

Computer Simulation of some Structural and Spectral Properties of Liquid and Rotator Phase t-Butyl Chloride

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The molecular motions and interactions in liquid- and rotator-phase t-butyl chloride have been simulated numerically with a 5×5 site-site potential derived from Lassier and Brot. The simulated a.c.f. are compared with spectral results from infrared, far-infrared, dielectric, Raman, Rayleigh, n.m.r. and incoherent neutron-scattering spectroscopy. The simulation is more successful in reproducing single- as opposed to multi-particle correlations. The results show that the computer-simulation method is a powerful means of self-consistent analysis, given the pair potential. The effects of rotation-translation coupling are investigated in a moving frame of reference defined by the principal moment-of-inertia axes. The computer simulation shows clearly that rotation is correlated to centre-of-mass translation in both the liquid and rotator phase at 228 K. The nature of this correlation is revealed in the moving frame of reference: its effects are present in the static frame.

In a remarkable and imaginative paper, Lassier and Brot¹ provided the first incisive account of the molecular dynamics of t-butyl chloride in its crystalline (III) and plastic (II and I) states:

$$T_{\text{III} \rightarrow \text{II}} = 182.9 \text{ K}; \quad T_{\text{II} \rightarrow \text{I}} = 219.25 \text{ K}; \quad T_{\text{I} \rightarrow \text{liq.}} = 247.53 \text{ K}.$$

Experimental results from dielectric relaxation ($\tau_c = 5.6$ ps at 274 K, 7.4 ps at 238 K, 7.7 ps at 233 K and 8.5 ps at 228 K) and far-infrared spectroscopy ($\bar{\nu}_{\text{max}} = 57 \text{ cm}^{-1}$ at 243 K and 26 cm^{-1} at 293 K) were interpreted with a modified Frenkel model with rotational jumps of finite duration and semi-quantitative agreement was obtained with the data.^{1a} Calculations of the lattice energies were carried out for phases II and I. The electrostatic energy was computed by summing up charge-charge interactions between atomic sites of pairs of t-butyl chloride molecules. Added to these were London dispersion energies. The lattices of each phase are partially disordered and averages were taken over samplings of the configurations in each phase. The difference between the computed energies of phases I and II was found to be equal to the observed enthalpy of transition. This is configurational in origin rather than purely electrostatic. Lassier and Brot calculated the configurational energy and energy of transition using (i) the energy of repulsion, (ii) the London attraction energy, (iii) the electrostatic energy between permanent charges, (iv) the energy of formation of the induced polarisation ($\frac{1}{2}\alpha E^2$), (v) the charge-induced dipole energy and (vi) the energy between induced dipoles. The first two terms were calculated with atom-atom Lennard-Jones parameters and amounted to ten times the electrostatic energy (iii), which in turn was an order of magnitude greater than the polarisation and induction energy.

t-Butyl chloride is therefore an ideal molecule to choose for a molecular-dynamics computer simulation of the dynamical (and thereby spectral) properties of the liquid and rotator phases, not least because of the detailed information about

the thermodynamic properties already available from Lassier and Brot. The electrostatic energy is so much smaller than the effective Lennard-Jones energy that periodic boundary conditions are not likely to be a problem, and it is also safe to ignore polarisation and induction effects in the first approximation. In this paper we aim to reproduce a variety of spectral data by computer simulation using the atom-atom Lennard-Jones and partial charge parameters of Lassier and Brot. These results will be compared with experimental data which have become available from a range of techniques since the appearance of the Lassier-Brot paper in 1968.

A great deal of the investigative effort in this field has concentrated on cold neutron scattering,²⁻⁵ culminating in a paper by Mansson and Larsson⁶ on phases I to III, whose main aim was to study the rotational motions which dominate the elastic and quasi-elastic scattering. 'Extreme' models (*sic*) ranging from free rotation to 'undamped libration' were used, but none fitted the data satisfactorily. Mansson and Larsson provide first- and second-rank orientational a.c.f. from the best fit of other models to the observed data. It is assumed that rotation is effectively decoupled from translation, *i.e.*

$$I_{\text{inc}}(\mathbf{K}, t) = I_{\text{cm}}(\mathbf{K}, t)I_{\text{rot}}(\mathbf{K}, t)I_{\text{tors}}(\mathbf{K}, t) \quad (1)$$

where $I_{\text{cm}}(\mathbf{K}, t)$, $I_{\text{rot}}(\mathbf{K}, t)$ and $I_{\text{tors}}(\mathbf{K}, t)$ are the symmetric forms of the incoherent, intermediate scattering functions for translational, rotational and torsional motions, respectively, \mathbf{K} is the momentum transferred in scattering and t is the time. This is a basic approximation which we can test with computer simulation by constructing the correlation matrix $\langle \mathbf{v}(0)\mathbf{J}^T(t) \rangle$ in a moving (molecular) frame of reference, where \mathbf{v} is the centre-of-mass linear velocity and \mathbf{J} the molecular angular momentum. If all its elements are small then rotation/translation interaction is small and eqn (1) is a good approximation.

Goyal *et al.*² have reported the quasi-elastic component of the neutron-scattering spectra of t-butyl chloride in the plastic phase and have attributed its origin to molecular orientation about the C-Cl axis. The mean time between successive reorientations is 1.0×10^{-11} and 1.4×10^{-11} s at 208 and 193 K, respectively. The dipole axis, according to Goyal *et al.*, is frozen and reorientation between individual sites occurs at 12 ps intervals. The different depths of the energy wells cause Davydov splitting³ of the infrared spectrum.

The first-rank orientational correlation time from neutron scattering⁶ appears to be 3.0 ps at 325 K, in comparison with the dielectric relaxation time¹ of 7.7 ps at 233 K. The second-rank orientational correlation time from neutron scattering⁶ is 1.2 ps. There is considerable uncertainty⁶ as to the ability of the neutron-scattering method to give a reliable estimate of the rotational diffusion dynamics.

N.m.r. relaxation has been studied in t-butyl chloride by a number of groups. Heatley⁷ provides a proton-¹³C magnetic resonance relaxation time for (assumed) isotropic rotational diffusion of 1.05 ± 0.10 ps in the liquid at 308 K. Boguslavskii *et al.*⁸ have measured the temperature dependence of the solid-state n.m.r. relaxation. There is an effect of large-amplitude reorientational and translational motions in the electric-field gradient of the resonant nucleus which persists over the temperature range of the phase transition. Koeksal⁹ has used H spin-lattice relaxation at 60 MHz between 100 and 330 K and discerned three types of motion: centre-of-mass translation, molecular tumbling and methyl-group torsion.

