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Laboratory Frame Cross Correlations in Chiral Liquids: Direct Observation of Rotation/Translation Coupling

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Abstract

Cross correlations of the type $\langle \mathbf{v}(t)\mathbf{J}^T(0)\rangle$ are observable in the laboratory frame of reference for chiral molecules in the liquid state. Here $\mathbf{v}$ is the molecular centre of mass linear velocity and $\mathbf{J}$ the molecular angular momentum. Some of these cross correlations are illustrated by computer simulation for the enantiomers and racemic mixture of fluorochloroacetonitrile. The Langevin equation is adapted for rototranslation and analytical expressions derived, in the first approximation, for the dominant elements of $\langle \mathbf{v}(t)\mathbf{J}^T(0)\rangle$.

1. Introduction

It is well known that the rotational theories of molecular diffusion, based on that of the Browian motion, are underdeveloped in that the statistical cross correlations that exist (for example) between the rotational and translational molecular motion are not described explicitly. In a previous letter [1] I have shown the importance of these cross correlation functions in explaining the observable spectral differences between liquid enantiomers of the type R (or S) and their equimolar (or racemic) mixture. In that letter I described a series of moving frame cross-correlation functions of the type $\langle \mathbf{v}(t)\mathbf{J}^T(0)\rangle_m$ between the molecular centre of mass velocity $\mathbf{v}$ and molecular angular momentum $\mathbf{J}$ both defined in the moving frame of the three principal molecular moments of inertia.

In this letter I report using computer simulation the important finding that for optically active molecules, these cross correlations also exist in the *laboratory* frame of reference. This means that cross-correlations of the type $\langle \mathbf{v}(t)\mathbf{J}^T(0)\rangle$ are observable *directly* in both R and S enantiomers and their racemic mixture. An appropriate combination of computer simulation and analytical theory [2, 3] may be used to extract information on the nature of the cross correlation. By carefully comparing the relevant spectral details in an enantiomer and racemic mixture information may be extracted directly about the matrix $\langle \mathbf{v}(t)\mathbf{J}^T(0)\rangle$.

I illustrate the result with reference to the enantiomers and racemic mixture of fluorochloroacetonitrile, which has recently been synthesised for the first time and has therefore become available for spectral investigation with a variety of methods [2].

2. Description of algorithm

The molecular dynamics algorithm is used to simulate the motions and interactions of R and S fluorochloroacetonitrile and of the RS (racemic) mixture with 108 molecules interacting pairwise with a six by six site–site potential described in Table I. The algorithm and numerical integration technique [3] are described fully elsewhere [4]. The laboratory frame cross correlation matrix $\langle \mathbf{v}(t)\mathbf{J}^T(0)\rangle$ is computed using a running time average in the usual way. In the racemic mixture, 54 molecules of enantiomer R are mixed with 54 of S, assuming that the site–site interaction terms are identical. This technique generates automatically the differences which are known to exist experimentally between the physical properties of an enantiomer and its racemic mixture [5–7].

3. Results and discussion

The novel result reported here for the first time is illustrated in Fig. 1 with reference to the elemental cross correlation functions $\langle v_x(t)J_y(0)\rangle$ and $\langle v_y(t)J_x(0)\rangle$ in the laboratory frame of reference for the R, S, and RS liquids. These cross correlation functions are normalised by $\langle v_x^2\rangle^{1/2}\langle J_y^2\rangle^{1/2}$ and $\langle v_y^2\rangle^{1/2}\langle J_x^2\rangle^{1/2}$ respectively, and are symmetric in their time dependence. There are nine elements of this type in the laboratory frame matrix $\langle \mathbf{v}(t)\mathbf{J}^T(0)\rangle$. The rotation translation coupling is accentuated by the application of an external electric field (Fig. 2). As described elsewhere [3] (see the accompanying letter), the electric field makes the sample birefringent and tends to align the molecules in one direction by the imposition of a torque of the type $\boldsymbol{\mu} \times \mathbf{E}$ where $\boldsymbol{\mu}$ is the molecular dipole moment and $\mathbf{E}$ the external field. The amplitude of the cross correlation function $\langle v_x(t)J_y(0)\rangle$ is dependent on the external field strength, (Fig. 2).

The field-off computer simulation results are illustrated with the following simple analytical theory of laboratory frame rotation translation coupling.

