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Computer Simulation of Some Spectral Properties of Liquid Acetone

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Computer simulation is used to produce a number of correlation functions and correlation times for liquid acetone at 293 K, 1 bar. These are compared with data from a range of techniques, including dielectric relaxation, far-infrared, infrared and Raman spectroscopy, depolarised Rayleigh scattering, spin–spin n.m.r. relaxation (both inter- and intra-molecular), Rayleigh wing 'power spectra', electro-optic and optical Kerr effect, resonance Raman spectroscopy and more specialised electro-optical techniques. The pattern of information from the computer simulation is similar, in general, to that from the spectroscopic measurements. There are some inconsistencies, namely in the n.m.r. translational correlation time and in the Raman C=O stretch correlation time. The simulation technique is used to produce elements of the rototranslational correlation matrix for acetone in the moving frame of reference.

The molecular dynamics of liquid acetone have been investigated with several complementary techniques, but it is difficult to obtain from these data a consistent overall viewpoint. In this paper we aim to produce a variety of dynamical data for liquid acetone from a simple model of the intermolecular potential between acetone molecules using the technique of computer simulation. This model is relatively crude, but is sufficiently realistic to support or contend some of the conclusions reached in the literature using spectroscopic data. Many of the spectroscopic techniques available to study molecular motion by bandshape transformation have been applied to liquid acetone.

Koga *et al.*[1] have used infrared bandshape analysis to study the anisotropy of rotational diffusion through three correlation times, τ_A, τ_B and τ_C, defined about the three inertial axes A, B and C (in conventional notation). In non-dipolar solvents the ratio $\tau_A : \tau_B : \tau_C$ does not vary very much from solvent to solvent. Reorientation about the B axis is more restricted, however. In dipolar solvents the correlation times are longer, especially τ_B. The Favro model[2] of rotational diffusion produces the result $\tau_A : \tau_B : \tau_C = 1.02 : 1.00 : 0.88$, in contrast to the observed $1.3 : 1.0 : 1.1$ (except in CS_2). Using[1] van der Waals radii the excluded volume about each axis is $V_A = 55.1$ Å^3, $V_B = 44.4$ Å^3 and $V_C = 48.5$ Å^3, which does not explain the order of the three correlation times. These authors observe that only motions about the A and C axes are restricted by dipole–dipole interactions. This is a relatively early paper, however, and it is unlikely that sufficient account was taken of vibration–rotation coupling, a difficult problem which remains to be solved satisfactorily.

The paper of Dill *et al.*[3] on the Rayleigh-scattered bandshape of liquid acetone under hydrostatic pressure remains one of the most useful in the available literature. These authors have provided angular position correlation functions and angular velocity correlation functions for liquid acetone at 1 bar, 293 K. We shall aim to compare the angular velocity correlation functions with the equivalent autocorrelation function (a.c.f.) obtained from computer simulation. The light-scattering data

were compared by Dill *et al.* with the n.m.r. relaxation results on liquid acetone reported by Jonas and Bull,[4] who obtained a separate translational correlation time $\langle\tau_t\rangle_{n.m.}$ rotational correlation time $\langle\tau_2\rangle_{n.m.r.}$ and their density dependence. The n.m.r. data in acetone show that $\langle\tau_t\rangle$ has the same density dependence as the viscosity, η, but $\langle\tau_2\rangle_{n.m.r.}$ and $\langle\tau_2\rangle_{l.s.}$, the Rayleigh correlation time, are much less density dependent than $\langle\tau_t\rangle$. It was discovered that, to a good approximation, $\langle\tau_2\rangle_{n.m.r.} = \langle\tau_2\rangle_{l.s.}$. This can be interpreted in two ways: either two components[3] (denoted $D_\parallel$ and $D_\perp$) of the diffusion tensor are equal or $\langle\tau_2\rangle_{l.s.}$ is related[3] to a mixture of $D_\parallel$ and $D_\perp$. We aim to resolve this question by computer simulation.

Schindler *et al.*[5] have just reported a Raman study of pressure effects in liquid acetone. The Raman bandshape of the symmetric C=O stretch at 1710 cm^{-1} was measured up to 4 kbar over a wide range of temperature. The consideration of the experimental linewidth and frequency data led to the conclusion that intermolecular dipole–dipole coupling is responsible for unusual effects as the hydrostatic pressure is increased. The frequencies of the polarised (VV) and depolarised (VH) bands in acetone differ by several wavenumbers. These authors point out that hydrodynamic theories usually consider repulsive forces as the main source of line broadening, but in reality the increase or decrease of half-width (and frequency) with pressure depends on the relative importance of attractive and repulsive intermolecular forces which influence a specific vibration. Schindler *et al.* expect that repulsive forces play a minor role in acetone compared with the attractive forces, and in the computer simulation we represent these by point charges from a recent MINDO/3 calculation by Wellington and Khowaiter.[6]

However, the interpretation of the Raman bandshapes measured by Schindler *et al.* was based on the simple Kubo stochastic bandshape theory.[7] Here the vibrational correlation function $\phi_v(t)$ is given by

$$\phi_v(t) = \exp\left(-\langle\Delta_\omega^2\rangle\{\tau_m^2[\exp(-t/\tau_m)-1]+\tau_m t\}\right) \quad (1)$$

where $\langle\Delta_\omega^2\rangle$ is the root-mean-square frequency displacement of the instantaneous transition frequency, sometimes equal to the vibrational second moment m_{2v}. The parameter τ_m is a modulation time. Schindler *et al.* define it as the correlation time for frequency fluctuations. It is rotovibrational, but confusion exists in the literature concerning its origin. Oxtoby *et al.*[8] have equated it to the duration time of a collision, Doge[9] and Wang[10] equate it to the rotational correlation time and Lynden-Bell[11] to the correlation time governing translational diffusion. Clearly these interpretations cannot all be correct, and a molecular dynamics simulation, even with a relatively simple model of the acetone pair-potential, will help in clearing the confusion.

