*a*) Centre-of-mass velocity ($\boldsymbol{v}$) auto-correlation functions in the laboratory frame. (——) Enantiomer (1), $\langle \boldsymbol{v}(t)\cdot\boldsymbol{v}(0)\rangle/\langle v^2\rangle$; enantiomer (2), $\langle \boldsymbol{v}(t)\cdot\boldsymbol{v}(t)\boldsymbol{v}(0)\cdot\boldsymbol{v}(0)\rangle/\langle v^4\rangle$. (– – –) Racemic mixture, levelling as for enantiomer. (*b*) As for (*a*), for molecular angular momentum, $\boldsymbol{J}$.

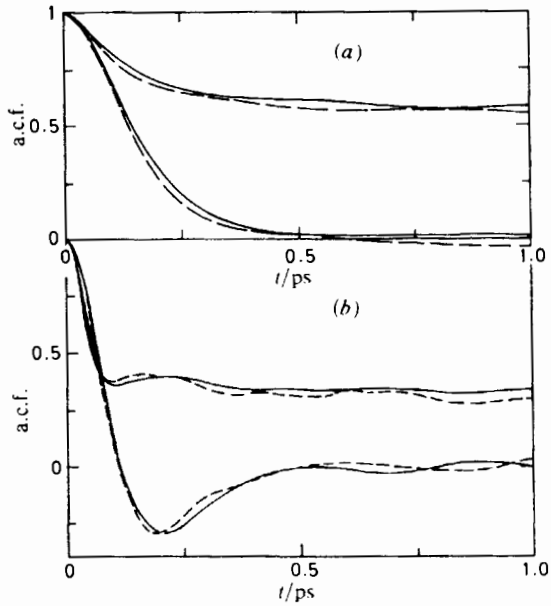

Fig. 3. (*a*) As for fig. 2(*a*) for molecular angular velocity, $\boldsymbol{\omega}$. (*b*) As for fig. 2(*a*), for molecular force, $\boldsymbol{F}(= m\dot{\boldsymbol{v}})$.

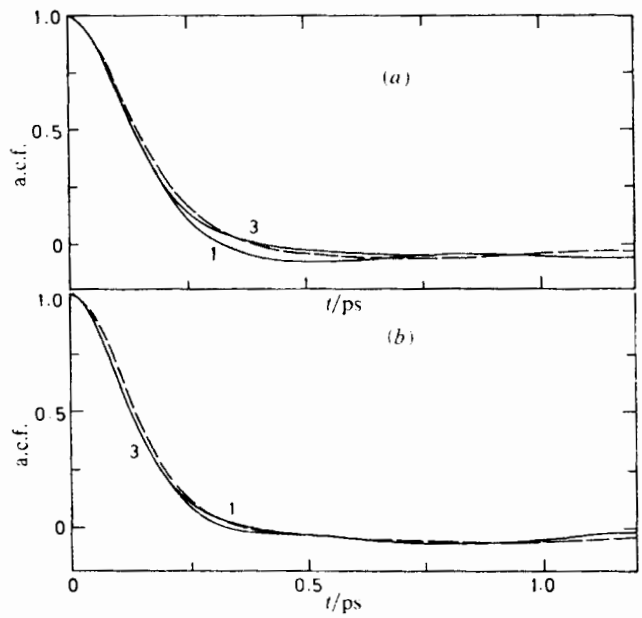

Fig. 4. (*a*) Rotational velocity a.c.f. for the enantiomer. (1) $\langle \dot{\boldsymbol{e}}_1(t) \cdot \dot{\boldsymbol{e}}_2(0) \rangle / \langle \dot{e}^2 \rangle$; (2) $\langle \dot{e}_2(t) \cdot \dot{\boldsymbol{e}}_3(0) \rangle / \langle \dot{e}_2^2 \rangle$; (3) $\langle \dot{\boldsymbol{e}}_3(t) \cdot \dot{\boldsymbol{e}}_3(0) \rangle / \langle \dot{e}_3^2 \rangle$. These may be related, by Fourier transformation, to the far-infrared spectrum.[5,6] (*b*) As for (*a*), racemic mixture.

