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Molecular dynamics of the bromochlorofluoromethanes in a right circularly polarized field

M.W. Evans*, **G.C. Lie**, and **E. Clementi**
IBM Corporation, Data Systems Division, Department 48B/MS 428,
Neighborhood Road, Kingston, NY 12401, USA

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The liquid state molecular dynamics of the chiral bromochloro-fluoromethanes have been investigated with computer simulation under the influence of an external right circularly polarized field of force. The field promotes the existence direct in the laboratory frame of time cross correlation functions which have a different symmetry for the enantiomer and racemic mixture. This may be used to measure cross correlation functions indirectly through the experimental observation of laboratory frame differences between the dynamical properties of the enantiomer and racemic mixture in a right circularly polarized field.

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I. Introduction

The molecular dynamics of one enantiomer of a chiral molecule are not identical in all respects with those of its mirror image. A difference has been found [1–3] using computer simulation in the frame of the principal molecular moments of inertia (1, 2, 3). One off-diagonal element of the cross-correlation matrix

$$C_1^{ij}(t)=\frac{\langle v_i(t)\,\omega_j(0)\rangle}{\langle v_i^2\rangle^{1/2}\langle\omega_j^2\rangle^{1/2}}$$

is the mirror image in time dependence of its equivalent in the other enantiomer of the chiral molecule. In the racemic mixture the element vanishes for all t.

Subsequent to this work many other new cross correlation functions have been identified [4–6] in the moving frame (1, 2, 3), and in the laboratory frame (x, y, z), but only the off-diagonal element referred to above switches sign between enantiomers, and then only in frame (1, 2, 3). In order to devise an experimental method which will give direct or indirect evidence on the difference between the dynamics of two enantiomers this paper attempts to use the special symmetry properties of a right circularly polarized external field to create cross-correlation functions in the laboratory frame of reference with different symmetry dependence on the field. The measurement of the properties of the enantiomers and racemic mixture in the presence and the absence of the external field might therefore lead to a method of providing indirect experimental information on dynamical cross-correlations. Circularly polarized fields applied to chiral media are also used in the well established [7] technique of circular dichroism, which could be utilized in combination with molecular dynamics to provide information on cross-correlation functions.

II. Molecular dynamics simulation methods

The algorithms is an adaptation of the standard constant volume computer simulation method to incorporate the effect of a right circularly polarized field of the type:

$$E_x=0;\quad E_y=E_0\cos\omega t;\quad E_z=E_0\sin\omega t;$$

on the molecular dynamics. The field is included in the forces loop of the algorithm as an extra torque of the type:

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* Permanent address: Department of Physics, University College of Swansea, Singleton Park, Swansea SA2 8PP, Wales (UK), and Visiting Academic, Department of Microelectronics & Electrical Engineering, Trinity College, Dublin 2, Republic of Ireland

$$\mathbf{T}_q = -\mu \times \mathbf{E}$$

where μ is the molecular dipole moment. The technique of temperature rescaling is then used to bring the system back to the input rotational and translational temperatures in the presence of the field. The reestablished equilibrium is then known as field-on equilibrium, which is reached at a higher internal potential energy than field-off equilibrium, although the kinetic energies in both cases are the same. The molecular dynamics of the sample in the presence of the field are then simulated with a model for the effective pair potential consisting of a five by five site-site product with partial charges as fully described elsewhere [8]. At field on equilibrium the system is then investigated for its "dynamical symmetry" through the use of time correlation functions in the laboratory frame of reference (x, y, z) and in the moving frame (1, 2, 3) defined by the three principal molecular moments of inertia. A comparison of these time correlation functions for the enantiomer and racemic mixture is then made to establish the different symmetry patterns for enantiomer and racemic mixture. Dynamical equilibrium is established in the presence of the field over 6000 time steps of 5.0 fs each. The time correlation functions are then computed over this total time span with running time averages using an efficient algorithm which eliminates data transfer from big disk to core.