Liquid acetone has been the object of a study by Perrot *et al.*[12] using depolarised Rayleigh light scattering. Denoting the intensity of the scattered light by $I(\omega)$, then the function $\omega^2 I(\omega)$ peaks at 64.5 cm^{-1} with a half-width of 92 cm^{-1}. These authors point out that $\omega^2 I(\omega)$ is comparable[13] with the far-infrared power absorption coefficient $\alpha(\omega)$ (in neper cm^{-1}). The latter has been measured by Reid and Evans[14] in 10% v/v decalin solution, where the peak absorption is at 52 cm^{-1}, with an Evans–Reid torque factor[15] of 1495 g m. We aim to computer-simulate the far-infrared band of liquid acetone in this paper and compare it directly with the far-infrared data and the Rayleigh scattering data $\omega^2 I(\omega)$ in the time domain. Liquid acetone is ideal for this kind of intertechnical comparison because its far-infrared and depolarised Rayleigh characteristics are clear of overlapping proper modes at high frequency. Pure liquid acetone is an intense absorber in the far-infrared, and we expect that collision-induced absorption effects[15] will be minimised.

This expectation is supported experimentally by the fact that the integrated absorption intensity (A) of the $\alpha(\omega)$ in the far-infrared is linearly dependent on the number density (N) of acetone solute molecules in non-dipolar solvents such as decalin.[14] Induced effects mean that A should be proportional to a power of N different from one. Our computer simulation does not involve molecular polarisability and cannot account for collision-induced absorption. It will be interesting to see, therefore, whether the experimental far-infrared $\alpha(\omega)$ and computer-simulated $\alpha(\omega)$ match up satisfactorily in pure liquid acetone.

Some of the new non-linear electro-optic techniques have been used to investigate the subtler equilibrium and dynamical properties of liquid acetone. It has been investigated using both electro-optic and picosecond optical Kerr-effect techniques developed, respectively, by Khanarian and coworkers[16] and Ho and Alfano.[17] Khanarian and coworkers point out that acetone is a strongly dipolar and optically anisotropic molecule and the electro-optical Kerr effect can be traced to the orientation of dipole moments. Burnham and Gierke[18] have used results from the optical Kerr effect, Cotton–Mouton effect and light scattering to obtain orientational pair correlation functions for liquid acetone from the theory of Ladanyi and Keyes.[19] Orientational pair correlation parameters for liquid acetone were derived but having values ranging from 0.5 (Kerr effect) to 1.4 (anisotropic Rayleigh scattering). [See also ref. (20).]

The dynamics of inhomogeneous Raman bandshapes have been treated by George *et al.*[20] employing the relatively simple Kubo theory[7] (as used by Schindler *et al.*[5]) to cover both the slow and fast processes present. Our far-infrared spectra and computer simulation show, at least for rotational motions in liquid acetone, that the Kubo theory is oversimplified. However, the computed molecular dynamics of liquid acetone are anisotropic,[21] and this supports the relatively large value of inhomogeneous bandwidth measured by George *et al.*

INTERCOMPARISON OF EXPERIMENTAL DATA

The traditional source of information concerning the rotational diffusion of dipolar molecules is dielectric relaxation.[15] At 293 K the relaxation time of pure liquid acetone is[22] 3.1 ± 0.1 ps decreasing to 2.5 ± 0.3 ps at 313 K. In 0.19 mole fraction CCl_4 solution the relaxation time decreases slightly to 2.9 ± 0.3 ps at 293 K. The effect of dilution is therefore not pronounced, and this is also true of the far-infrared, the high-frequency adjunct[15] of the dielectric dispersion curve. It is sometimes remarked that the dielectric relaxation time and the rotational correlation time obtainable from infrared bandshapes (Koga *et al.*[1]) contain the same information. This is at best an approximation, because the dielectric relaxation time is multimolecular in origin,[15] and the infrared correlation time is a single molecule property more properly termed a rotovibrational correlation time. The dielectric relaxation time as reported in the literature is often merely the inverse of the measured dielectric loss peak frequency, and care must be exercised before any meaning can be attached to this on the intermolecular level. In dilute CCl_4 solution the three correlation times calculated by Koga *et al.*[1] are $\tau_A = 1.29$ ps, $\tau_B = 1.01$ ps and $\tau_C = 1.11$ ps. These contrast with the dielectric relaxation time of acetone in CCl_4: 2.9 ± 0.3 ps.