Raman^{10,11} and Rayleigh¹² light scattering have been used to study liquid t-butyl chloride. First- and second-rank orientational correlation times have been reported by Czarniecka *et al.*,¹⁰ and accurately derived correlation functions by Constant *et al.*¹¹ Czarniecka *et al.*¹⁰ used the totally symmetric C-CH₃ stretch at 812 cm^{-1}

for their analysis, so that the subsequent rotational correlation time is a mixture of all three correlation times about the principal moment-of-inertia axes, which we compute in this paper. They also used the symmetric C—Cl stretch at 570 cm^{-1} , providing the second-rank orientational correlation time of the dipole unit vector. The C—CH₃ stretch correlation time in liquid t-butyl chloride at room temperature is reported as 1.49 ps. The correlation function of the C—Cl stretch agreed with that of Constant *et al.*¹¹ within the experimental uncertainty. Czarniecka *et al.* compare their results with dielectric relaxation times with and without a correction for the internal field. The relaxation time is 4.9 ± 0.5 ps at room temperature. Constant and Fauquembergue¹³ have also made a study of the Raman C—Cl stretch over a wide temperature range for neat liquid t-butyl chloride and in carbon tetrachloride and hexane solution. Orientational correlation times and functions were obtained on the assumption that (i) orientational and vibrational processes are mutually independent, (ii) there are no vibrational cross-correlations between molecules and (iii) collision-induced scattering can be neglected. The second-rank orientational correlation time is defined as the area beneath the correlation function, and these data supplement the earlier work of Constant *et al.*¹¹ with infrared, depolarised Rayleigh and dielectric relaxation as well as Raman spectroscopy. The second-rank orientational correlation time at 298 K of the Raman C—Cl stretch is 1.2 ± 0.1 ps in pure liquid t-butyl chloride, in fair agreement with Heatley's n.m.r. correlation time of 1.05 ± 0.10 ps. Constant *et al.*¹¹ made a direct comparison of the Raman and Rayleigh correlation functions in pure liquid t-butyl chloride at room temperature (298 K). The (second-rank) Rayleigh correlation time is 1.3 ± 0.05 ps, slightly longer than the C—Cl Raman correlation time. According to Constant *et al.* these two times should be the same if cross-correlations and other effects, such as induced scattering,¹¹ were absent. At 'long times' (*sic*) the two correlation functions are different in magnitude but have the same slope, meaning that cross-correlations narrow the observed Rayleigh band. There are no significant differences between the two correlation functions at short times. This is taken by Constant *et al.* to mean that collision-induced effects are too weak to be detected. However, this conclusion is contested by Carlson and Flory,¹² who report that the depolarised Rayleigh band contains 'copious' (*sic*) induced scattering over a range of frequencies. In pure liquid t-butyl chloride at 298 K, Carlson and Flory assert that no less than 50% of the absolute intensity of the depolarised Rayleigh spectrum is collision-induced. There is therefore serious disagreement on this point. The results of Carlson and Flory for polarisability anisotropies agree with independent estimates¹² from the Kerr effect and absolute Raman intensities.

The computer-simulation method does not take account of the induced effects, and a comparison of the simulated and observed¹¹ Raman and Rayleigh second-rank correlation functions will allow us to estimate the effect of induced scattering on the correlation times. This does not seem to be great, despite the points made by Carlson and Flory, because of the good agreement between the n.m.r.⁷ and Raman¹¹ correlation times mentioned earlier.

The 'first-rank' procedure equivalent to comparing Raman and Rayleigh bands is to compare infrared bands with far-infrared and dielectric absorption. 'Cross-comparison' can also be made¹⁴ of the far-infrared spectrum with the Rayleigh 'power spectrum', obtained by multiplying the Rayleigh band by $\bar{\nu}^2$, where $\bar{\nu}$ is the wavenumber.

Constant *et al.*¹¹ have reported at 288 K an infrared (C—Cl stretch) correlation time of 4.2 ps for pure liquid t-butyl chloride, decreasing to 2.0 ps in 20 mol% in n-hexane solution. (The corresponding second-rank correlation times are 1.2 and

0.8 ps, respectively.) The infrared time can be compared with the dielectric relaxation time reported by Czarniecka *et al.*¹⁰ of 4.9 ps. Reid and Evans¹⁵ have measured the effect of dilution on the relaxation time of t-butyl chloride in the liquid and glassy phases. In 10% decalin solution at room temperature the dielectric relaxation time is 3.6 ps and in the glassy state¹⁶ it is increased to the μs range.

t-Butyl chloride is one of the most intensively studied liquids in the far-infrared, both experimentally^{1,15} and theoretically. Larkin¹⁷ has applied the well-jumping model of Lassier and Brot¹ to the far-infrared and dielectric spectrum in both the liquid and rotator phases, and has force-fitted the spectrum by adjusting model parameters. Subsequently Reid and Evans¹⁵ and Reid¹⁸ have studied the rotational velocity a.c.f. of t-butyl chloride both in the rotator phase I at 243 K, where the far-infrared peak is at 57 cm^{-1} ($\tau_D = 8.1\text{ ps}$), and in the pure liquid at 296 K, where the peak shifts to 26 cm^{-1} . The integrated intensity of the band is 325 cm^{-2} , while the Gordon sum rule¹⁹ produces 266 cm^{-2} . This result is similar to that of Carlson and Flory¹² for the Rayleigh integrated intensity. Reid and Evans¹⁵ have discussed the validity of the Gordon sum rule in this context and Bossis²⁰ has recently extended the analysis to involve anisotropic cavities and the internal field effect. The integrated intensity of the t-butyl chloride absorption is linear with dilution, so that collision-induced effects are not likely seriously to distort the far-infrared spectrum due to the cancellation of symmetrically disposed molecular fields around a centrally placed reference.

Comparing the infrared correlation time of 4.2 ps with the dielectric relaxation time of 4.9 ps in liquid t-butyl chloride at room temperature one may suppose that cross-correlation effects are small, a supposition supported by the similarity of the Raman and Rayleigh correlation times. The success of the pair-additivity approximation of Lassier and Brot¹ also seems to support this view, non-pair additive multi-body effects (such as that of polarisability) being small. (Induced absorption or scattering in the liquid phase is not a pair-additive effect.¹⁶) The evidence points towards the validity of a molecular-dynamics simulation using the usual approximation of the computer method, which should therefore be able to reproduce the far-infrared bands fairly accurately.

Kluk²¹ has produced a one-particle stochastic theory of dipolar dielectric relaxation which takes into account the problem of the local field. For molecules or groups of molecules with C_2 or higher symmetry a single-exponential macroscopic decay function is obeyed. This is the case in t-butyl chloride. The restricted rotator model^{22,23} of Kalmykov and Gaiduk provides good agreement with the spectral data over a range of far-infrared and lower frequencies, and Reid and Evans¹⁵ have analysed the complete range of absorption of t-butyl chloride with their itinerant oscillator model. This analysis was carried out both in the frequency and time domains and provided a model-predicted Debye relaxation time of 3.0 ps for t-butyl chloride in decalin solution. This compares with a measured relaxation time of 3.7 ps. [A full description of this work is given in ref. (16), chap. 4.]