The intermolecular pair potential used in the simulation was a five by five Lennard-Jones atom-atom potential composed of site-site parameters as follows:

$\varepsilon/k(\mathrm{H-H}) = 10.0\,\mathrm{K}$; $\sigma(\mathrm{H-H}) = 2.8\,\mathrm{A}$;
$\varepsilon/k(\mathrm{Cl-Cl}) = 158\,\mathrm{K}$; $\sigma(\mathrm{Cl-Cl}) = 3.6\,\mathrm{A}$;
$\varepsilon/k(\mathrm{F-F}) = 54.9\,\mathrm{K}$; $\sigma(\mathrm{F-F}) = 2.7\,\mathrm{A}$;
$\varepsilon/k(\mathrm{Br-Br}) = 218.0\,\mathrm{K}$; $\sigma(\mathrm{Br-Br}) = 3.9\,\mathrm{A}$;
$\varepsilon/k(\mathrm{C-C}) = 35.8\,\mathrm{K}$; $\sigma(\mathrm{C-C}) = 3.4\,\mathrm{A}$;

Additionally the electrostatic interactions between two molecules were modelled with partial electronic charge of: −0.16 for Br; 0.335 for C; 0.225 for H; −0.18 for Cl; and −0.22 for F.

III. Results and discussion

a) Laboratory frame of reference (x, y, z)

In general the effect of the external field is to make possible the existence in the laboratory frame of off diagonal elements of time correlation tensors of the type

$$\langle \mathbf{A}(t)\,\mathbf{A}^T(0)\rangle = \begin{bmatrix} \langle A_x(t)\,A_x(0)\rangle & \langle A_y(t)\,A_x(0)\rangle & \langle A_z(t)\,A_x(0)\rangle \\ \langle A_x(t)\,A_y(0)\rangle & \langle A_y(t)\,A_y(0)\rangle & \langle A_z(t)\,A_y(0)\rangle \\ \langle A_x(t)\,A_z(0)\rangle & \langle A_y(t)\,A_z(0)\rangle & \langle A_z(t)\,A_z(0)\rangle \end{bmatrix}$$

where A is a dynamical vector quantity on the molecular scale. In this section the properties of these tensors are given at field on equilibrium for different vectors of the S enantiomer and the racemic mixture. It is observed that certain off-diagonal elements of the correlation tensors have distinctly different time

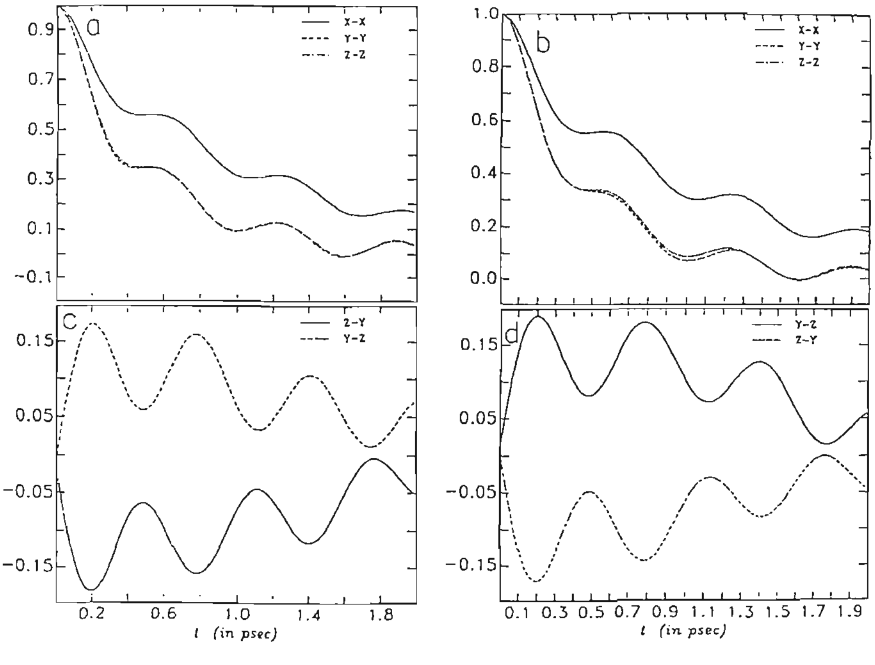

Fig. 1a–d. Field induced anisotropy in the laboratory frame orientational correlation tensor, $\langle \mu_i(t)\,\mu_j(t)\rangle_{x,y,z} / \langle \mu_i^2\rangle^{1/2}\langle \mu_j^2\rangle^{1/2}$, of CHBrClF: **a** diagonal elements for the s enantiomer; **b** diagonal elements for the racemic mixture; **c** off-diagonal elements (z, y) and (y, z) for the s enantiomer; **d** off-diagonal elements (z, y) and (y, z) for the racemic mixture