The infrared and dielectric correlation times are first-rank Legendre in nature,[15] whereas spin–spin n.m.r. and depolarised Rayleigh correlation times are second rank. Bull and Jonas[4] provide a reorientational spin–spin n.m.r. correlation time of 0.75 ps for pure liquid acetone at 296 K and 1 bar, which increases to 1.0 ps at

2 kbar and 296 K. The translational correlation times under the same conditions are 4.8 and 11.0 ps, respectively, *i.e.* more dependent on density.[3] In deriving these times Bull *et al.* made use of rotational diffusion theory[15] assuming isotropic diffusion. This means that the mean first-rank correlation time should be three times the mean second-rank correlation time. Comparing the dielectric relaxation time in pure liquid acetone at 1 bar (3.1 ± 0.1 ps) with the n.m.r. spin–spin time (0.75 ps) this seems to be roughly the case, but our earlier remarks imply that such a comparison, often made, is almost meaningless and any conclusion drawn therefrom spurious. The only self-consistent source of data for such a comparison comes from computer simulation. The measurements and analysis of Koga *et al.*[1] produce first-rank rotational correlation times which are roughly the same as the n.m.r. spin–spin times, and these and the depolarised Rayleigh scattering investigations of Dill *et al.*[3] clearly show that the theory of rotational diffusion does not explain the molecular-dynamical properties in liquid acetone.

Another traditional method of analysis reported in the literature is to compare depolarised Rayleigh correlation times[3] with Raman[5] and n.m.r.[4] correlation times. Rayleigh times are multimolecular in origin,[15] and those from the other two techniques are supposed to be unaffected directly by intermolecular cross-correlations. Dill *et al.*[3] report that the Rayleigh and n.m.r. correlation times for pure liquid acetone are the same at both 1 bar and 2.0 kbar. This result contrasts markedly with that of the equivalent 'first-rank' procedure, which is to compare dielectric[22] and infrared[1] rotational correlation times. We have mentioned already that the former is three times the latter at 293 K and 1 bar in dilute CCl_4 solution, where cross-correlations between acetone molecules are *a priori* small, given no dimer formation. The Raman correlation times of Schindler *et al.*[5] (using Kubo's theory[7]) are 0.27 ps for pure liquid acetone at 1 bar and 298 K, and 0.55 ps at 2 kbar and 298 K. These are considerably shorter than those from the spin–spin n.m.r. and depolarised Rayleigh scattering and seem to have little significance in terms of rotational dynamics, except that they are considerably more dependent on density. They are derived from the C=O stretch. We have mentioned that the Kubo correlation times derived by Schindler *et al.* have variously been attributed different origins.[5,8–11] It seems clear that they cannot be translational, because the n.m.r. results[4] produce a translational correlation time at 296 K and 1 bar of 4.8 ps (and 11.0 ps at 2 k bar). These are an order of magnitude longer than the Raman correlation times of Schindler *et al.* but interestingly have a similar density dependence. They are too short to be purely rotational in origin, and are most likely best regarded as empirical parameters resulting from the application of data of complex origin of an oversimplified bandshape theory. The shortcomings of the Kubo theory are clearly exposed in the far-infrared[15] and by the use of computer simulation. It has been developed considerably by Evans *et al.*[15] in an attempt to explain the far-infrared data. We mention that the picosecond laser-induced inhomogeneous broadening of Raman bands reported by George *et al.*[20] clearly shows that the rotovibrational diffusion in liquid acetone is anisotropic, and our computer simulation must also aim to produce this result self-consistently.

There is therefore some inconsistency in the available literature concerning the molecular dynamics of liquid acetone, and we shall attempt to clarify matters with a relatively simple computer simulation of the relevant dynamical properties.

MOLECULAR-DYNAMICS ALGORITHM

The rotational and translational equations of motion are integrated with basically the same numerical method, which we have described more fully

elsewhere.[23a] The interaction between $(CH_3)_2CO$ molecules is modelled with a 4×4 Lennard-Jones atom–atom 'core' with point charges localised at each site. The CH_3 group is taken as an entity and the complete set of parameters are as follows: $\sigma(CH_3—CH_3) = 3.92$ Å; $\sigma(C—C) = 3.00$ Å; $\sigma(O—O) = 2.80$ Å; $\varepsilon/k(CH_3—CH_3) = 72.0$ K; $\varepsilon/k(C—C) = 50.0$ K; $\varepsilon/k(O—O) = 58.4$ K. The cross-terms are evaluated with the Lorentz–Berthelot combining rules. The $—CH_3$ parameters are taken[23b] from a paper by Bellemans *et al.*[23c] on the molecular-dynamics simulation of n-alkanes, the O—O parameters from molecular crystal data,[22c] and the C—C parameters from our previous work on CH_2Cl_2, $CHCl_3$, $CHBr_3$ and CH_3OH. We adhere to our method of using literature values without adjustment. The value of this general approach is that it will allow us to see, eventually, whether atom–atom parameters are transferable between molecules in the first approximation. Refinement of the intermolecular pair potential is, in our opinion, a separate issue, requiring an intense experimental effort to obtain vapour-phase data on constants such as dielectric virial coefficients, viscosity, *etc.*, since molecular interactions in the liquid are not pairwise additive. Simulation algorithms use an effective pair potential.

Electrostatic interactions are important in liquid acetone, the latest piece of experimental evidence coming from Schindler *et al.*[5] We have attempted to represent these with the simple approximation of point charges, taken from a MINDO/3 calculation by Wellington *et al.*[6] This provides $q_{CH_3} = -0.032|e|$; $q_C = 0.566|e|$; $q_O = -0.502|e|$, where e is the electric charge. The magnitude of these charges means that our use of only 108 molecules with periodic boundary conditions introduces artificial ordering. The importance of this artifact can only be judged *a posteriori* by how well the simulation fits the appropriate experimental spectral data, such as those in the far-infrared, or by simulating the Kirkwood correlation factors, for example of Khanarian and coworkers.[16] If the periodic boundary conditions are affecting the computation we might expect the computed values of g_1, g_2 and g_3 to be over-emphatic.