Therefore, a great deal of work has been carried out on t-butyl chloride liquid and rotator phases I and II since the appearance of the Brot-Lassier paper of 1968. The outcome of this work is not entirely clear, especially in the area of collision-induced absorption or scattering. In what follows we aim to use a submillimetre laser system to provide spot-frequency absorption measurements in the far-infrared and fix the absolute absorption intensity accurately. This will provide us with more insight into this phenomenon. The molecular-dynamics computer-simulation method is used to produce as wide a variety of spectral data as possible in the liquid and rotator phase I.

EXPERIMENTAL

The intensity of the far-infrared band in *t*-butyl chloride in the liquid at 293 K and in the rotator phase at 228 K was checked with a tunable Apollo Instruments submillimetre laser at 61, 84 and 103.6 cm^{-1} . The results agreed well with the interferometric data reported by Reid.^{16,18} It is clear therefore that the Gordon sum rule does not reproduce the observed far-infrared integrated intensity. A similar outcome was observed in the rotator at 228 K.

MOLECULAR-DYNAMICS SIMULATION

The rotational and translational equations of motion are integrated numerically with an algorithm which we have described elsewhere.²⁴ The translational equations are integrated with a two-step Verlet algorithm and the rotational equation in two stages, the total torque being first computed from the atomic forces and the angular momentum secondly by a cubic interpolation over the four previous values in time sequence. The orientation of the *t*-butyl chloride molecules is defined with three unit vectors, l_A , l_B and l_C , directed along the principal moment-of-inertia axes of the molecule (a C_{3v} symmetric top).

The intermolecular pair potential is that of Lassier and Brot,¹ excluding the very small polarisability and induction effects. The Lennard-Jones parameters are $\sigma(\text{C}-\text{C}) = 3.4 \text{ \AA}$, $\sigma(\text{CH}_3-\text{CH}_3) = 4.0 \text{ \AA}$, $\sigma(\text{Cl}-\text{Cl}) = 3.6 \text{ \AA}$, $\epsilon/k(\text{C}-\text{C}) = 35.8 \text{ K}$, $\epsilon/k(\text{CH}_3-\text{CH}_3) = 158.6 \text{ K}$ and $\epsilon/k(\text{Cl}-\text{Cl}) = 127.9 \text{ K}$. The Lorentz-Berthelot combining rules used by Lassier and Brot provide the cross-terms. The partial charge parameters of Lassier and Brot are: $q_{\text{CH}_3} = 0.054|e|$; $q_{\text{C}} = 0.038|e|$ and $q_{\text{Cl}} = -0.201|e|$.

The simulations were carried out at 293 K, 1 bar in the liquid and at 228 K, 1 bar in rotator phase I. Haffmans and Larkin²⁵ have provided a density of 0.96 gm cm^{-3} for rotator phase I at 228 K (f.c.c., $a = 8.62 \text{ \AA}$, 4 molecules per unit cell) and this was used to calculate the input molar volume for the computer simulation.

At both state points the *t*-butyl chloride molecules were arranged on a face-centred cubic lattice, which melted over some 2000 or 3000 time steps of 0.005 ps each. The sample of 108 molecules was monitored for residual ordering through the Verlet parameter, which is zero for a random distribution of orientations/positions. Total energy was conserved to approximately one part in a thousand.

At equilibrium, samples of *ca.* 2000 time steps were taken for the computation of auto-correlation functions by running-time averaging. A.c.f. of l_A , l_B and l_C (the orientation vectors), v (the centre-of-mass linear velocity), ω (the molecular angular velocity) and J (the angular momentum) were constructed, and of l_A , l_B and l_C (the rotational velocity a.c.f. for comparison with far-infrared data); also cross-correlations were constructed between v and J in a moving frame of reference fixed in the principal moment-of-inertia frame. Correlation times are the areas of these auto-correlation functions.

Long-range corrections to the virial sum and to the potential energy have been incorporated for the Lennard-Jones interactions only, because such sums diverge for the electrostatic contributions. For Lennard-Jones interactions atomic sites were considered independently of what molecules they belonged to. The electrostatic interaction was considered as a molecular property, and the minimum image convention and cut-off criterion were applied to the centre-of-mass-centre-of-mass distance, accounting for all 25 contributions for each pair of molecules. For relatively small partial charges, as in *t*-butyl chloride, there is apparently no need for an elaborate correction for long-range electrostatic forces, such as the Ewald

Table 1. Comparison of experimental and computer-simulated correlation times for t-butyl chloride

technique	experimental correlation times	simulated auto-correlation times (293 and 228 K)/ps
infrared	C—Cl stretch, 288 K ¹¹ pure liquid TBC: 4.2 ps 20% mole fraction TBC in n-hexane: 2.0 ps totally symmetric C—CH ₃ stretch: ¹⁰ 1.49 ps	$\tau_1(I_C) = 4.0$ a weighted mean of: $\tau_1(I_C) = 4.0$; $\tau_1(I_A) = \tau_1(I_B) = 3.2$
Raman	C—Cl stretch: ¹¹ 1.2 ps	$\tau_2(I_C) = 1.5$; $\tau_2(I_A) = \tau_2(I_B) = 1.2$
Rayleigh	20% mole fraction in n-hexane: ¹¹ 0.8 ps pure liquid at 298 K: ¹¹ 1.3 ps	a weighted mean of: $\tau_2(I_C) = 1.5$; $\tau_2(I_A) = \tau_2(I_B) = 1.2$ $\tau_1(I_C) = 4.0$; $\tau_1(I_A) = \tau_1(I_B) = 3.2$
dielectric relaxation	pure liquid: ¹⁰ 4.9 ps 10% decalin solution: ¹⁰ 3.6 ps rotator phase I: 274 K: 5.6 ps rotator phase I: 238 K: 7.4 ps rotator phase I: 233 K: 7.7 ps rotator phase I: 228 K: 8.5 ps	$\tau_1(I_C) = 9.5$; $\tau_1(I_A) = \tau_1(I_B) = -$
n.m.r. relaxation	¹ H— ¹³ C spin-spin: ⁷ 1.05 ± 0.1 ps	$\tau_2(I_C) = 1.5$; $\tau_2(I_A) = 1.2$
neutron scattering	mean time between successive reorientations: ³ 10 ps at 208 K. (rotator II): 14 ps at 193 K. <i>P</i> ₁ (dipole vector): ⁶ 235 K: 3.0 ps <i>P</i> ₂ (dipole vector): ⁶ 235 K: 1.2 ps	$\tau_1 = 9.5$ $\tau_2 = 5.2$ at 228 K

