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Cross correlation between rotation and translation in spherical tops

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The nature of statistical cross correlation between center-of-mass molecular translation and rotation of the same molecule is investigated for carbon tetrachloride liquid by molecular dynamics computer simulation. It is shown that rotation and translation in this T_d-symmetry spherical top are indeed correlated through the existence of the molecular Coriolis, centripetal, and nonuniform accelerations of the rigid molecule, thus invalidating the Debye theory of rotational diffusion under the conditions for which it was originally proposed. The *simple* cross-correlation function

$$\langle \omega(t)\mathbf{v}^T(0)\rangle/[\langle \omega^2(0)\rangle^{1/2}\langle v^2(0)\rangle^{1/2}]$$

vanishes, however, for all t and in *all* frames of reference for the spherical top diffusing in three dimensions in a bath of other spherical tops.

I. INTRODUCTION

It is now well established[1-5] that the center-of-mass translational motion of a diffusing molecule is dependent statistically on its own rotation, and that the effect of translation should be introduced into the theory of rotational diffusion[6,7] in asymmetric and also in spherical tops. These results have been obtained from computer simulation and might catalyze some further work into extending the theory of molecular diffusion to involve the new correlations now becoming available from simulation. This paper therefore explores the nature of statistical cross correlation between rotation and translation in the T_d spherical top carbon tetrachloride using molecular-dynamics computer simulation.[8] The various cross correlations now known through the new rotating-frame theory of molecular diffusion are evaluated using this numerical technique at an ambient temperature of about 300 K and a pressure of 1 b. The numerical results show clearly that such cross correlations do in fact exist, thus proving the need to extend basic theory, such as the great theory of rotational diffusion due to Debye.[6,7] At present, computer simulation appears to be producing results that the analytical methods can only follow, showing the power of the simulation technique. The methods currently available[9,10] for extending the Debye theory through the use of memory functions and matrix-continued fractions,[10] for example, still leave open the formidable problem of statistical cross correlation for molecular diffusion in three dimensions.

II. COMPUTER-SIMULATION METHODS

The classical equations of rotational and translational motion for 108 interacting CCl_4 molecules were investigated with the algorithm TETRA whose details have been made available elsewhere in the literature.[11] This algorithm is valid for three-dimensional diffusion in the asymmetric top and is adaptable straightforwardly for the spherical top. The potential energy was assumed to be pairwise additive as usual, and was made up of atom-atom Lennard-Jones terms as follows:

$$\sigma(\text{C-C})=3.20\ \text{Å},\quad \epsilon(\text{C-C})/k=51.0K\ ;$$

$$\sigma(\text{Cl-Cl})=3.35\ \text{Å},\quad \epsilon(\text{Cl-Cl})/k=175.0K\ ;$$

$$\sigma(\text{C-Cl})=\tfrac{1}{2}[\sigma(\text{C-C})+\sigma(\text{Cl-Cl})]\ ;$$

$$\epsilon(\text{C-Cl})/k=\left[\frac{\epsilon(\text{C-C})}{k}\frac{\epsilon(\text{Cl-Cl})}{k}\right]^{1/2}.$$

A time step of 5.0×10^{-15} s was used to construct the dynamical trajectory of each molecule over a span of about 1000 of these. After equilibration, these were dumped on to magnetic tape every two time steps and running-time averages were used to construct autocorrelations and cross correlations of time for the molecular center-of-mass linear velocity and angular momentum and velocity. These were computed in two frames of reference, the laboratory frame (x,y,z) and the moving frame (1,2,3) of the principal molecular moments of inertia. The definition of any vector $\mathbf{A}$ in the latter frame is

$$\begin{aligned}A_1&=A_xe_{1x}+A_ye_{1y}+A_ze_{1z}\ ,\\ A_2&=A_xe_{2x}+A_ye_{2y}+A_ze_{2z}\ ,\\ A_3&=A_xe_{3x}+A_ye_{3y}+A_ze_{3z}\ ,\end{aligned}\qquad(1)$$

where $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ are unit vectors in the principal moment of inertia axes. Therefore the center-of-mass position vector $\mathbf{r}$, for example, would be defined by Eqs. (1) in frame (1,2,3). The new rotating-frame theory of molecular diffusion involves $\mathbf{r}$ in a range of new cross correlations in this frame, and these are explored for carbon tetrachloride in this work.