The simulation run was initiated at 293 K, with a molar volume of 73.5 cm^3 at 1 bar. The 108 acetone model potentials were arranged initially on an f.c.c. lattice in a cube of half-side 11.81 Å, the potential cut-off distance. This is about three times the largest Lennard-Jones σ value used. According to Bossis *et al.*,[23e] who have initiated a method of computer simulation with no periodic boundary conditions, medium-range correlations between intensely dipolar molecules disappear at *ca.* 10 Å from a given molecule; however, properties that specifically depend on longer-range correlations, such as the absolute magnitude of the static permittivity, cannot be calculated with periodic boundary conditions, and we have not attempted to do so.

Different minimum-image criteria were employed for Lennard-Jones and charge–charge interactions. For these former, atomic sites were considered independently of which molecules they belonged to. For charges, the minimum-image convention and cut-off criterion were applied to the inter-centre-of-mass distance, accounting for all 16 contributions for each pair of molecules.

The time step employed, 0.0025 ps, helped to conserve total energy to within 0.5%. *Ca.* 3000 time steps were used for equilibration before starting to store data on disk for the evaluation of statistical functions for comparison with spectral results.

The acetone molecule is an asymmetric top. The three principal moments of inertia used in the computer-simulation program were calculated from structural data. This produced $I_A = 71.2\times10^{-40}$ g cm^2, $I_B = 83.0\times10^{-40}$ g cm^2 and $I_C = 154.2\times10^{-40}$ g cm^2. The dipole axis in this notation is that of I_B, and the dipole unit vector $\boldsymbol{e}_B$ (see table 1 later).

TABLE 1.—COMPARISON OF EXPERIMENTAL AND COMPUTER-SIMULATED CORRELATION TIMES FOR LIQUID ACETONE

technique	experimental correlation time/ps	simulated autocorrelation time[a]/ps (at 293 K and 1 bar)
dielectric relaxation (i) pure acetone[15,22] (ii) 20% mole fraction in CCl_4[22]	(i) 3.1 ± 0.1 (ii) 2.9 ± 0.3	$\tau_{1A} = 3.2$; $\tau_{1B} = 2.2$; $\tau_{1C} = 2.2$
infrared bandshapes[1] in dilute solution	$\tau_{1A} = 1.29$, $\tau_{1B} = 1.01$, $\tau_{1C} = 1.11$	$\tau_{1A} = 3.2$; $\tau_{1B} = 3.3$; $\tau_{1C} = 2.2$
spin–spin n.m.r.,[4] rotational correlation time	0.75	$\tau_{2A} = 0.75$; $\tau_{2B} = 0.6$; $\tau_{2C} = 0.6$
n.m.r. translational[4]	4.80	$\tau_t \doteqdot 1.0$ ps
Raman, C=O stretch[5]	0.27	$\tau_{2B} = 0.6$
Rayleigh scattering[3]	0.75	$\tau_{2A} = 0.75$; $\tau_{2B} = 0.6$; $\tau_{2C} = 0.6$
	frequency maximum/cm^{-1}	
far-infrared power absorption (i) pure acetone (this work) (ii) 10% acetone in decalin[14]	(i) 57 (ii) 52	see fig. 4
Rayleigh scattering[12] 'power spectrum'	64.5	see fig. 4

[a] The dipole unit vector is e_B.

EXPERIMENTAL

For comparison with the computer simulation we have recorded the far-infrared spectrum of acetone using interferometric techniques and a new Apollo Instruments far-infrared laser system. Five spot-frequency measurements are reported that agree well with the broad band produced by Fourier-transform spectroscopy. Spot frequencies were chosen in the region of maximum absorption and at higher frequencies to define accurately the decay of the band. This is essential to produce a reliable correlation function, by subsequent transformation to the time domain, which may then be directly compared with results from the simulation (see fig. 4 later).

Details of our interferometric system have been published elsewhere. Our Apollo model 120 laser system is a tunable, optically pumped system designed for peak power output on the 84 cm^{-1} line of methyl alcohol. The laser is pumped by a model 560 tunable flowing carbon dioxide laser with outputs >40 W in the c.w. mode on many of the stronger transitions. It is tunable over 85 wavelengths. The complete system is electronically stabilized, thus maintaining the CO_2 laser at optimum pumping frequency and the far-infrared cavity length at the peak of cavity resonance.

RESULTS AND DISCUSSION

The correlation times from the computer simulation at 293 K and 1 bar are listed in table 1 and compared with some of the available experimental data. Fig.

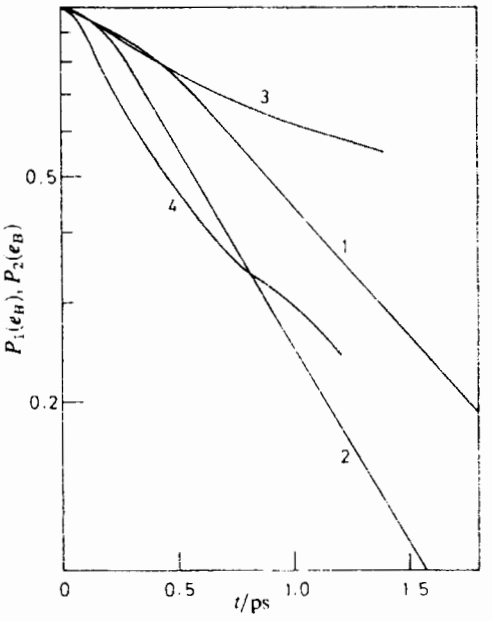

FIG. 1.—First-rank orientational autocorrelation functions $P_1(e_B)$. (1) Acetone in acetonitrile[1] in infrared bandshape analysis; (2) as for (1) but in n-hexane; (3) computer simulation; (4) as for (3) but second-rank orientational a.c.f. $P_2(e_B)$.