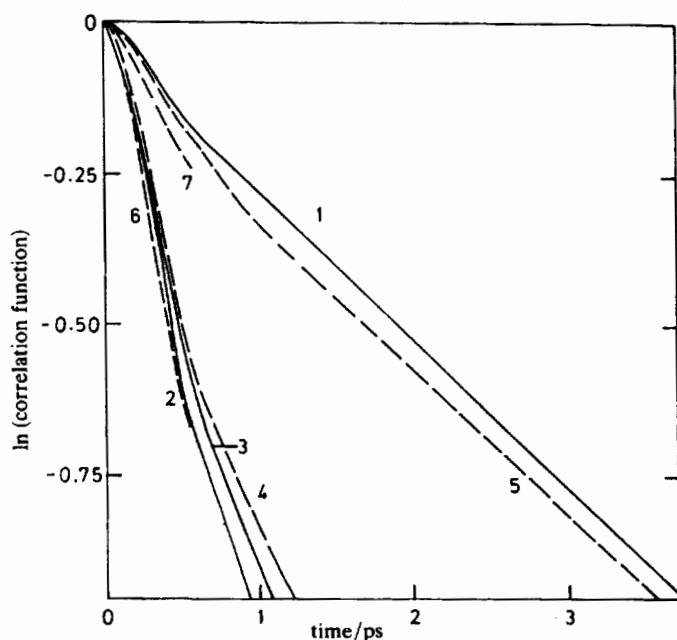


Fig. 1. Comparison of computer-simulation results with the experimental data of Constant *et al.*¹¹ for liquid t-butyl chloride at 293 K. 1, First-rank orientational a.c.f. from infrared bandshape analysis; 2, second-rank orientational a.c.f. from Raman scattering; 3, second-rank orientational cross c.f. from Rayleigh scattering; 4, computer-simulated second-rank orientational a.c.f. of the dipole vector (C_{3v} symmetry axis); 5, as for 4, first-rank a.c.f.; 6, as for 4, vector $\perp C_{3v}$ axis; 7, as for 5, vector $\perp C_{3v}$ axis.

sum, because the dominant forces, as calculated by Lassier and Brot,¹ are those from the anisotropy of the total Lennard-Jones potential.

RESULTS AND DISCUSSION

Table 1 is a comparison of some of the correlation times from the simulation with experimental results at 293 K, 1 bar and 228 K, 1 bar. In fig. 1 we illustrate the results of the computer simulation with the infrared, Raman and Rayleigh orientational correlation functions of Constant *et al.*¹¹ The agreement is probably within the experimental error in all three cases; this implies that (i) reorientational effects have probably been factorised-out correctly from vibrational dephasing effects in the liquid,¹¹ (ii) the same remark applies to the Raman, second-rank orientational auto-correlation function and (iii) Carlson *et al.*¹² have pointed out the large effects on their result of collision-induced scattering. This conflicts with the view of Constant *et al.*¹¹ The results of the computer simulation indicate that the theoretical, $P_2(I_A)$, auto-correlation function has a similar time dependence to the multi-molecule correlation function derived by Constant *et al.* from the Rayleigh wing. The only possible way of reconciling all three sources of evidence is to assume that the time dependence of the collision-induced effects is the same as that of the scattering due to the permanent molecular polarisability anisotropy.

By comparing the Raman and Rayleigh correlation functions with the results of the computer simulation (fig. 1), it seems that cross-correlations are short-ranged

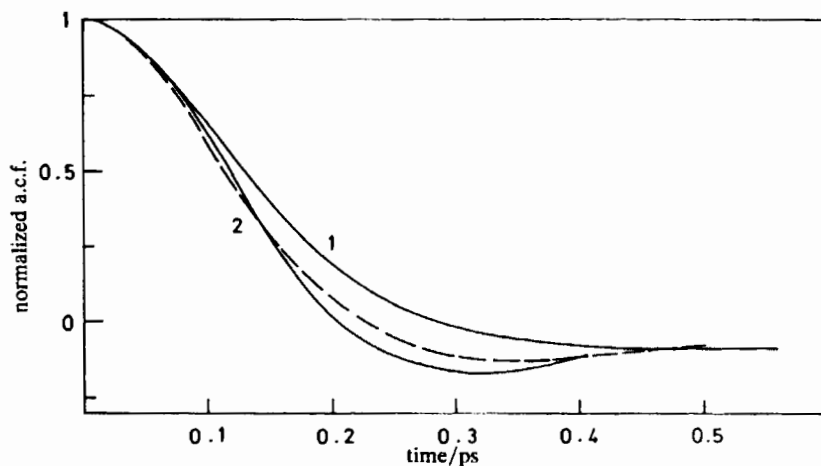


Fig. 2. Curve 1, computer-simulated rotational velocity a.c.f., $\langle I_C(t) \cdot I_C(0) \rangle / \langle I_C^2 \rangle$; curve 2, Fourier transform of the far-infrared spectrum of liquid t-butyl chloride;¹⁶ $\langle I_A(t) \cdot I_A(0) \rangle / \langle I_A^2 \rangle$, illustrating the anisotropy of the rotational motion.

in liquid t-butyl chloride, so that auto-correlation functions and many-particle correlation functions have a similar time dependence. This is corroborated by the similarity of the orientational infrared (auto-) correlation time for the C—Cl stretch,¹¹ 4.2 ps, to the dielectric relaxation time, 4.9 ps. The computer-simulated correlation time is 4.0 ps. The role of orientational cross-correlation in liquid t-butyl chloride can be investigated further by use of far-infrared data.^{17,18} In fig. 2 we compare simulated and measured rotational velocity correlation functions. The former is an auto-correlation function ($\langle I_C(t) \cdot I_C(0) \rangle / \langle I_C^2 \rangle$) and the latter a multi-particle property¹⁶ in the same sense as the dielectric relaxation time.

Initially, the decay of the two functions is the same, but thereafter the multi-particle correlation function decays more quickly and has a slightly deeper negative over-shoot. The structure of the collision-induced far-infrared absorption spectrum¹⁶ is dependent on the structure of the spectrum due to cross-correlation, because collision-induction is a multi-body, non-pair-additive effect. The effect of dilution¹⁶⁻¹⁸ on the far-infrared peak frequency is small and the integrated intensity of the far-infrared spectrum is linear in the molecular number density (N).¹⁶ This implies that multi-body effects (dependent on a power of N) are very small. On the other hand, the Gordon sum rule¹⁶ produces only a part of the total integrated intensity even in dilute solution, so we are led to the conclusion that our knowledge of intensity effects, both in the far-infrared and in Rayleigh scattering,¹² is insufficient at present to obtain a consistent view with more than one technique. However, we have obtained a consistent view of the orientational dynamics in t-butyl chloride liquid with the 5×5 site-site model of Lassier and Brot.¹

Having tested the numerical method against experimental data we can proceed now to use the computer simulation to investigate dynamical properties which are not accessible to straightforward experimental evaluation but which are, nevertheless, fundamentally important to an understanding of the liquid state of matter. One of the basic steps in the theory of neutron scattering is represented in eqn (1). If the rotational motion of liquid t-butyl chloride is not independent of its centre-of-mass translation then eqn (1) becomes approximate. Ciccotti *et al.*²⁶ have