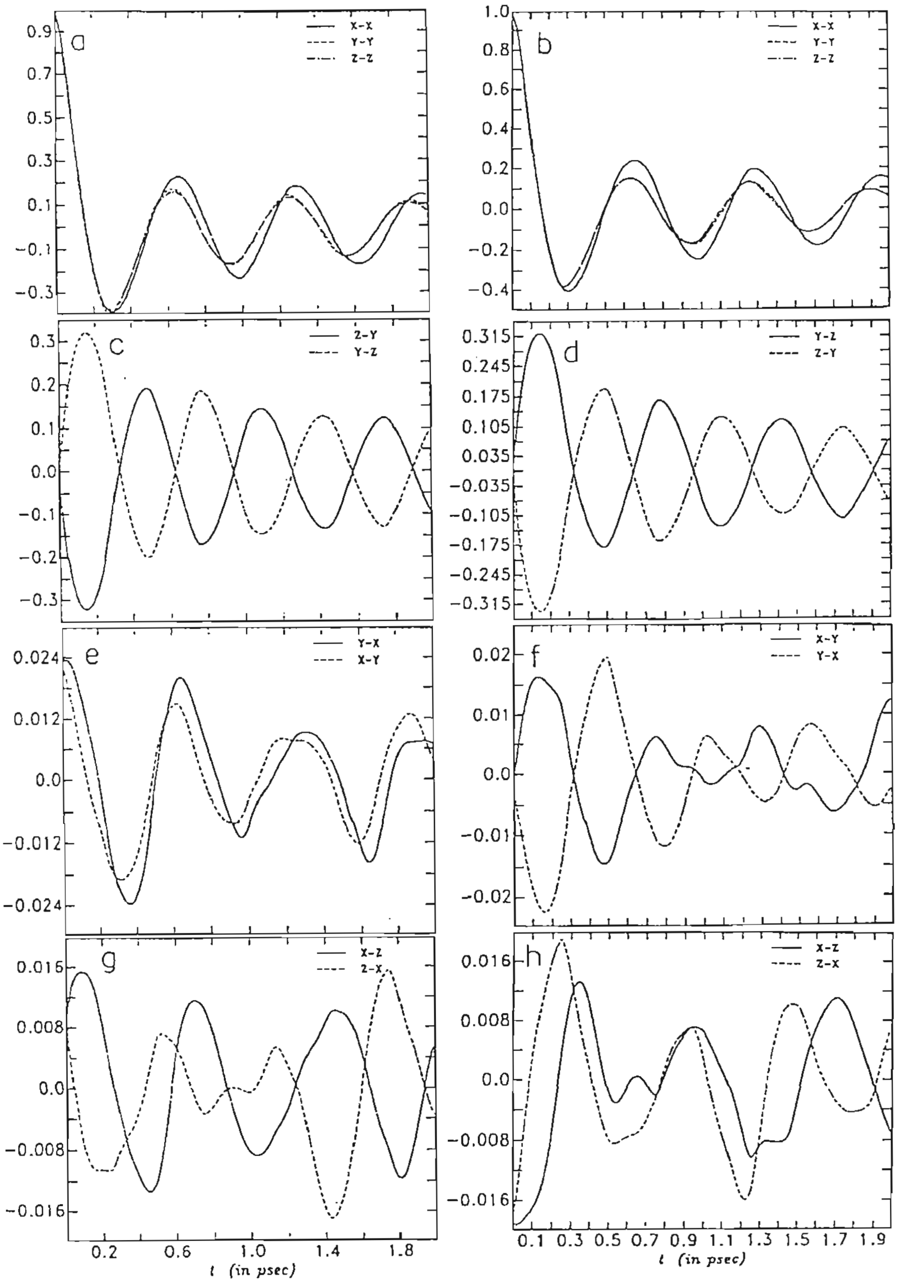

Fig. 2a–h. Field induced anisotropy in the laboratory frame rotational velocity correlation tensor, $\langle \dot{\mu}_i(t)\,\dot{\mu}_j(t)\rangle_{x,y,z}/\langle \dot{\mu}_i^2\rangle^{1/2}\langle \dot{\mu}_j^2\rangle^{1/2}$, of CHBrClF: **a** diagonal elements for the *s* enantiomer; **b** diagonal elements for the racemic mixture; **c** off-diagonal elements (*z*, *y*) and (*y*, *z*) for the *s* enantiomer; **d** off-diagonal elements (*z*, *y*) and (*y*, *z*) for the racemic mixture; **e** off-diagonal elements (*x*, *y*) and (*y*, *x*) for the *s* enantiomer; **f** off-diagonal elements (*x*, *y*) and (*y*, *x*) for the racemic mixture; **g** off-diagonal elements (*z*, *x*) and (*x*, *z*) for the *s* enantiomer; **h** off-diagonal elements (*z*, *x*) and (*x*, *z*) for the racemic mixture

dependences in the enantiomer and mixture direct in the laboratory frame itself. The appearance of off-diagonal elements direct in the laboratory frame is accompanied by a measurable birefringence in the orientational and rotational velocity a.c.f.'s, (Figs. 1 and 2), which could be used experimentally to measure the off-diagonal elements with the interpretative power of computer simulation.

b) Orientational time correlation tensor

The overall symmetry effect of the field in this case is

$$\mathbf{C}_2(t)=\begin{bmatrix} + & 0 & 0\\ 0 & + & 0\\ 0 & 0 & + \end{bmatrix}_{(x,y,z)} \to \begin{bmatrix} + & \delta & \delta\\ \delta & + & +\\ \delta & - & + \end{bmatrix}_{(x,y,z)}$$

i.e. the (*z*, *y*) and (*y*, *z*) off diagonal elements appear as mirror images (Fig. 1b), and the time dependence of the (*x*, *x*) element becomes different from those of the (*y*, *y*) and (*z*, *z*) diagonal elements of the matrix. The Fourier transform of the orientational autocorrelation function is related to the dielectric loss through the Green/Kubo/Cole equations [9–11] and the results of Fig. 