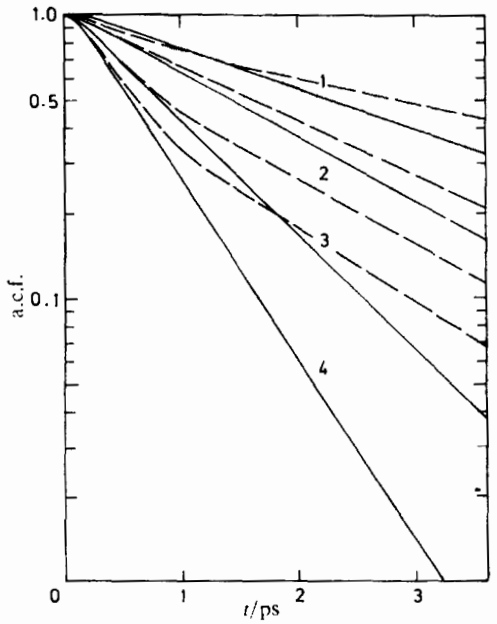

Fig. 5. Orientational a.c.f. of e_3 and e_2. (——) (1) $P_1(e_3) = \langle e_3(t) \cdot e_3(0) \rangle$, enantiomer; (2) $P_1(e_2)$; (3) $P_2(e_3) = \frac{1}{2}\langle 3[e_3(t) \cdot e_3(0)]^2 - 1 \rangle$; (4) $P_2(e_2)$. (– – –) As for (1)–(4), racemic mixture.

relaxation or infrared bandshape analysis leads to $P_1(\boldsymbol{u})$, the Legendre a.c.f. of the dipole unit vector, $\boldsymbol{u}$. Raman and Rayleigh scattering may be used to measure $P_2(\boldsymbol{u})$, the second Legendre a.c.f.[5]

We have reported already[6] the far-infrared and inverse Raman spectra of (+)3-methylcyclohexanone and the racemic mixture, and fig. 4 and 5 corroborate the small differences measured spectrally in, of course, the laboratory frame of reference.

STATISTICAL CORRELATION IN THE MOVING FRAME OF REFERENCE

The off-diagonal elements of $\langle \boldsymbol{v}(t)\boldsymbol{J}^{\mathrm{T}}(0) \rangle_m$ are illustrated in fig. 6 for the enantiomer and racemic mixture. These are all normalised in the same way and should all vanish by symmetry at $t = 0$. The fact that they do not do so is due to 'computer noise'. A (2,1) element, for example, is defined as:

$$(2,1) = \frac{\langle v_2(t)J_1(0) \rangle_m + \langle v_2(0)J_1(t) \rangle_m}{2\langle v_2^2(0) \rangle_m^{1/2} \langle J_1^2(0) \rangle_m^{1/2}}.$$

These cross-correlation functions are reliable to *ca.* 0.4 ps, when the 'noise' level becomes commensurate with the 'signal'.

It is clear from fig. 6(*a*) and (*b*) that there is substantial translation/rotation correlation in four of the diagonal elements (2,1), (1,2), (3,2) and (2,3) of the matrix $\langle \boldsymbol{v}(t)\boldsymbol{J}^{\mathrm{T}}(0) \rangle_m$ in the enantiomer. Fig. 6(*c*) shows, however, that the translation/rotation correlation in the elements (1,3) and (3,1) is much smaller and barely distinguishable from the underlying noise.

This is crucial to our understanding of the laboratory-frame differences of fig. 2–5. The important point is that the only molecular-dynamical difference between