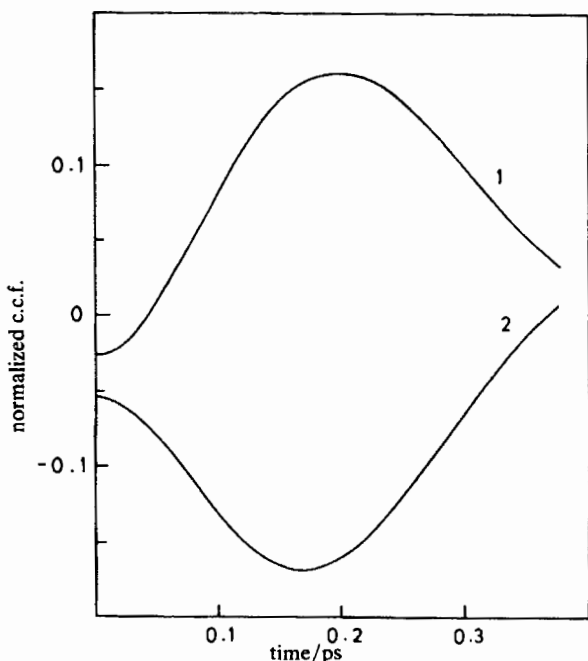


Fig. 3. Elements of $\langle \mathbf{v}(t)\mathbf{J}^T(0) \rangle$ in the moving, principal-moment-of-inertia frame. 1, $\langle v_2(t)J_1(0) \rangle / [(\langle v_2^2 \rangle^{1/2} \langle J_1^2 \rangle^{1/2})]$, the (2, 1) element; 2, the (1, 2) element. The noise level is demonstrated by the $t = 0$ intercept, which is zero by symmetry in the absence of noise.

shown recently that the correct way of investigating rototranslational correlation is to look at the dynamics in a moving frame of reference. We have transformed the centre-of-mass linear velocity vector, \mathbf{v} , into the moving frame of reference defined by the principal moments of inertia of t-butyl chloride and constructed the correlation function of this quantity with \mathbf{J} , the angular momentum in the same frame of reference. The (1, 2) and (2, 1) elements of this matrix, $\langle \mathbf{v}(t)\mathbf{J}^T(0) \rangle$, do not vanish (by symmetry²⁶) for $t > 0$. The result is shown in fig. 3, suitably normalised. Despite the statistical noise, it is clear that there is a true statistical correlation between rotation and translation on the basis of the 5×5 site-site model.¹ This means that eqn (1) is, strictly speaking, inapplicable because it produces $\langle \mathbf{v}(t)\mathbf{J}^T(0) \rangle = 0$ for all elements. Looking for appropriate explanations, without involving a detailed mathematical analysis,²⁷ it is interesting to remark that the decays of $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle / \langle v^2(0) \rangle$ and $\langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle / \langle J^2(0) \rangle$ in the laboratory frame of reference (fig. 4) are very similar. Each a.c.f. is transiently non-Gaussian,²⁷ although each eventually attains its Gaussian limit at equilibrium.

The role of rotation/translation correlation may be investigated further in the rotator phase at 228 K. However, before turning to a detailed consideration of that state we would like to remark on an interesting paper by Delker *et al.*²⁸ In very dilute solutions the absorption of t-butyl chloride in n-heptane, cyclohexane and decalin may be fitted within experimental error by three-variable Mori theory,¹⁶ because ϵ , the dielectric loss, finally decreases with the fifth power of frequency. In the terminology of Delker *et al.*,²⁸ there is 'no Poley absorption' in dilute t-butyl chloride solution. This implies that the rotational freedom in dilute solution is pronounced, and this, coupled with the fact that there is no pronounced shift in

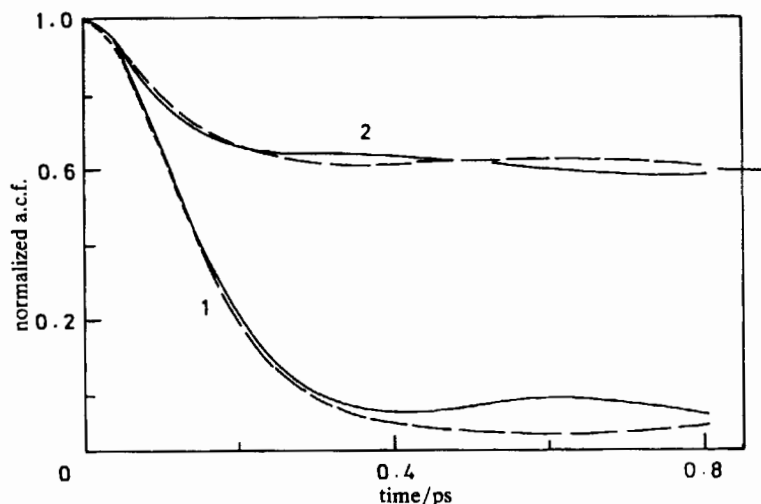


Fig. 4. (1, —) $\langle \mathbf{J}(t) \cdot \mathbf{J}(0) \rangle / \langle J^2 \rangle$, angular momentum a.c.f.; (1, ---) $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle / \langle v^2 \rangle$, linear centre-of-mass velocity a.c.f. (both in the laboratory frame). (2, —) $\langle \mathbf{J}(t) \cdot \mathbf{J}(t) \mathbf{J}(0) \cdot \mathbf{J}(0) \rangle / \langle J^4 \rangle$; (2, ---) $\langle \mathbf{v}(t) \cdot \mathbf{v}(t) \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle / \langle v^4 \rangle$. Computer simulation, t-butyl chloride at 293 K.

the power absorption coefficient on dilution, means that dynamic cross-correlations are either short range or negligible.

By constructing atom-atom probability density functions, the equilibrium structures of the liquid at 293 K or the rotator phase at 228 K may be compared over a short range ($< 10 \text{ \AA}$) where correlations persist. These functions measure the probability of finding an atom of molecule B at a distance r from an atom of molecule A given the position of this latter atom relative to the origin in the laboratory frame of reference.

These probability density functions are illustrated in fig. 5, where we compare the liquid- and rotator-phase curves on the same scale. It is clear that the stronger correlations disappear on the whole within the 10 \AA range of the first coordination shell, and that the structure in this range does not differ greatly between the two phases. There is a lack of long-range order in the rotator phase as measured through these probability density functions, which seems to suggest that they are incapable of supporting phonon modes as usually observed in the crystalline phase below 182.9 K.

The mean Verlet parameter in the rotator phase is 35 ± 10 , so there is positional ordering, as in a cubic lattice, but no significant orientational ordering. For a perfectly ordered sample the Verlet parameter in our case would be 108 and zero for a perfectly disordered sample.