1 therefore imply that the dielectric loss in the x axis is different from that in the y and z axes both for the enantiomer and the racemic mixture at field-on equilibrium. The Fourier transform of the off-diagonal elements is also a spectrum, by the fundamental theorem of Fourier transformation. This spectrum would be related to a dielectric loss and the off-diagonal elements of the complete correlation tensor might therefore be expected to contribute to the observable dielectric loss in a right circularly polarized laser field. There seem to be no Green/Kubo relations available for this type of cross correlation function, which might also be expected to play a role in the well known phenomenon of circular dichroism.

For $C_2(t)$ the off diagonal structure is dominated by the (z, y) and (y, z) elements, these being mutually perpendicular to the x axis of the applied circularly polarized field. The other four off diagonal elements in this case vanish in the noise of the simulation, and are therefore marked with a delta function as above. For this reason there is no overall discernible symmetry change between enantiomer and racemic mixture for the orientational correlation tensor. The symmetry in both cases is therefore

$$\begin{bmatrix} + & 0 & 0 \\ 0 & + & - \\ 0 & - & + \end{bmatrix}_{(x,y,z)} \rightarrow \begin{bmatrix} + & \delta & \delta \\ \delta & + & + \\ \delta & - & + \end{bmatrix}_{(x,y,z)} .$$

c) Rotational velocity correlation tensor

The symmetry of the cross correlation tensor is similar to that of the orientational tensor just described, and the elements are illustrated in Fig. 2. However, in this case there is an interesting difference between the off-diagonal elements for the enantiomer and the racemic mixture in the (x, y) and (y, x) and (x, z) and (z, x) diagonals. This is therefore a laboratory frame difference induced by the application of the right circularly polarized laser field.