1 compares the simulated dipole autocorrelation function $\langle e_B(t) \cdot e_B(0) \rangle$ with the results of Koga *et al.*[1] in (1) acetonitrile and (2) n-hexane. Results from other solvents[1] fall between these limits. Curve 4 of fig. 1 is the computer-simulated P_2 function, *i.e.* $\frac{1}{2}\langle 3e_B(t) \cdot e_B(0)^2 - 1 \rangle$. The area beneath this gives the simulated correlation time, labelled τ_B in table 1 and compared with the n.m.r., Raman (C=O stretch) and Rayleigh scattering results. The simulated infrared rotational correlation time τ_B is 2.2 ps, which is compared with the infrared and dielectric relaxation measurements in table 1. Note that the dielectric relaxation time is a weighted mean[2,15] of the three simulated correlation times about the three principal moments of inertia axes. The experimentally measured dielectric relaxation time is longer than the simulated correlation times. This conforms with a pattern now emerging among parallel computer simulations[23] on CH_2Cl_2, $CHCl_3$, $CHBr_3$, CH_3F, CH_3CN and CH_3I. This is probably due to our calculation of autocorrelation functions rather than the cross-correlation functions observed[15] in dielectric relaxation. However, it is clear from table 1 that even in the intensely dipolar acetone, the simulation produces results which are capable of describing the trend observable with a number of different techniques.

The anisotropy of the rotational diffusion in acetone, as observed by Koga *et al.*[1] and by George *et al.*,[20] for example, produces a pattern of correlation times (table 1) which are reproduced by the computer simulation. The ratio $\tau_A : \tau_B : \tau_C$ is *ca.* 1.3 : 1.0 : 1.1 from infrared band-shapes and *ca.* 1.5 : 1.0 : 1.0 from the simulation. Fig. 2 is a repeat of fig. 1 for the e_C vector autocorrelation functions. The experimental results[1] refer to (1) carbon tetrachloride and (2) cyclohexane. As in fig. 1, experimental results[1] in other solvents fall between these extremes.

Dill *et al.*[3] have produced an angular velocity correlation function from their work on the depolarised Rayleigh wing of acetone, and in fig. 3 this is compared

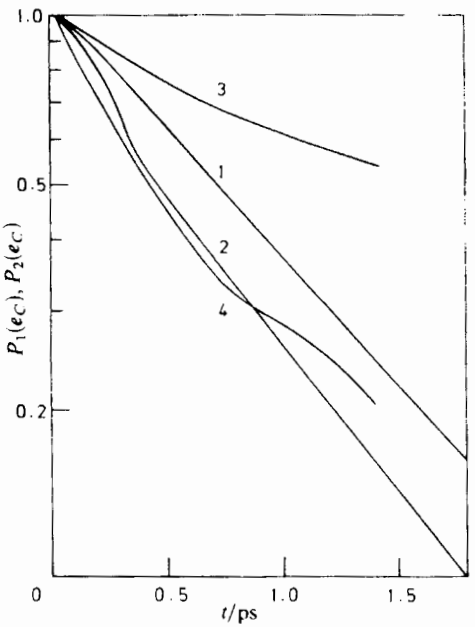

FIG. 2.—As for fig. (1) for the unit vector e_C. (1) Infrared bandshape analysis,[1] acetone in carbon tetrachloride; (2) in cyclohexane; (3) computer simulation; (4) second-rank orientational a.c.f. $P_2(e_C)$.

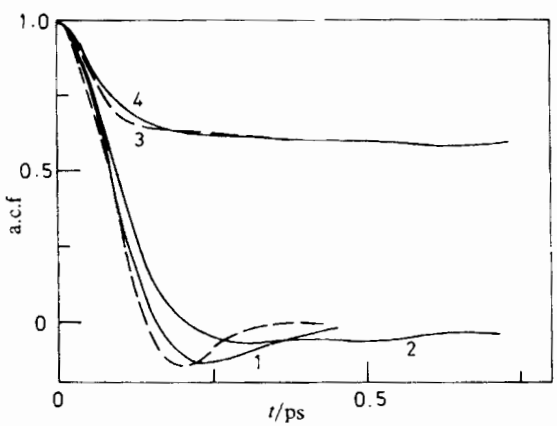

FIG. 3.—(– – – –) Angular velocity correlation function from depolarised Rayleigh scattering.[3] (1) Simulated angular-velocity a.c.f. (——); (2) simulated angular-momentum a.c.f. (——); (3) simulated second-moment angular-velocity a.c.f.: $\langle \boldsymbol{\omega}(t)\cdot\boldsymbol{\omega}(t)\boldsymbol{\omega}(0)\cdot\boldsymbol{\omega}(0)\rangle/\langle\omega^4(0)\rangle$ (– – –); (4) simulated second-moment angular-momentum a.c.f.: $\langle \boldsymbol{J}(t)\cdot\boldsymbol{J}(t)\boldsymbol{J}(0)\cdot\boldsymbol{J}(0)\rangle/\langle J^4(0)\rangle$ (——).