The rotator phases I and II of t-butyl chloride have been studied in depth with thermal neutron scattering,²⁻⁶ and in the paper of Mansson *et al.* first- and second-rank orientational correlation functions are derived at 235 K. In fig. 6 these are compared with the results from the computer simulation. It is clear that the functions derived by neutron scattering decay far more quickly than the computer-simulated auto-correlation functions. The dielectric relaxation time at 238 K measured by Lassier and Brot¹ (7.0 ps) is also longer than the area beneath the P_1 function from the neutron-scattering result at the same temperature. The area beneath the

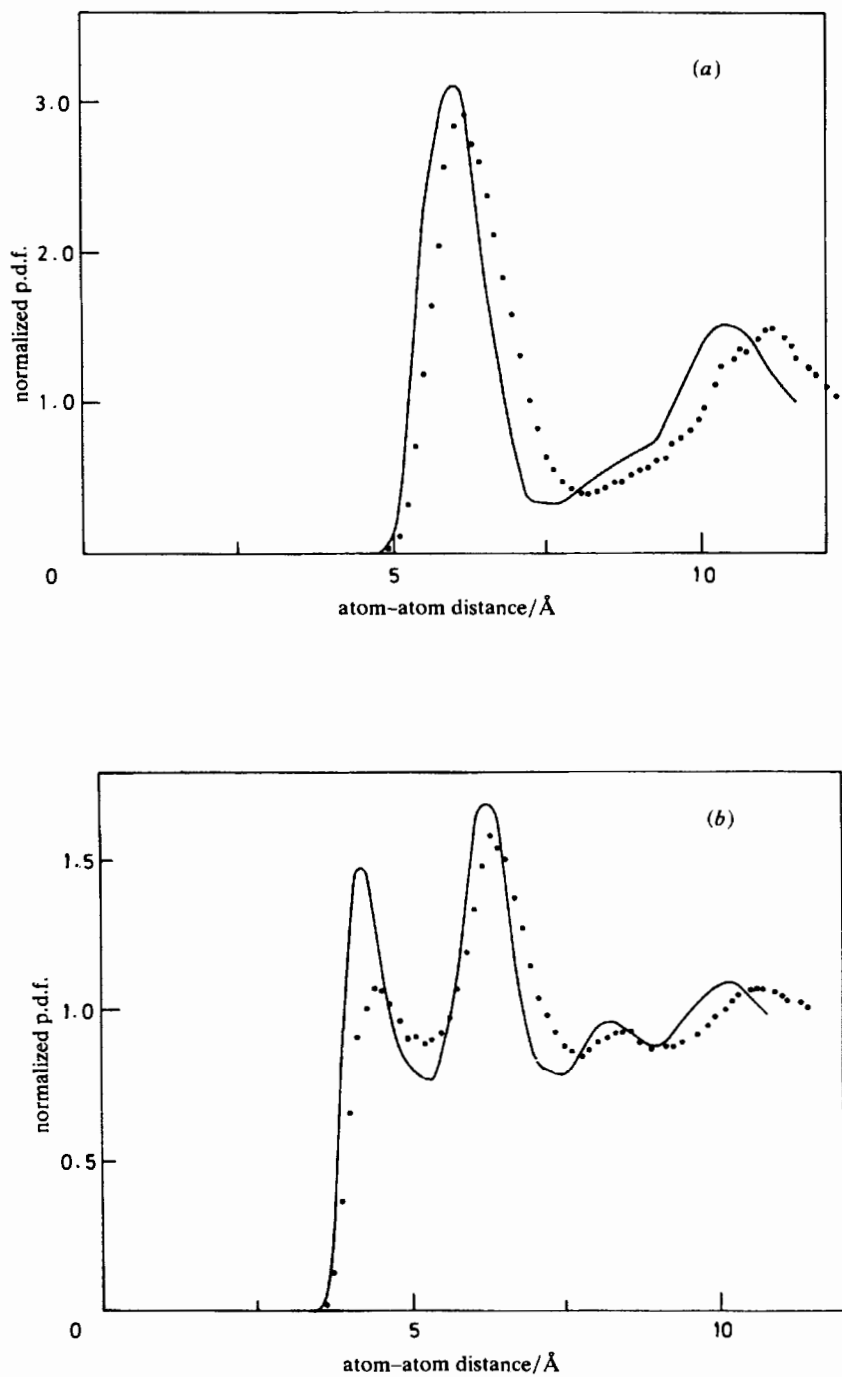
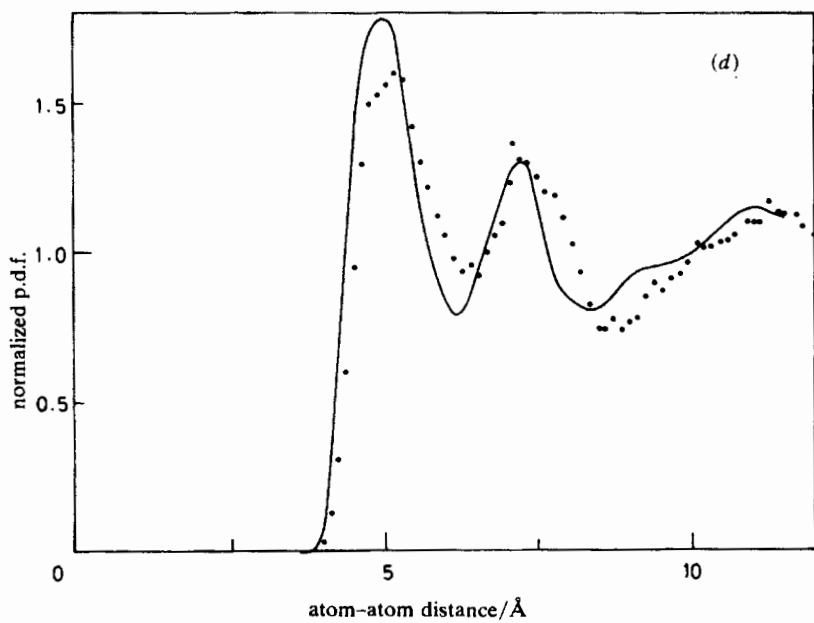
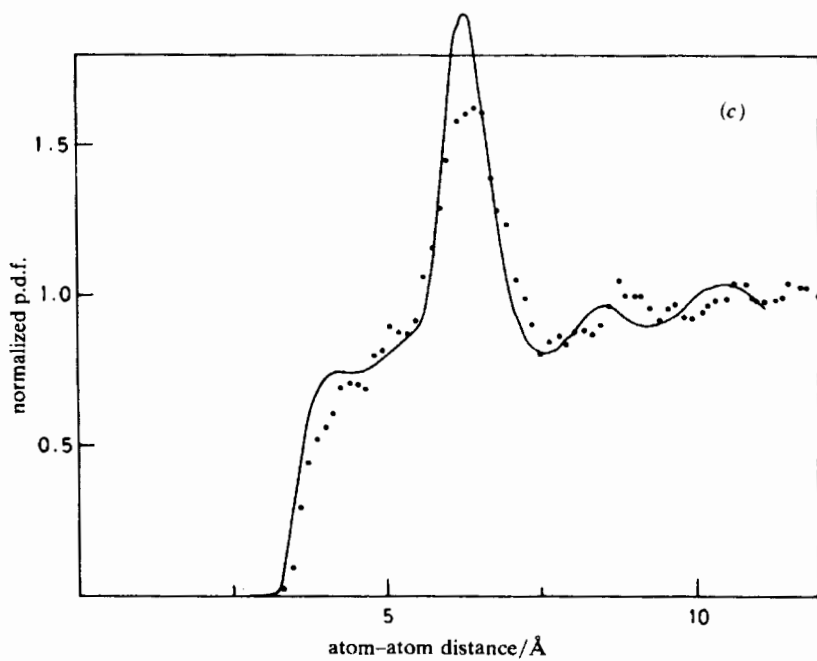