4. Analytical theory

To a first approximation, the inertial dynamics of the chiral asymmetric top may be described by those of a spherical top with embedded dipole. (For fluorochloroacetonitrile $I_x =$

Table I. *Intermolecular pair potential for fluorochloroacetonitrile: Lennard–Jones and partial charge terms*

Atom*	$x(e_3)$	$y(e_1)$	$z(e_2)$ R	$z(e_2)$ S	$\epsilon/k/K$	$\sigma/$A	$q/\lvert e\rvert$
N	0.75	−2.28	0.35	−0.35	47.8	3.0	−0.16
C	0.27	−1.29	−0.03	0.03	35.8	3.4	−0.02
C	−0.34	−0.05	−0.51	0.51	35.8	3.4	0.03
H	−0.34	−0.38	−1.59	1.59	10.0	2.8	0.51
Cl	0.61	1.33	0.07	−0.07	127.9	3.6	−0.16
F	−1.64	0.06	0.02	−0.02	54.9	2.7	−0.20

*Atom coordinates relative to centre of mass: frame of the molecular principal moments of inertia.

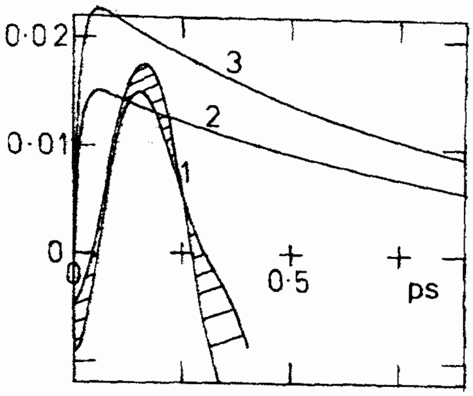

Fig. 1. The $\langle v_y(t)J_x(0)\rangle$ element of the laboratory frame cross correlation matrix $\langle \mathbf{v}(t)\mathbf{J}^T(0)\rangle$ for S fluorochloroacetonitrile at 133 K; computer simulation. (1) ▨ Normalised cross correlation function from the computer simulation, showing the noise level. (2) —— Analytical theory: (rototranslational Langevin equation with $\gamma_v = 8.0$ THz; $\gamma_J = 10.0$ THz; $\gamma_{vJ} = 0.5$ THz $\langle v_y^2\rangle^{1/2}\langle J_x^2\rangle^{1/2} = 0.044$ in reduced units. (3) As for (2), $\gamma_{vJ} = 0.75$ THz.

137×10^{-40} g cm^2; $I_y = 386 \times 10^{-40}$ g cm^2; $I_x = 273 \times 10^{-40}$ g cm^2.) The Langevin equation for rototranslation in this case is [2]:

$$\left.\begin{aligned}\dot{\mathbf{J}} &= -\boldsymbol{\gamma}_J\cdot\mathbf{J} - \boldsymbol{\gamma}_{Jv}\cdot\mathbf{v} + \boldsymbol{\Gamma}(t)\\ \dot{\mathbf{v}} &= -\boldsymbol{\gamma}_{vJ}\cdot\mathbf{J} - \boldsymbol{\gamma}_v\cdot\mathbf{v} + \mathbf{F}(t)\end{aligned}\right\} \tag{1}$$

where the friction grand-matrix is described as

$$\boldsymbol{\gamma} = \begin{bmatrix}\boldsymbol{\gamma}_J & \boldsymbol{\gamma}_{Jv}\\ \boldsymbol{\gamma}_{vJ} & \boldsymbol{\gamma}_v\end{bmatrix} \tag{2}$$

The off-diagonal elements of this matrix are measures of the rototranslational interaction. Auto and cross-correlation functions may be calculated from eq. (1) as the inverse Laplace transform of

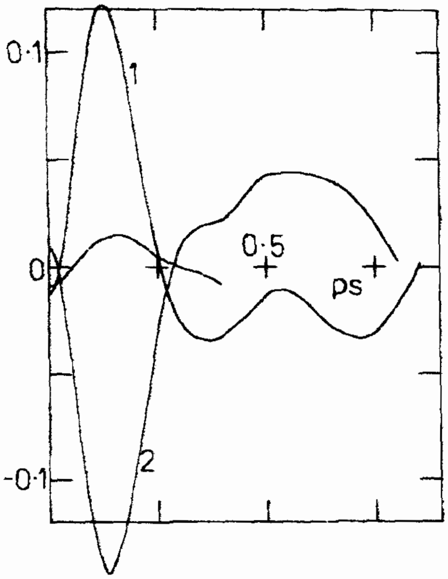

Fig. 2. The effect of a strong external electric field on the characteristics of the cross correlation functions in Fig. 1. (1) $\langle v_y(t)J_x(0)\rangle$ element in the laboratory frame. $\mu E/kT = 38$. (2) As for (1), the $\langle v_x(t)J_y(0)\rangle$ element. ----, As for (1), with no external field.