The effect of the field applied to the enantiomer is

$$\mathbf{C}_3(t) = \begin{bmatrix} + & 0 & 0 \\ 0 & + & 0 \\ 0 & 0 & + \end{bmatrix}_{(x,y,z,R)} \rightarrow \begin{bmatrix} + & - & + \\ - & + & + \\ - & - & + \end{bmatrix}_{(x,y,R)}$$

and for the racemic mixture

$$\mathbf{C}_3(t) = \begin{bmatrix} + & 0 & 0 \\ 0 & + & 0 \\ 0 & 0 & + \end{bmatrix}_{(x,y,z,RS)} \rightarrow \begin{bmatrix} + & + & + \\ - & + & + \\ + & - & + \end{bmatrix}_{(x,y,z,RS)}$$

i.e., there is a different symmetry in the field-on c.c.f.'s for the two cases in four of the off-diagonal elements. This is attributable to the different response of enantiomer and mixture to the aplied right (or left) circularly polarized field and is a dynamical phenomenon connected with the appearance in the laboratory frame of circular dichroism and the birefringence clearly visible in fig. 2.

d) Angular velocity autocorrelation function

In this case the symmetry of the four off-diagonal elements is opposite to that for the rotational velocity a.c.f. and the effect of the field on the enantiomer is

$$\mathbf{C}_4(t) = \begin{bmatrix} + & 0 & 0 \\ 0 & + & 0 \\ 0 & 0 & + \end{bmatrix}_{(x,y,z,R)} \rightarrow \begin{bmatrix} + & + & - \\ + & + & + \\ + & - & + \end{bmatrix}_{(x,y,z,R)}$$

in contrast to that on the racemic mixture

$$\begin{bmatrix} + & 0 & 0 \\ 0 & + & - \\ 0 & - & + \end{bmatrix}_{(x,y,z,RS)} \rightarrow \begin{bmatrix} + & \delta & \delta \\ \delta & + & + \\ \delta & - & + \end{bmatrix}_{(x,y,z,RS)} .$$

There is therefore a direct laboratory frame difference observable between the time dependent properties of four off diagonal elements of the angular velocity cross correlation tensor for enantiomer and racemic mixture. This is again related to the dynamics of circular dichroism.

e) Center of mass velocity

In this case there is no pronounced anisotropy in the time dependence of the diagonal elements, and the off-diagonals are dominated by the (y, z) and (z, y) elements. The effect of the right circularly polarized field on the emantiomer is therefore:

$$\mathbf{C}_5(t) = \begin{bmatrix} + & 0 & 0 \\ 0 & + & 0 \\ 0 & 0 & + \end{bmatrix}_{(x,y,z,R)} \rightarrow \begin{bmatrix} + & \delta & \delta \\ \delta & + & - \\ \delta & + & + \end{bmatrix}_{(x,y,z,R)}$$

and is the same on the racemic mixture. It is interesting in this context to note that the field induces no elements of the simple cross correlation matrix

$$\mathbf{C}_6^{ij}(t) = \frac{\langle v_i(t)\,\omega_j(0)\rangle}{\langle v_i^2\rangle^{1/2}\langle \omega_j^2\rangle^{1/2}}$$

direct in the laboratory frame (x, y, z). This is in contrast to the effect of a simple z axis uniaxial electric field, which induces the appearance of the (x, y) and (y, x) elements of the tensor $C_6(t)$. The simple electric field also induces anisotropy in the center of mass linear velocity correlation tensor, while the right circularly polarized field used here does not seem to do so. Therefore this may be indicative of the fact that anisotropy in the diagonal elements of the tensor is linked to the off diagonal elements of $C_6(t)$. It seems clear from this work that anisotropy in the diagonal elements of the orientation, rotational velocity, and angular velocity tensors is linked to the appearance of off diagonal elements caused by the circularly polarized field.

f) Cross correlation tensor

Recently, a new class of cross correlation tensors has been reported [14] which exists direct in the laboratory frame of reference and whose members involve simultaneously angular variables, such as molecular angular velocity or torque, and linear variables such as force or linear velocity. The significance of these "exotic" time correlation functions is that they indicate the complete inapplicability of classical diffusion theory [15] to molecular dynamics in the liquid state of matter if the theory is based on concepts of "rotational" or "translational" diffusion. The "exotic" c.c.f.'s seem complicated in structure but are determined by well-defined symmetry rules [16] on the existence of time correlation functions in the laboratory frame of reference. Cross correlation functions less complicated in structure, such as the simple C_6 vanish for all t in isotropic media (even chiral media) because of the different parity reversal properties of v and ω in the laboratory frame of reference. One of the least "exotic" cross-correlation functions to survive the symmetry constraints is