Fig. 5. Atom-atom p.d.f. for *t*-butyl chloride. (—) Liquid at 293 K; ●, rotator 1 at 228 K. (a) Carbon-carbon; (b) methyl-methyl; (c) chlorine-chlorine; (d) carbon-chlorine; (e) carbon-methyl; (f) methyl-chlorine.

**Fig. 5.** (continued)

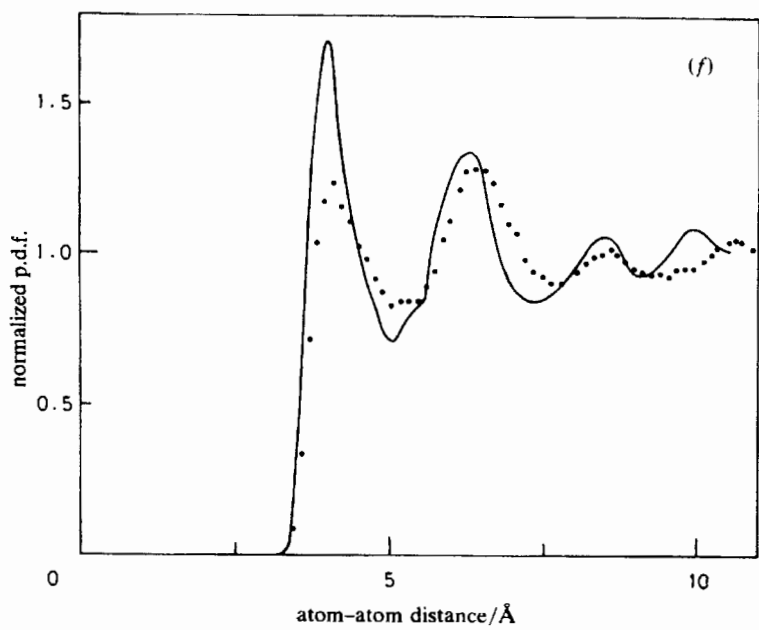
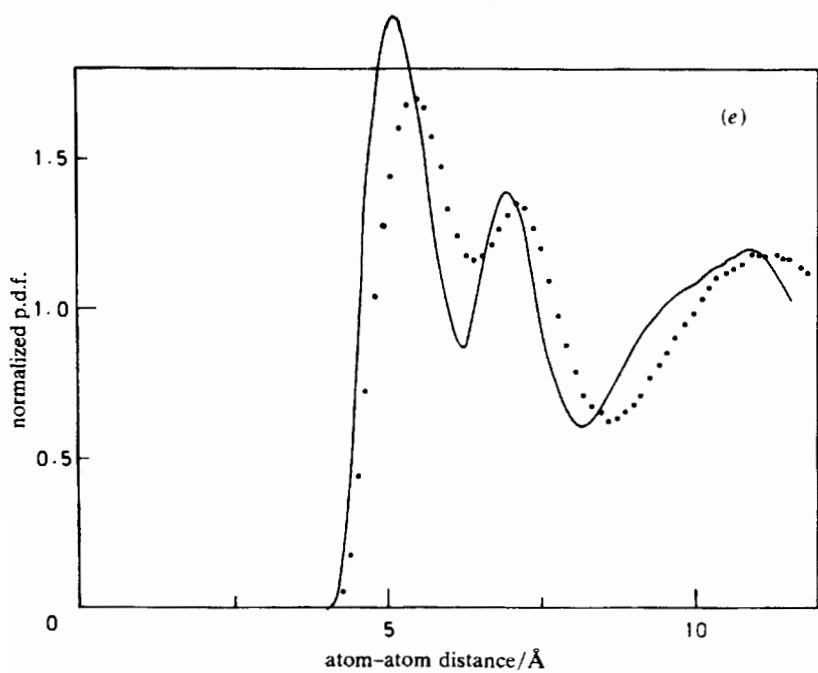


Fig. 5. (continued)

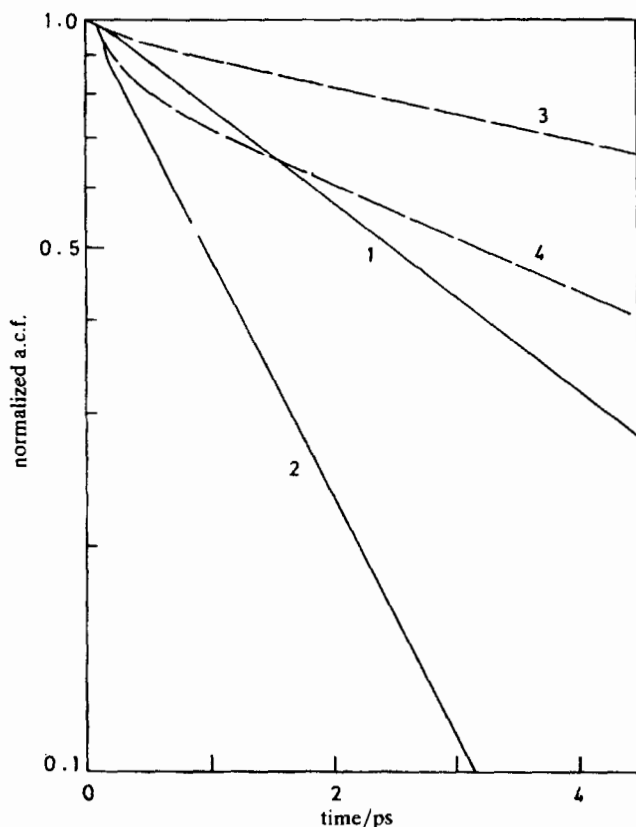


Fig. 6. (—, 1) P_1 (first-rank) a.c.f. from neutron inelastic scattering⁶ in the rotator phase I at 235 K; (—, 2) as for 1, second-rank a.c.f. (P_2); (---, 3) $P_1(I_C)$, computer simulation at 228 K; (---, 4) $P_2(I_C)$, computer simulation at 228 K.

computer-simulated P_1 function (at 228 K) agrees well (table 1) with the measured (228 K) dielectric relaxation time¹ (8.5 ps).