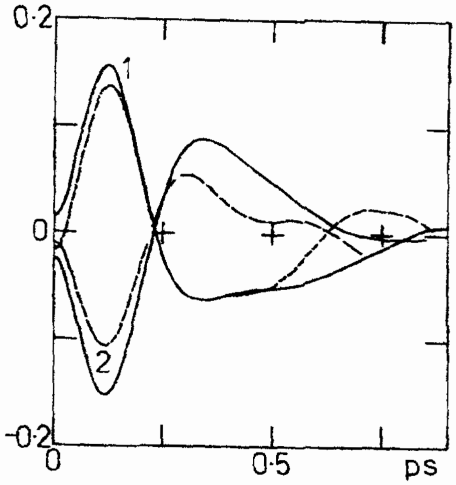

Fig. 3. Dominant cross-correlation elements under a $10.0kT$ field. (1) (y, x) element; ——, Racemic mixture; ----, R enantiomer. (2) As for (1), (x, y) element. Here (x, y, z) is the laboratory frame. The other elements of $\langle \mathbf{v}(t)\mathbf{J}^T(0)\rangle$ exist but are much smaller in magnitude. *Ordinate*: Normalised cross-correlation function.

$$\begin{bmatrix}L_a\langle \mathbf{v}(t)\mathbf{v}^T(0)\rangle & L_a\langle \mathbf{v}(t)\mathbf{J}^T(0)\rangle\\ L_a\langle \mathbf{J}(t)\mathbf{v}^T(0)\rangle & L_a\langle \mathbf{J}(t)\mathbf{J}^T(0)\rangle\end{bmatrix} = \begin{bmatrix}\langle \mathbf{v}(0)\mathbf{v}^T(0)\rangle & \mathbf{0}\\ \mathbf{0} & \langle \mathbf{J}(0)\mathbf{J}^T(0)\rangle\end{bmatrix}[p\mathbf{1} + \boldsymbol{\gamma}]^{-1} \tag{3}$$

In order to account for the fact that we are dealing with left or right handed molecules R or S enantiomers and their racemic mixtures) we have to write each of the elements of $\boldsymbol{\gamma}$ as matrices. The grand matrix $\boldsymbol{\gamma}$ therefore has elements which are themselves matrices. From eq. (3)

$$L_a\langle \mathbf{v}(t)\mathbf{J}^T(0)\rangle = \boldsymbol{\gamma}_{Jv}\langle \mathbf{v}(0)\mathbf{v}^T(0)\rangle\,\mathbf{D}^{-1} \tag{4}$$

$$L_a\langle \mathbf{J}(t)\mathbf{v}^T(0)\rangle = \boldsymbol{\gamma}_{vJ}\langle \mathbf{J}(0)\mathbf{J}^T(0)\rangle\,\mathbf{D}^{-1} \tag{5}$$

where

$$\mathbf{D} = (\mathbf{1}p + \boldsymbol{\gamma}_v)(\mathbf{1}p + \boldsymbol{\gamma}_J) - \boldsymbol{\gamma}_{Jv}\boldsymbol{\gamma}_{vJ}$$

and $\mathbf{1}$ is the unit matrix. Note that $\boldsymbol{\gamma}_{Jv}$ and $\boldsymbol{\gamma}_{vJ}$ must be matrices in eq. (4) and (5) in order to account for the computer simulation results qualitatively, let alone quantitatively. This is because each element of $\langle \mathbf{v}(t)\mathbf{J}^T(0)\rangle$ from the computer simulation has its own individual characteristics such as time dependence and normalised intensity (Figs. 1 and 2). These characteristics depend on the details of the intermolecular potential energy and individual atoms making up the diffusing molecule. We need detailed independent information on the nature of before the rototranslational Langevin equation (1) can be used to interpret experimental spectra. As much supplementary information as needed can be supplied by computer simulation, given the assumptions inherent in the technique [2, 3], such as pairwise additivity and periodic boundary conditions. A detailed account of the nature of $\boldsymbol{\gamma}$ and its 36 elemental correlation functions (e.g., those in Fig. 3) will be published elsehwere. In this letter we arrive at the following first approximation to the solution of eq. (1) using a combination of numerical and analytical methods.

(i) To a first approximation $\boldsymbol{\gamma}_v = \gamma_v\mathbf{1}$; $\boldsymbol{\gamma}_J = \gamma_J\mathbf{1}$ where $\mathbf{1}$ is the unit matrix.

(ii) The first results of our investigation show that all the elements of $\boldsymbol{\gamma}_{vJ}$ and $\boldsymbol{\gamma}_{Jv}$ exist, in principle, in the laboratory frame [8]. The dominant elements however are those illustrated in Fig. 2. The analytical expressions for $\langle \mathbf{v}(t)\mathbf{J}^T(0)\rangle$ or $\langle \mathbf{J}(t)\mathbf{v}^T(0)\rangle$ from eqs. (4) or (5) involve an inverse Laplace transformation as described in the appendix. This comparison is illustrated briefly in Fig. 1.