with (1) the computer simulated (and normalised) angular velocity autocorrelation function $\langle \boldsymbol{\omega}(t)\cdot\boldsymbol{\omega}(0)\rangle/\langle\omega^2(0)\rangle$ and (2) the normalised angular-momentum autocorrelation function $\langle \boldsymbol{J}(t)\cdot\boldsymbol{J}(0)\rangle/\langle J^2(0)\rangle$. (In an asymmetric top with C_{2v} symmetry such as acetone these two functions do not have the same time dependence.) Up to 0.2 ps the experimental and simulated functions decay similarly (fig. 3), which is possibly fortuitous, because the Rayleigh wing is a multimolecular phenomenon

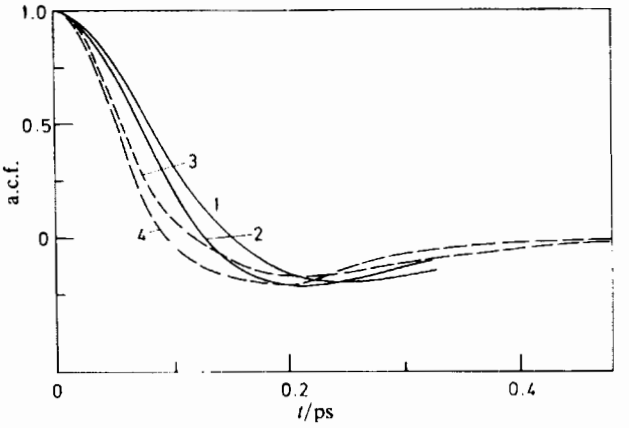

FIG. 4.—(1) Computer-simulated rotational velocity a.c.f.[15] of the dipole unit vector: $\langle \dot{\boldsymbol{e}}_B(t) \cdot \dot{\boldsymbol{e}}_B(0) \rangle / \langle \dot{e}_B^2(0) \rangle$ (——); (2) as (1) but $\langle \dot{\boldsymbol{e}}_C(t) \cdot \dot{\boldsymbol{e}}_C(0) \rangle / \langle \dot{e}_C^2(0) \rangle$ (——); (3) Fourier transform of the far-infrared power coefficient of a 10% solution of acetone in decalin[14] (– – – –); (4) Fourier transform of the far-infrared band of pure liquid acetone (this work) (– – – –).

in the sense that cross-correlations of molecular orientation are supposed to play an intrinsic part in its make-up, while the simulated function in fig. 3 is constructed from autocorrelations. Nevertheless, there is independent evidence that cross-correlations are relatively unimportant in pure liquid acetone. The shift of the dielectric relaxation time on dilution (table 1) is small, and Dill *et al.* have produced a Rayleigh-wing relaxation time identical with the single-particle spin–spin n.m.r. correlation time (0.75 ps). Using Kerr-effect methods, Beevers and Khanarian[16] have produced a Kirkwood factor for liquid acetone at 293 K of 0.8. In the complete absence of cross-correlations this is 1.0. They also produce second- and third-order Kirkwood factors incorporated in a quantity G, which is unity in the hypothetical absence of nearest-neighbour interactions. At 293 K this is measured as 1.32. Finally, the shift on dilution of the far-infrared peak in acetone (table 1) is relatively small.

In the purely dynamic sense, the simulated second-moment autocorrelation functions of fig. 3 are transiently non-Gaussian, but go to the correct Gaussian limit[24] of *ca* 0.6.

In fig. 4 we illustrate two of three computer-simulated rotational velocity autocorrelation functions[15] $\langle \dot{\boldsymbol{e}}_B(t) \cdot \dot{\boldsymbol{e}}_B(0) \rangle / \langle \dot{e}_B^2 \rangle$ and $\langle \dot{\boldsymbol{e}}_C(t) \cdot \dot{\boldsymbol{e}}_C(0) \rangle / \langle \dot{e}_C^2 \rangle$. These are compared with the Fourier transforms of the far-infrared power spectra of pure liquid acetone (this work), acetone in 10% v/v decalin,[14] and of the 'Rayleigh power spectrum', $\omega^2 I(\omega)$, obtained by Perrot *et al.*[12] The shapes of these functions are similar, with characteristic[15] long negative tails. The similarity seems to suggest that cross-correlations and collision-induced phenomena[15] are *not* contributing significantly in pure liquid acetone to either the far-infrared or Rayleigh wing spectrum. These effects are, of course, absent in the autocorrelation function computer simulation. The result, illustrated in fig. 4, again falls into a pattern which is now beginning to establish itself in several computer simulations;[23] the far-infrared (or 'Rayleigh power spectrum') bandshapes are similar, when scaled, to the results from simulation. This suggests that periodic boundary conditions are not a deterrent in this kind of work, even with long-ranging charge–charge interactions.