III. RESULTS AND DISCUSSION

Previous work[1,2] with the rotating-frame theory of rotation and/or translational diffusion in the asymmetric top has uncovered the existence of several new types of cross-correlation and autocorrelation functions involving simultaneously both types of motion. The autocorrelation functions (acf's) are the following:

(i) the acf of the Coriolis acceleration is $2\boldsymbol{\omega}\times\mathbf{v}$;

(ii) the acf of the centripetal acceleration is $\boldsymbol{\omega}\times(\boldsymbol{\omega}\times\mathbf{r})$;

(iii) the acf of the nonuniform acceleration is $\dot{\boldsymbol{\omega}}\times\mathbf{r}$.

These are illustrated for CCl_4 in Fig. 1 both in the laboratory frame (x,y,z) and in the moving frame (1,2,3). The vectors (i)—(iii) are accelerations which involve the rotational and translational motion of the molecule simultaneously, and therefore find no place in the simple theories of rotational diffusion,[7] where the center-of-mass linear velocity $\mathbf{v}$ and the position vector $\mathbf{r}$ are undefined. Similarly, theories based on linear diffusion leave the angular velocity $\boldsymbol{\omega}$ out of consideration. The new rotating-frame theory of diffusion[1,2] involves both types of motion, but there seems to be no contemporary method of solution apart from analogue-circuit simulation.[12–15] This is work in progress.[16] The existence of the acf's of these accelerations is in itself sufficient to show that computer simulation is capable of producing more information than both the analytical theory and the various experimental probes now available.[17,18]

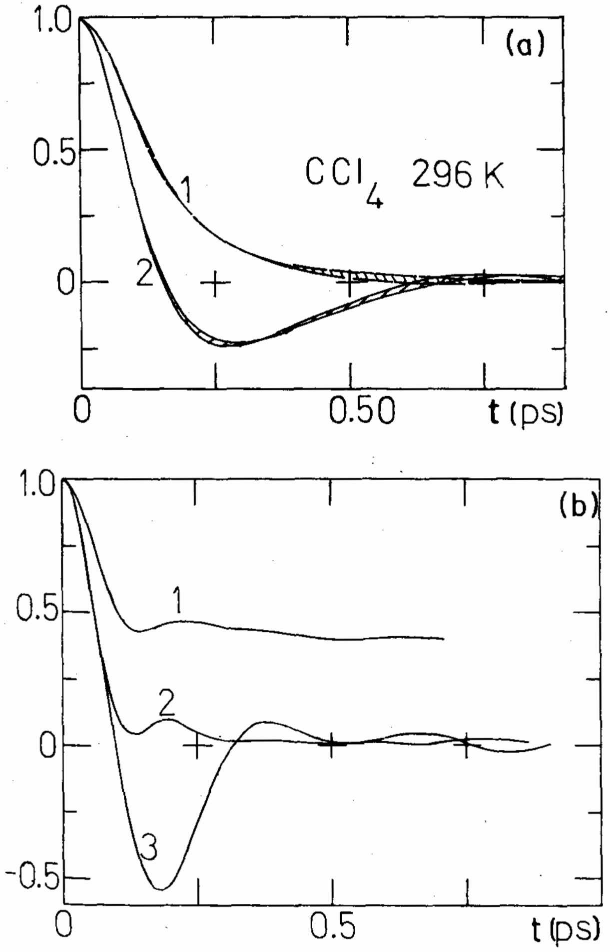

FIG. 1. (a) Autocorrelation functions for liquid CCl_4 at 296 K. Curve 1, the acf of the Coriolis force in the moving (1,2,3) and laboratory (x,y,z) frames of reference; curve 2, the acf of the nonuniform force. (b) Same as in (a) at 100 K. Curve 1, the acf of the Coriolis force; curve 2, the acf of the centripetal force; curve 3, the acf of the nonuniform force in frame (1,2,3).