$$\mathbf{C}_7^{ij}(t)=\frac{\langle\{\mathbf{v}(t)\times\boldsymbol{\omega}(t)\}_i\rangle\langle\{\mathbf{T}_q(0)\times\mathbf{v}(0)\}_j\rangle}{\langle(\mathbf{v}(0)\times\boldsymbol{\omega}(0))_i^2\rangle^{1/2}\langle(\mathbf{T}_q(0)\times\mathbf{v}(0))_j^2\rangle^{1/2}}$$

where T_q is the net torque on the molecule at time t. The net effect of the right circularly polarized field on this cross correlation tensor is, for the enantiomer

$$\mathbf{C}_7(t)=\begin{bmatrix}+ & 0 & 0\\ 0 & + & 0\\ 0 & 0 & +\end{bmatrix}_{(x,y,z,R)}\rightarrow\begin{bmatrix}+ & \delta & \delta\\ \delta & + & -\\ \delta & + & +\end{bmatrix}_{(x,y,z,R)}$$

and the same for the racemic mixture.

Therefore the off diagonal elements (y, z) and (z, y) of $C_7(t)$ appear direct in the laboratory frame again in the presence of the electric field component of the right circularly polarized laser field. (The complete analysis can be repeated, of course, for the interaction of the magnetic field component [13] with the molecular magnetic dipole moment.)

IV. Field strength dependence

Some exploratory work was completed on the dependence of the results given in this paper on the strength of the applied field for a given frequency, ω. The birefringence noted in Fig. 1 is approximately proportional to field strength, and this implies that the amplitude of the off-diagonal elements in the cross correlation tensors are also dependent in some way on the strength of the applied field.

More intricate is the dependence of the birefringence and cross correlation functions on the frequency of the circularly polarised field. This is not a straightforward proportionality and needs a considerable amount of further work in order to determine the precise consequences of varying the frequency.

V. Effects due to higher multipoles: quantum effects

The effects discussed above are all first order effects of the electromagnetic field interacting directly with the molecular electric dipole moment in the laboratory frame (x, y, z). The "transverse" off-diagonal elements reported in this section might well play a role in the theory of dynamic light scattering [17] from a circularly polarized laser field, although this is usually second order in the field intensity E, interaction occurring via the molecular polarizability. The intermolecular pair potential used in this work includes in one sense all higher multipoles in the effective pair potential through the use of point charges. The computation is however restricted to the consideration of pair interactions and polarisability effects cannot be easily considered without introducing multi-body effects and charge distributions which are dependent on molecular geometry, thus undermining the site-site concept of the intermolecular potential. The successful treatment of polarisability effects of nature would also need a quantum mechanical approach to the problem of molecular dynamics, particularly in the context of chirality. These quantum effects cannot be ignored but require an advance in the state of the art of molecular dynamics computer simulation. In the context of circular dichroism, for example, this type of work would be expected to reveal the transitions involved in the field induced circular dichroism. A discussion of quantum transitions is obviously not possible with a purely classical dynamical algorithm as used in this paper. These are used here to indicate the types of new phenomena that become available in chiral media treated with a circularly polarised field.

The results of this section show that certain laboratory frame differences in the dynamics of liquid state enantiomers and racemic mixtures are expected in the off-diagonal elements of certain cross correlation tensors, cited above. The observation of dielectric and far infrared spectra under optimum conditions might lead to a method of observing the time dependence of these cross correlation functions experimentally, with the interpretative help of computer simulation.

a) Moving frame of reference (1, 2, 3)

The moving frame of reference is defined by the frame of the molecular principal moments of inertia (1, 2, 3). In this frame the simple cross correlation function $C_1(t)$ exists for $t > 0$ and is different in time dependence for enantiomer and racemic mixture. In the presence of the right circularly polarized field the (3, 2) and (2, 3) elements in each case are not symmetric in time dependence, but otherwise are similar for enantiomer and racemic mixture. Substantial differences begin to appear between enantiomer and racemic mixture in the (1, 3) and (3, 1) elements, for which the (1, 3) element attains twice the normalized value at $t = 0$ for the enantiomer compared with the mixture. The main overall effect of the field on these moving frame c.c.f. elements is to remove the well known symmetry difference at field off equilibrium mentioned in the introduction to this paper, and reported elsewhere [1]. These effects are illustrated in Fig. 3.