Note to end with that the analytical expressions for the autocorrelation functions $\langle \mathbf{v}(t)\mathbf{v}^T(0)\rangle$ and $\langle \mathbf{J}(t)\mathbf{J}^T(0)\rangle$ from eqs. (3)–(5) contain in general all the cross elements of $\boldsymbol{\gamma}_{vJ}$ and $\boldsymbol{\gamma}_{Jv}$. This implies that with the aid of computer simulation a variety of spectral methods can be used to investigate the nature of the phenomenological parameters $\boldsymbol{\gamma}_{vJ}$ and $\boldsymbol{\gamma}_{Jv}$.

Acknowledgement

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Appendix

The matrices $\boldsymbol{\gamma}_{vJ}$ and $\boldsymbol{\gamma}_{Jv}$ for fluorochloroacetonitrile have dominant elements according to the results illustrated in Figs. 1 and 2. In the first approximation they may be written therefore as

$$\boldsymbol{\gamma}_{vJ} \doteqdot \begin{bmatrix} 0 & \gamma_{xy}^{Jv} & 0 \\ \gamma_{yx}^{Jv} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\boldsymbol{\gamma}_{Jv} \doteqdot \begin{bmatrix} 0 & \gamma_{xy}^{vJ} & 0 \\ \gamma_{yx}^{vJ} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \qquad \text{(A1)}$$

With these approximations, together with those for $\boldsymbol{\gamma}_v$ and $\boldsymbol{\gamma}_J$ made in the text we arrive at the following first approximations to the cross-correlation elements:

$$L_a\langle v_x(t)J_y(0)\rangle = \gamma_{xy}^{Jv}\,[(p+\gamma_v)(p+\gamma_J)-\gamma_{xy}^{Jv}\gamma_{xy}^{vJ}]^{-1} \qquad \text{(A2)}$$

$$L_a\langle v_y(t)J_x(0)\rangle = \gamma_{yx}^{Jv}\,[(p+\gamma_v)(p+\gamma_J)-\gamma_{xy}^{Jv}\gamma_{xy}^{vJ}]^{-1} \qquad \text{(A3)}$$

The computer simulation implies that:

$$\gamma_{xy}^{Jv} = -\gamma_{yx}^{Jv}$$

within the noise illustrated in Fig. 1.

The inverse Laplace transform of eqs. (A2) (or A3) may be obtained as

$$\begin{aligned}\langle v_x(t)J_y(0)\rangle &= \frac{\langle v^2\rangle\gamma_{xy}^{Jv}}{(c-b^2)^{1/2}}\,e^{-bt}\sin[(c-b^2)^{1/2}t] \qquad c > b^2 \\ &= \langle v^2\rangle\gamma_{xy}^{Jv}\,e^{-bt}\sinh[(b^2-c)^{1/2}t] \qquad b^2 < c \qquad \text{(A4)}\end{aligned}$$

where $b = 2(\gamma_v + \gamma_J)$; $c = \gamma_v\gamma_J - \gamma_{xy}^{Jv}\gamma_{xy}^{vJ}$. Assuming that $\gamma_{xy}^{Jv} = \gamma_{xy}^{vJ}$ and taking a numerical value for $\langle v^2\rangle$ from the computer simulation it is possible to express $\langle v_x(t)J_y(0)\rangle$ or $\langle v_y(t)J_x(0)\rangle$ in terms of three parameters γ_v, γ_J, and γ_{xy}^{Jv}. Rough estimates of γ_v and γ_J may be obtained from the computer simulations of $\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle$ and $\langle \mathbf{J}(t)\cdot\mathbf{J}(0)\rangle$ by decoupling the Langevin equations (1), i.e., by neglecting completely, in the first approximation, *r/t* coupling. This decoupling procedure implies from eq. (1)

$$\langle \mathbf{v}(t)\cdot\mathbf{v}(0)\rangle = \langle v^2\rangle e^{-\gamma_v t}$$

$$\langle \mathbf{J}(t)\cdot\mathbf{J}(0)\rangle = \langle J^2\rangle e^{-\gamma_J t} \qquad \text{(A5)}$$

providing a very rough numerical fix for γ_v and γ_J. Computer simulated a.c.f.'s [2, 3] are very much more complicated than the simple exponential of eq. (A5). They have negative overshoots and inclusion of *r/t* coupling automatically accounts for these, even in the Markovian approximation of eq. (1). Having fixed γ_v and γ_J in this way, an estimate γ_{xy}^{Jv} may be obtained by differentiating eq. (A4) for its maximum value ($0 < t < \infty$). In this way the free parameters in the analytical theory may be determined. The analytical and computational results are matched in Fig. 1. The analysis may be extended to racemic mixtures, and to investigate chiral discrimination in a molecular dynamical context.

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