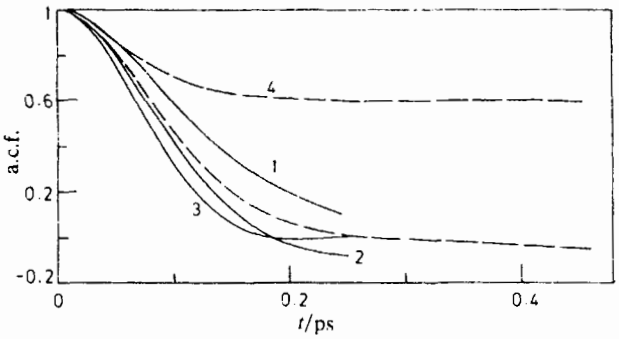

FIG. 5.—Centre-of-mass velocity autocorrelation functions simulated in the laboratory and moving frames of reference: (– – – –) $\langle \boldsymbol{v}(t)\cdot\boldsymbol{v}(0)\rangle/\langle v^2\rangle$, laboratory frame; (1) $\langle v_A(t)v_A(0)\rangle/\langle v_A^2\rangle$, principal moment of inertia frame: the moving frame (——); (2) $\langle v_C(t)v_C(0)\rangle/\langle v_C^2\rangle$ (——); (3) $\langle v_B(t)v_B(0)\rangle/\langle v_B^2\rangle$ (——) (note that the component autocorrelation functions are not isotropic in the moving frame of reference); (4) the kinetic-energy a.c.f. $\langle v^2(t)v^2(0)\rangle/\langle v^4\rangle$, which goes to the Gaussian limit[24] of 3/5 in any frame of reference (– – –).

There are some inconsistencies in table 1. The most serious is that in the velocity correlation time, measured by Jonas and Bull[4] to be 4.80 ps. In contrast, the laboratory frame velocity autocorrelation function simulated by computer (fig. 5) is not exponential, as assumed by Jonas and Bull in their derivation. It cuts the abcissa at 0.2 ps, and shows the characteristic long negative tail. This pattern is repeated in a parallel simulation[23] of $CHBr_3$, where the n.m.r. correlation time measured by Sandhu[25] is far longer than the computer simulated centre-of-mass velocity correlation time (the area beneath the a.c.f.). This may be due to definition. In the extreme narrowing limit the translational n.m.r. correlation time sometimes quoted in the literature (τ_t) is not τ_v, but rather

$$\tau_t = \frac{ma}{12kT\tau_v}$$

where m is the molecular mass and a the radius. Using $a = 2.0$ Å and our simulated τ_v of *ca.* 0.08 ps we obtain $\tau_t = 1.0$ ps. This is recorded in table 1. It is well established by now[15] that the centre-of-mass velocity a.c.f. does not decay exponentialiy, but is oscillatory, with a long negative tail and positive longer time tail decaying as $t^{-3/2}$. The correlation time or area beneath the a.c.f. is always small. The n.m.r. data reduction on the other hand[4,25] assumes a Stokes-law behaviour, implying that the a.c.f. is an exponential, with, of course, a finite correlation time.

The other inconsistency in table 1 is interexperimental in nature. The Raman (C=O stretch)[5] band, after data reduction with Kubo's model,[7] produces a correlation time of 0.27 ps, which compares with a simulated τ_B value of 0.6 ps and a spin–spin n.m.r. rotational correlation time[4] of 0.75 ps. Clearly the Raman correlation time is too short. The reason may be that it measures a rotovibrational phenomenon rather than a purely rotational one. Even if the latter were the case, however, the Kubo model is not an adequate description of molecular dynamics in liquids.[15] This is seen clearly in the far-infrared,[14,15] where the power absorption is effectively a second moment of the dielectric-loss spectrum. The Kubo model does not produce the basic features of the Poley absorption[15] in the far-infrared, and only appears to work in the Raman case because of the relative insensitivity of the latter to short-time details (*e.g.* fig. 4) of what is actually going on. However,

the Raman spectrum of molecular liquids can be useful when interpreted more simply and straightforwardly, *e.g.* by taking the correlation time as the inverse half-width of the band under study, making sure that rotational and vibrational effects are adequately decoupled. A referee has pointed out that the correlation time for the second-order orientational process derived from ref. (5) is from the isotropic band. This is very uncertain in origin. Schindler *et al.*[5] provide an anisotropic spectrum of half-width 6.5 cm^{-1}. Taking the inverse half-width gives us an isotropic correlation time of 0.82 ps.

Clearly therefore, the computer simulation method (oversimplified as it is) is capable of distinguishing correctly for acetone between experimental methods which produce sensible descriptions at one state point of liquid-state molecular dynamics and those which do not. Furthermore the pattern emerging from intertechnical comparison is broadly similar to that coming out of the computer (table 1). At the same time, the representation we have used of the acetone–acetone pair potential is empirical, and there are sensitive methods available in the gas phase which should be used to refine our knowledge in this area. Prominent among these is the measurement of dielectric virial coefficients.[26] An attempt should also be made to involve polarisability in the molecular-dynamics simulation. However, the pair-additivity concept for intermolecular potentials with or without polarisability is a dubious one in the liquid state, and for this reason the most accurate of gas-phase pair potentials may not work in the liquid. It is nonetheless clear that our empirical potential is a basis upon which the available spectroscopic data seem to rest fairly solidly (table 1). It is equally clear that the available analytical theory (*e.g.* the Favro or Kubo models) is not capable of dealing with the range of data covered in this paper without considerable and complex elaboration.[15] Therefore it seems justifiable to continue to use site–site (or atom–atom) models as a basis for the computer simulation of some of the more accessible spectroscopic properties of molecular liquids. It is no coincidence that the r.i.s.m. models of Chandler *et al.*[27] seem to have been the most successful in describing the structural properties of molecular liquids, as opposed to their dynamic (or frequency dependent, spectroscopic) properties.