In the moving frame of reference it has been observed in this simulation that the right circularly polarized field has no effect on the overall symmetry of cross correlation functions. In contrast to the laboratory frame of reference no new off diagonal elements appear in frame (1, 2, 3) in the presence of the field. The field has a small effect on the already existing diagonal elements, which become different in time dependence for the enantiomer and the racemic mixture. It is therefore advantageous, in conclusion, to work

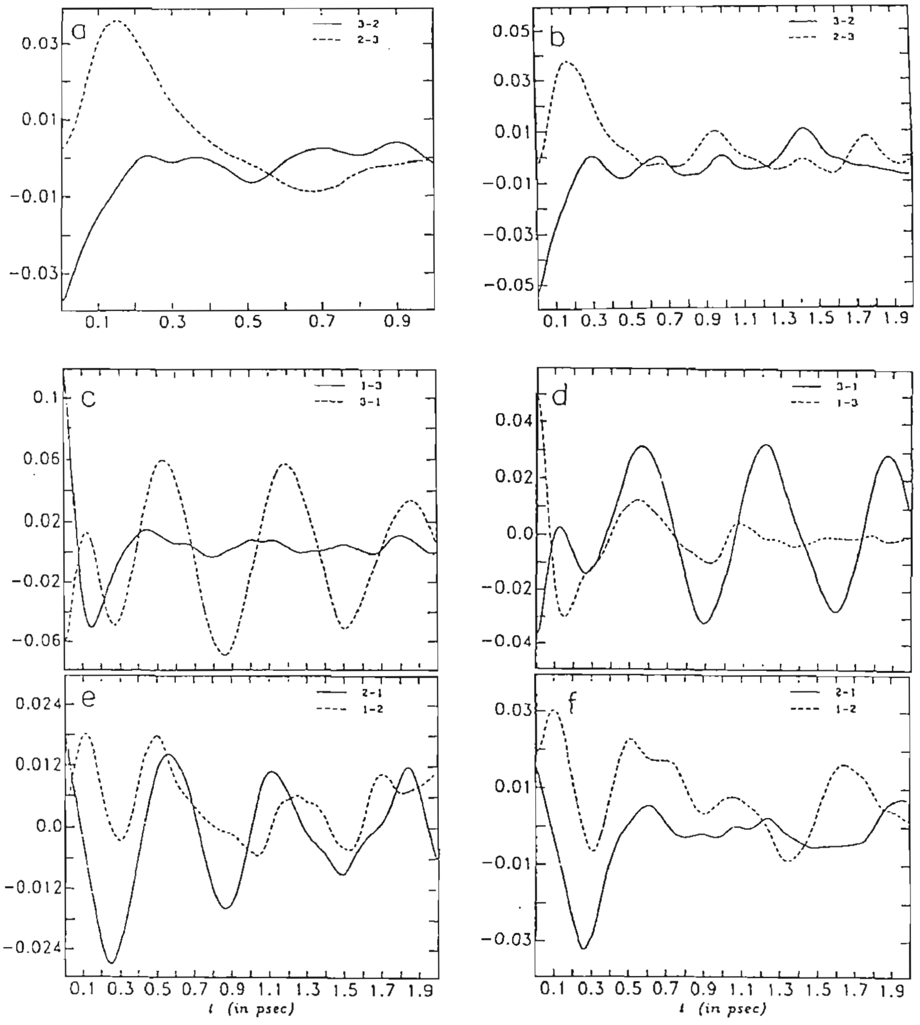

Fig. 3a–f. Moving frame off-diagonal elements of the cross correlation tensor C_1, $\langle v_i(t)\,\omega_j(t)\rangle_{1,2,3}/\langle v_i^2\rangle^{1/2}\langle\omega_j^2\rangle^{1/2}$. **a**, **c**, and **e** are for the *s* enantiomer;. whereas **b**, **d**, and **f** are for the racemic mixture

in the laboratory frame when simulating the effect of external fields on the dynamics of chiral molecules, and this of course allows direct comparison with and implementation of experimental data on the same liquid system.

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