The basic assumption made in deriving the results of fig. 6 from incoherent neutron scattering is that there is no interaction between molecular rotation and translation either in the laboratory or any moving frame of reference. This is not supported by the computer simulation because the relevant elements of $\langle v(t)J^T(0) \rangle$ exist (fig. 7) in the moving principal-moment-of-inertia frame. They are more structured in the computer-simulated rotator phase at 228 K than in the liquid at 293 K. This might explain why the P_1 and P_2 orientational auto-correlation functions of Mansson *et al.*⁶ (at 235 K) appear to decay too quickly in comparison with the computer-simulation results (at 228 K) or in comparison with the dielectric relaxation¹ (at 238 K). If we remind ourselves that the atom-atom and charge-charge parameters used in this computer simulation produce¹ the correct enthalpy of transition for more than one phase change in t-butyl chloride then it becomes clear that the atom-atom simulation method is a powerful and successful method of probing the details of what is really going on in these phases on a molecular scale. These results imply quite clearly that the fundamental theory of incoherent neutron scattering must be extended to account properly for rototranslation. This

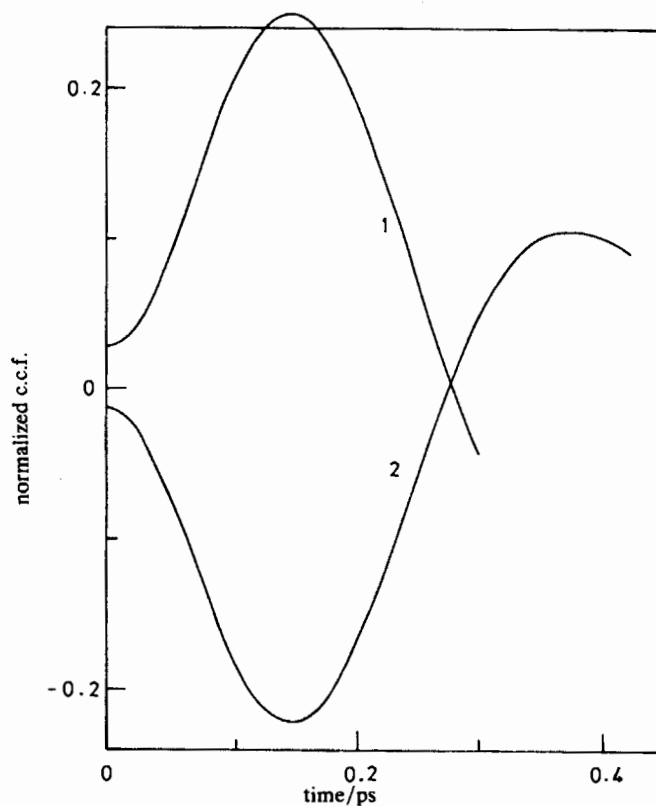


Fig. 7. As for fig. 3, rotator phase at 228 K, computer simulation.

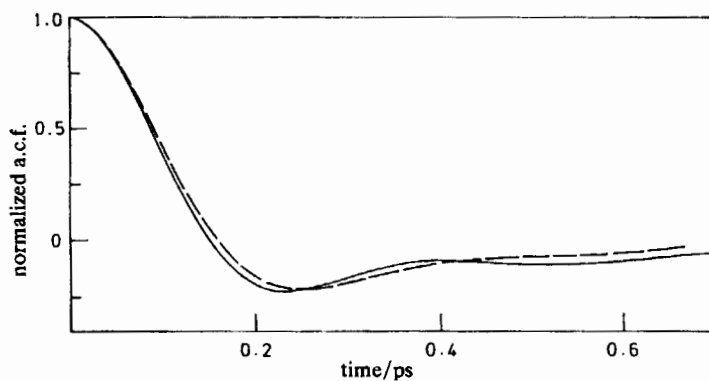


Fig. 8. As for fig. 4, rotator phase at 228 K, computer simulation.

is true even in the 'rotator' phase, a misnomer because centre-of-mass oscillation is a correlated part of the overall motion. The last point is illustrated in fig. 8, by the angular momentum and centre-of-mass linear velocity a.c.f., computed this time in the static, laboratory frame of the observer.

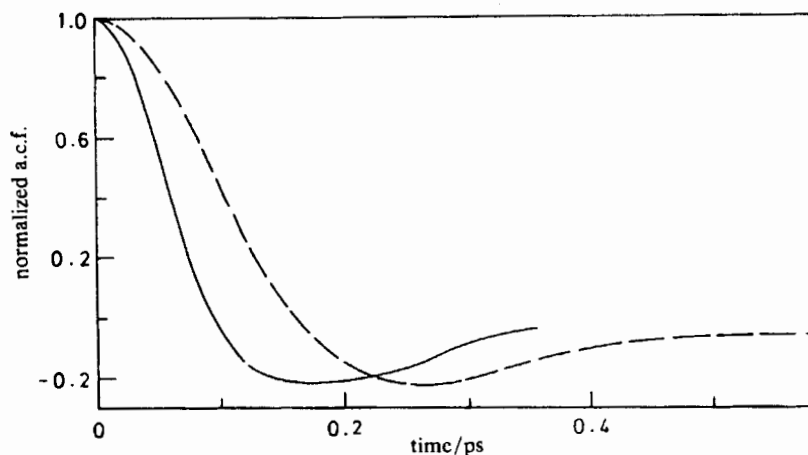


Fig. 9. (---) $\langle l_c(t) \cdot l_c(0) \rangle / \langle l_c^2 \rangle$, rotator phase at 228 K, computer simulation; (—) Fourier transform of the f.i.r. spectrum¹⁸ at 243 K.

Finally, in fig. 9, we compare the rotational velocity a.c.f. computed at 228 K with the straight Fourier transform of the far-infrared spectrum of the rotator phase taken by Reid.¹⁸ The simulated a.c.f. seems to decay, as in the liquid, faster than the measured cross-correlation function, although the shift in the time at which these functions cut the abscissa is the same in both experimental and theoretical cases, *ca.* 50%.

A referee has raised the point of whether or not the computer simulation supports the existence of potential wells in the liquid or rotator phase. This is answered in detail by the existence and nature of rotation/translation correlation in both phases. This implies the existence of potential wells because of its detailed dependence on molecular structure and symmetry. In other words, the shape of the t-butyl chloride molecule is critically important in determining the nature of the collective molecular dynamics. The profile of the interaction potential between two t-butyl chloride molecules therefore contains maxima and minima. The existence of a well defined peak in the computer-simulated far-infrared spectrum also points to the existence of barrier-well structure, as discussed by Haffmans *et al.*²⁵

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