Thus having attempted to compare our simulation with experimental data, if only at one state point, 293 K and 1 bar, we can now attempt to use the computer as a means of producing information about the molecular dynamics of liquid acetone otherwise inaccessible. A satisfying example is the interaction of rotation with translation, important in the theory of thermal neutron scattering, although usually ignored and implicitly important in that of other techniques of table 1. Recently Bellemans *et al.*[28] have cleared up a great deal of confusion in this area by using computer simulation to look at correlation functions of the type $\langle \boldsymbol{v}(0)\boldsymbol{J}^{\mathrm{T}}(t)\rangle$ in a *moving* frame of reference. Depending on the molecular symmetry, some elements of the matrix $\langle \boldsymbol{v}(0)\boldsymbol{J}^{\mathrm{T}}(t)\rangle$ exist for $t>0$ and quantify the nature of rotation–translation coupling. In fig. 6 we illustrate some of these non-vanishing elemental correlation functions for acetone at 293 K and 1 bar. The non-vanishing elements are (1, 2), (2, 1) and possibly (3, 1). The noise level is indicated by the arrows at $t = 0$. By symmetry all elements should vanish at $t = 0$. For convenience, our moving frame is defined as that of the principal moments of inertia, so that $(1, 2) = (A, C)$, $(2, 1) = (C, A)$ and $(3, 1) = (B, A)$. Each correlation function is normalised by $\langle v_i^2\rangle^{1/2}\langle J_j^2\rangle^{1,2}$.

We remark that the elements are not symmetric with respect to each other, *e.g.* $(A, C) \neq (C, A)$, $(B, A) \neq (A, B)$, for C_{2v} symmetry. In a parallel simulation[23] of the C_{3v} molecules $CHCl_3$ and $CHBr_3$ the (A, C) and (C, A) elements are symmetric.

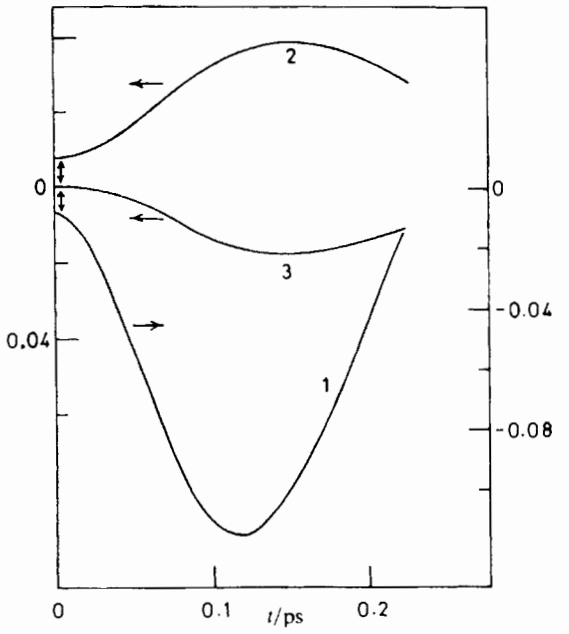

FIG. 6.—Elements of the rototranslational matrix: (1) $[\langle v_C(0)J_A(t)\rangle + \langle v_C(t)J_A(0)\rangle]/(2\langle v_C^2\rangle^{1/2}\langle J_A^2\rangle^{1/2})$, the (C, A) element $2\langle v_C^2\rangle^{1/2}\langle J_A^2\rangle^{1/2}$; (2) as for (1), (A, C) element; (3) (B, A) element. All other elements vanish for all t.

The pattern for acetone is similar[29] to that for the C_{2v} molecule CH_2Cl_2, and it is becoming clear that these moving-frame elements are sensitive to changes in molecular symmetry, moment of inertia, mass, dipole moment *etc.*: in other words, to details of the intermolecular potential of interaction working in a dynamical context. The existence of a phase change[23] in $CHBr_3$ (from liquid to plastic crystal) is dependent on the fact that the (A, B) and (B, A) elements are very small, so that rotation is almost wholly decoupled from translation, allowing the formation at 281 K and 1 bar of the aptly termed 'rotator' phase solid. In acetonitrile,[23] in contrast, the same normalised elements for the same (C_{3v}) symmetry are at least an order of magnitude bigger, peaking at ±0.21. Acetonitrile has no known rotator phase. In acetone and CH_2Cl_2 the (C, A) elements peak at −0.11 and −0.12, respectively, and these again do not form a rotator phase.

When it comes to the analytical description of these moving-frame elements (as opposed to the numerical) the traditional approach, based on the Langevin or Fokker–Planck–Kramers equations,[15] must either be rejected or elaborated. A constraint on any attempt in this direction is that $\langle \boldsymbol{v}(0)\boldsymbol{J}^{\mathrm{T}}(t)\rangle$ vanishes for all t in the laboratory frame of reference,[28] owing to the fact that the parity of $\boldsymbol{J}$ is opposite to that of $\boldsymbol{v}$. Although Grigolini *et al.*[30] have made several attempts to develop the Langevin or Fokker–Planck equation for rototranslation it is becoming clear that the answer lies in the new, non-linear methods of theoretical physics, basically because these lead us naturally towards a truer description of the intermolecular potential than the simple Langevin equation, for example, can supply. At present the situation as regards an analytical description of the curves in fig. 6 is very simple, there is none. In this case one cannot argue against the computer-simulation method as a means of understanding the subtleties of the liquid state of molecular matter.

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