IV. CROSS-CORRELATION FUNCTIONS

Many hundreds of new types of cross-correlation functions (ccf) have recently been reported[1,2] for the CH_2Cl_2 molecule modeled with a simple 3×3 site-site potential. Of the many possibilities available from the rotating-frame theory it turns out that only a few exist. Therefore the rules governing cross correlations between rotation and translation are highly selective in nature. In this section we report the existence of three of these types for liquid carbon tetrachloride in the moving frame of reference. This provides further evidence that the rotational and translational motions even of a spherical top molecule are correlated as intricately as those of the asymmetric top. For example, Figs. 2—4 illustrate for comparison the relevant (diagonal) moving-frame elements of ccf's such as

$$C_1(t)=\langle \mathbf{v}(t)\times\boldsymbol{\omega}(t)\mathbf{v}^T(0)\rangle/[\langle v^2(0)\rangle\langle\omega^2(0)\rangle)^{1/2}]\;, \tag{2}$$

$$C_2(t)=\langle \mathbf{r}(t)\times\boldsymbol{\omega}(t)\mathbf{r}^T(0)\rangle/[\langle r^2(0)\rangle\langle\omega^2(0)\rangle)^{1/2}]\;, \tag{3}$$

$$C_3(t)=\frac{\langle\boldsymbol{\omega}(t)\times[\boldsymbol{\omega}(t)\times\mathbf{r}(t)][\boldsymbol{\omega}(0)\times\mathbf{r}(0)]^T\rangle}{[\langle\omega^2(0)\rangle\langle\omega^2(0)\rangle^{1/2}\langle r^2(0)\rangle]}\;, \tag{4}$$

for both CCl_4 and for a five-by-five atom-atom model of CH_2Cl_2 described elsewhere in the literature. It can be seen from these figures that the same types of cross correlation exist in the moving frame both for the spherical and for the asymmetric top. The fine details of time dependence and amplitude are different but otherwise rotational or purely translational diffusion theory is equally inapplicable in both symmetries. The basic and simple kinematic reason for such a seemingly unexpected result is that the ccf's above are correlating an acceleration into a velocity in the moving frame (1,2,3). For example, the Coriolis acceleration can be cross correlated into the linear velocity $\mathbf{v}$ with the result that the three diagonal elements of the ccf tensor exist. The Coriolis acceleration is, of course, a real acceleration in both frames, and is very well known in other contexts, such as rotation and/or vibration coupling in infrared and Raman spectra.[8,17] It seems to have escaped detailed consideration in the theory of three-dimensional molecular diffusion. The same can be said of the centripetal and nonuniform accelerations. These can all be cross correlated into the linear and angular velocity of the same molecule with positive results in frame (1,2,3). Without a detailed analytical description of these statistical cross correlations we do not in reality have much knowledge of the molecular dynamics of a liquid.

One of the significant results of this work is that the simple ccf

$$C_4(t)=\langle\boldsymbol{\omega}(t)\mathbf{v}^T(0)\rangle/[\langle\omega^2(0)\rangle^{1/2}\langle v^2(0)\rangle^{1/2}] \tag{5}$$

disappears for all t in both frames (1,2,3) and (x,y,z). This has been checked by computing each element of the matrix in Eq. (5) separately over at least two independent segments of about 1000 time steps each. This is the first conclusive evidence that simple cross correlations vanish in both frames for the spherical top but, as shown, other ccf's such as C_1, C_2, and C_3 do not. Therefore the theory of rotational diffusion has no validity in the spherical top. This result agrees with the theoretical predictions made in Ref. 2 based on the rotating-frame theory of asymmetric-top diffusion.[1–5]

It is worth noting that the other consequence of T_d symmetry is visible in Fig. 1. This is that the acf's of the Coriolis, centripetal, and nonuniform accelerations in CCl_4 are identical in time dependence in frame (1,2,3) and (x,y,z). Once we depart from spherical-top geometry this is no longer true, and evidence for this is available from the molecular-dynamics simulation of dichloromethane, reported in full elsewhere.[1,2]