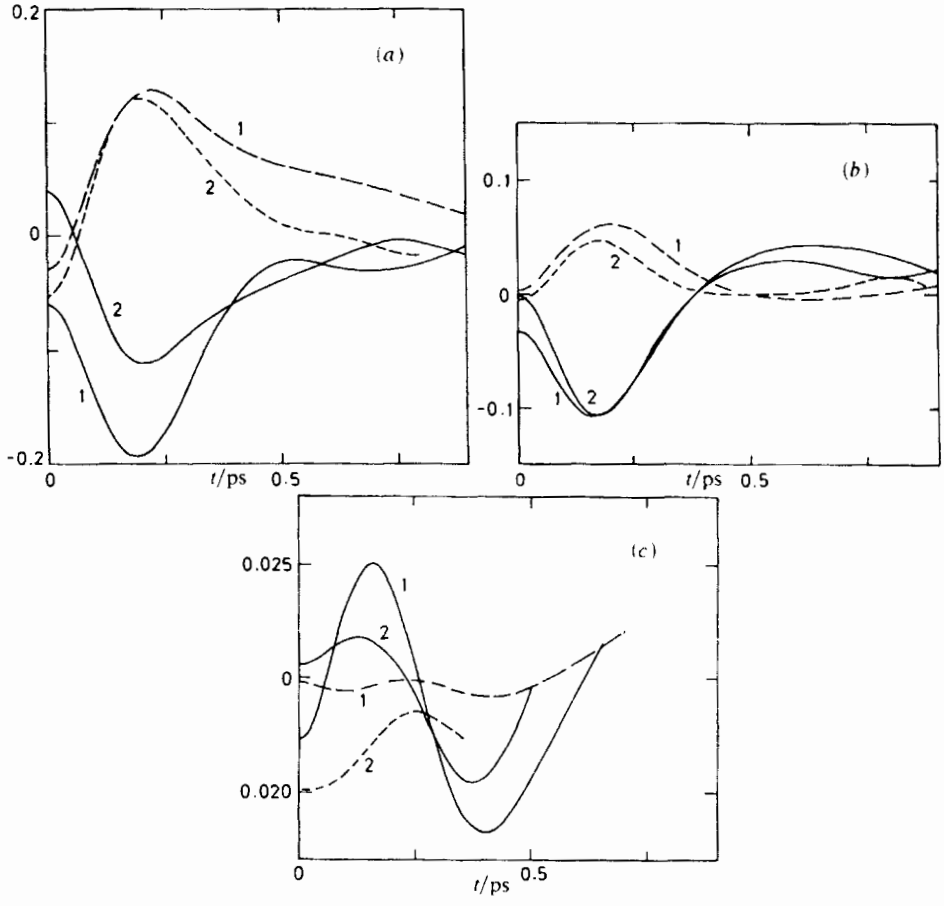

Fig. 6. Off-diagonal elements of $\langle \boldsymbol{v}(t)\boldsymbol{J}^{T}(0)\rangle_m$ in enantiomer (1) and racemic mixture (2). (*a*) (– – –) (2,1); (——) (1,2). (*b*) (– – –) (3,2); (——) (2,3). (*c*) (– – –) (3,1); (——) (1,3).

enantiomer 1 and its mirror image, enantiomer 2, is in these (1,3) and (3,1) elements of $\langle \boldsymbol{v}(t)\boldsymbol{J}^{T}(0)\rangle_m$. The two enantiomer liquids are identical in all other respects, including the time dependence of the other four off-diagonal elements. The only possible explanation for the distinct behaviour of the racemic mixture must be based on the different moving-frame elements (1,3) and (3,1) of either enantiomer. The effect of these moving-frame correlations is carried through into the laboratory frame, although the direct correlation $\langle \boldsymbol{v}(t)\boldsymbol{J}^{T}(0)\rangle_l$ of the laboratory frame vanishes for all t because the response of $\boldsymbol{v}$ to parity inversion is different from that of $\boldsymbol{J}$ in this frame.[17]

A vivid example of this point is provided by the enantiomers and racemic mixture of a simple liquid such as 2-chlorobutane. The mixture melts at 142 K while each enantiomer melts at 133 K. In this range of temperature each enantiomer is a liquid, whose molecular-dynamical properties in the laboratory frame of reference are identical to techniques such as dielectric relaxation or far-infrared spectroscopy. When mixed in equal proportions, however, the result is a solid

racemic modification. It is not possible to explain this without the use of cross-correlation functions exemplified by $\langle \boldsymbol{v}(t)\boldsymbol{J}^{\mathrm{T}}(0)\rangle_m$.

The moving frame elements of the racemic mixture are illustrated in fig. 6(*c*), and there are some interesting differences with respect to their counterparts of fig. 6(*a*) and (*b*). As in our previous simulation[6] of C_2H_4FI, these tend to be larger than the corresponding difference in the auto-correlation functions of the laboratory frame, illustrated by fig. 2–5.

There seems to be no firm evidence that individual atom–atom terms in pair potentials are different when a molecule of enantiomer 1 interacts with one of enantiomer 2 as opposed to another molecule of enantiomer 1. This would mean that atom–atom Lennard-Jones terms are not transferable and not pairwise additive in general. The nature of the pair potential in a racemic modification [18] as compared with that in the pure enantiomer should be investigated by measuring the second and higher virial coefficients in optically active molecules. An *ab initio* quantum-mechanical calculation of the pair potential in the enantiomer and racemic mixture would add to our knowledge in this area.

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