V. CONCLUSION

Rotational and translational diffusion in liquid carbon tetrachloride are correlated through the existence of the Coriolis, centripetal, and nonuniform accelerations of the diffusing molecule. Therefore the theory of rotational

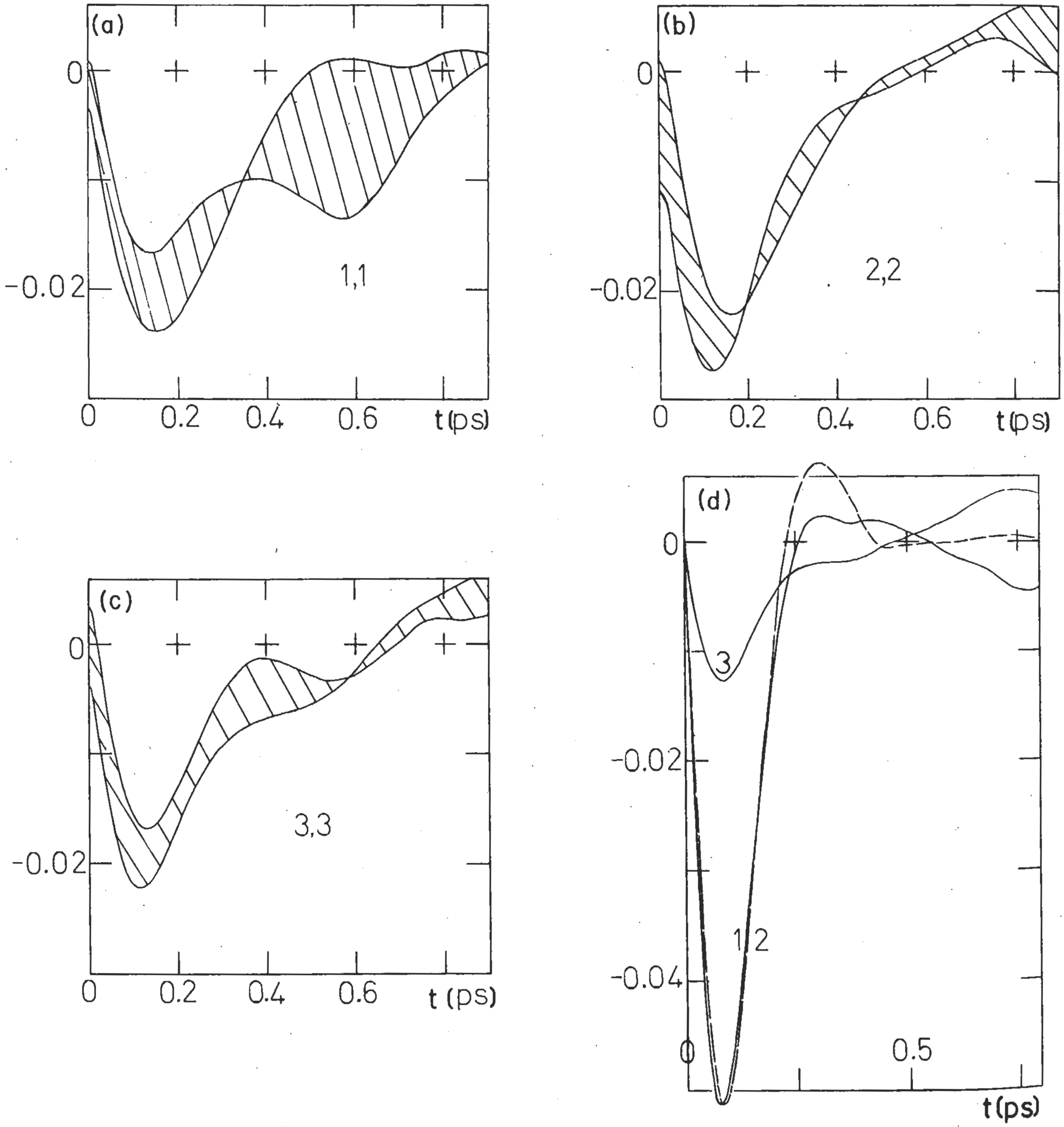

FIG. 2. Diagonal elemental ccf's of $C_1(t)$ in frame (1,2,3) in liquid CCl_4 for the spherical top. (a) The (1,1) element; (b) the (2,2) element; (c) the (3,3) element. The off-diagonal elements in frame (1,2,3) vanish for all t. All elements vanish in frame (x,y,z). (d) Off-diagonal liquid dichloromethane for the C_{2v} symmetry asymmetric top (see Fig. 1). Curve 1, the (1,1) element; curve 2, the (2,2) element; curve 3, the (3,3) element in frame (1,2,3).

diffusion has to be extended to include these results. This is despite the fact that simple cross correlations such as $C_4(t)$ vanish for all t in both frames of reference.

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APPENDIX: GROUP-THEORETICAL ANALYSIS OF CROSS CORRELATIONS IN FRAME (1,2,3)

Within the noise, each of the cross-correlation functions in the text has equal elements on the diagonal of the

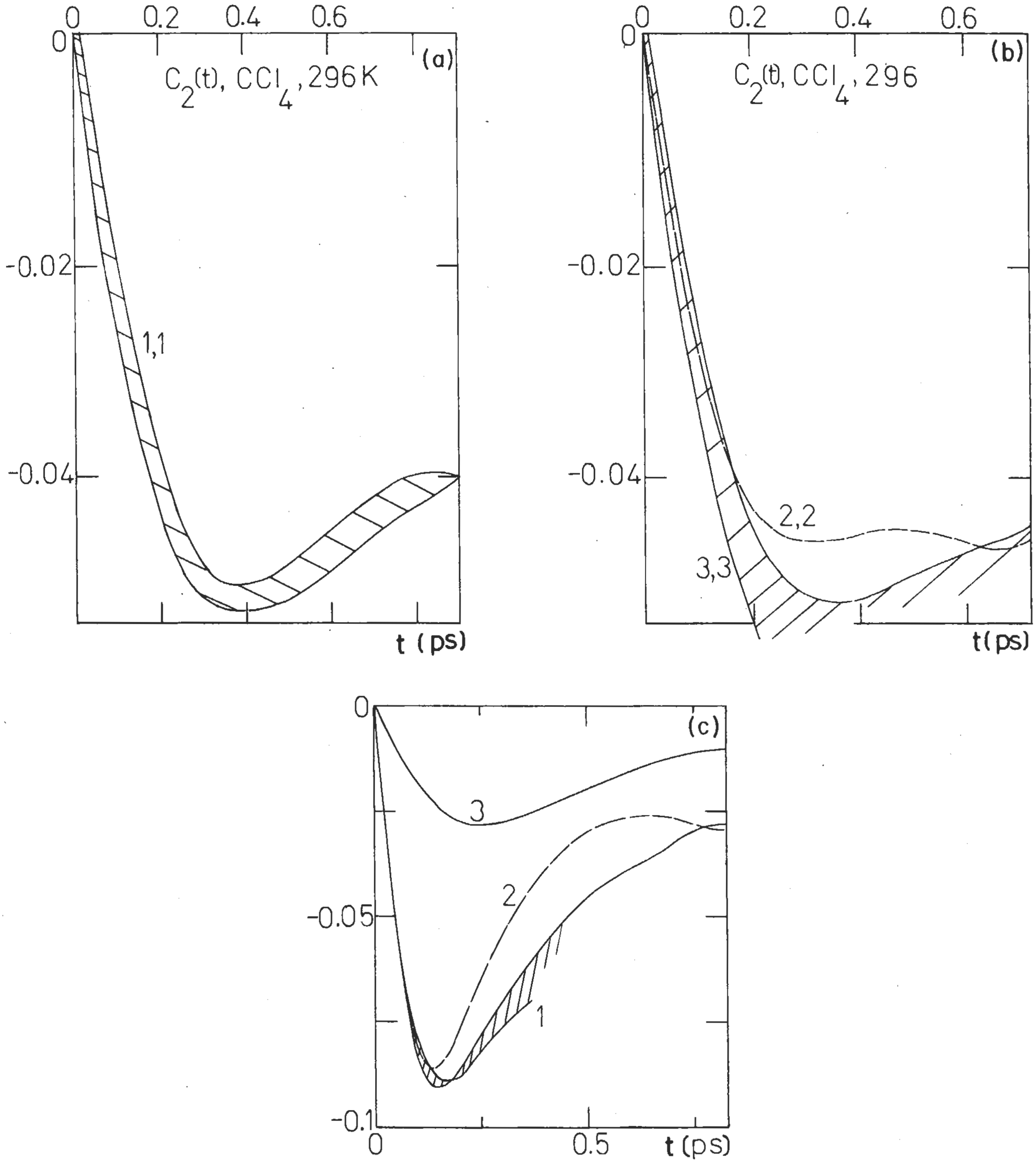

FIG. 3. The ccf of $C_2(t)$ for CCl_4 (see Fig. 2).

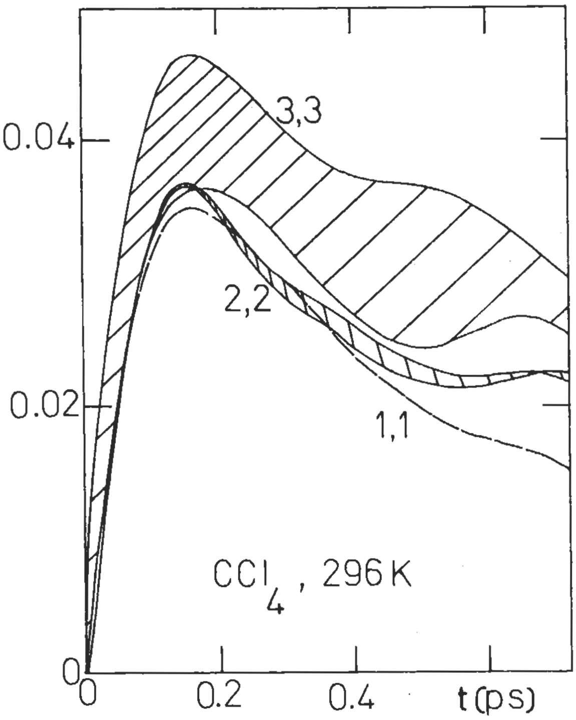

FIG. 4. The ccf of $C_3(t)$ for CCl_4 (see Fig. 2). For clarity the noise level on (1,1) is not shown.

correlation tensor in frame (1,2,3). This result has been predicted in private correspondence with Professor D. H. Whiffen. For example, $C_1(t)$ is reducible in frame (1,2,3) in an isotropic environment as A_1 (or A_2)$+E+T_1+T_2$, nine elements, of which A_1 is the only property which survives after averaging in isotropic surroundings. For example, if the tensor is the outer product of two vectors (both polar or both axial) A_1 applies and refers, for example, to the triple product $\langle \mathbf{v}(t)\times\boldsymbol{\omega}(t)\cdot\mathbf{v}(0)\rangle$ which is a scalar. The A_2 case refers to a pseudoscalar which might be the product of an axial and a polar vector. These products are only nonzero on average for point groups which embrace optically active molecules. Consequently, $C_1(t)$ reduces to the renormalized triple product multiplied by the unit tensor. This implies that the (1,1), (2,2), and (3,3) elements must be equal in magnitude and time dependence in the spherical top in frame (1,2,3,) in isotropic surroundings. At the time origin the triple product must separately vanish for all the molecules in ensemble because two out of the three vectors in the product are parallel.

The application of group theory in this way shows therefore that those elements which appear in this computer simulation are precisely those expected on the grounds of symmetry. It is concluded therefore that the computer simulation provides the necessary evidence to show the presence of rotation to translation cross correlation in spherical tops.[19]

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