

MOLECULAR DYNAMICS AND STRUCTURE OF LIQUID ACETONITRILE - A REVIEW AND COMPUTER SIMULATION.

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ABSTRACT

Most of the last decade's literature on liquid acetonitrile (dynamics and structure) is reviewed briefly and analysed with a computer simulation. This uses a 6 x 6 site-site model for the pair potential with electrostatics approximated by point charges. The NMR relaxation data are fairly consistent with the results of the simulation, whereas the data from infra-red and dielectric spectroscopy are not. The major sources of this disagreement are a) long-ranged orientational cross-correlation due to association and b) polarisability effects, which are not accounted for in the computer simulation.

INTRODUCTION

The molecular dynamics of liquid acetonitrile may be investigated with a range of complementary techniques. The problem now facing us is that of obtaining a consistent overall view based on what these various sources of information individually contain. It is well known that individual spectroscopic methods provide us with distorted images of the molecular motion, and a combination of experimental optics is needed to give each contributory aspect due prominence. This implies the need for a theory of the liquid state capable of reproducing this mass of structural and dynamical data self-consistently. No such analytical theory is yet available, but the computer simulation [1]

of spectral properties in liquids has now reached the stage where many different correlation functions can be produced consistently from a model of the effective pair potential.

The interaction potential between a pair of acetonitrile molecules is not known, and in any case would not be appropriate for use in the liquid state, where interaction potentials are not additive pairwise. In computer simulation a model of the pair potential is therefore chosen on semi-empirical grounds, and used in the calculation with virial-sum corrections for multi-body effects. If we attempt to use transferable parameters in these model calculations and carry out computer simulations for a number of different molecular liquids, a general method of interpretation will begin to emerge. The computer simulation technique is a stage on the way to a general theory of the liquid state of matter based on molecular dynamics and interactions.

We have been pursuing this methodology in a series of recent articles[2] using the Lennard-Jones atom-atom model potential with point charges placed at the atomic sites simulating the electrostatic part of the inter-molecular potential. The molecules chosen for this series of computer simulations are dipolar, substituted methanes whose spectroscopic properties have been investigated intensively. The six atoms in acetonitrile place this molecule at the limits of capability of our present computer power and speed, because there are 36 atom-atom interactions per pair of molecules. On the other hand, there are at least seventy recent papers available on the spectroscopic study of acetonitrile molecular structure and dynamics in the liquid phase, and this makes worthwhile any attempt at understanding the outcome of this work with computer simulation.

In this paper we first aim to review the formidable research literature in this area, then outline our numerical methods and finally compare the results of our numerical exercise with the experimental data.

Infra-red, Raman and Rayleigh Bandshapes

Liquid acetonitrile, and solutions of acetonitrile, have been investigated intensively in the last decade with infra-red, Raman and Rayleigh spectroscopy [3-38].

Bien et al [38] use NMR spin-lattice relaxation, Raman and infra-red spectroscopy to obtain orientational correlation functions [1] from the degenerate (E) bands of acetonitrile. For parallel bands ($\nu_1(\text{C-H}) = 2944 \text{ cm}^{-1}$; $\nu_2(\text{C}\equiv\text{N}) = 2253 \text{ cm}^{-1}$; $\nu_3(\text{C-H stretch}) = 1376 \text{ cm}^{-1}$ and $\nu_4(\text{C-C}) = 917.5 \text{ cm}^{-1}$) the shapes are distorted by hot-bands [9]. For perpendicular bands ($\nu_5(\text{as. C-H s.}) = 3002 \text{ cm}^{-1}$; $\nu_6(\text{as. C-H b.}) = 1444 \text{ cm}^{-1}$; $\nu_7(\text{C-C bend}) = 1039 \text{ cm}^{-1}$; $\nu_8(\text{C}\equiv\text{N bend}) = 378.5 \text{ cm}^{-1}$) the interpretation is complicated by i) vibration-rotation coupling; ii) the fact that the Raman profile is the sum of two rotovibrational components; iii) strong first-order Coriolis coupling.

In principle, however, the \perp bands provide a correlation time for motion about the C_{3v} symmetry axis ($I_A = 5.5 \times 10^{-40} \text{ gm cm}^2$; ($I_B = I_C = 91.22 \times 10^{-40} \text{ gm cm}^2$)). In contradiction to the NMR relaxation work of Bull [39], Bien et al [38] provide an angular momentum correlation time (τ_ω) for motion about the mutually perpendicular axes (of I_B or I_C). They report $\tau_\omega = 0.063 \text{ ps}$ for a nuclear quadrupole coupling constant (NQC) of 172.5 kHz and $\tau_\omega = 0.044 \text{ ps}$ (NQC = 160.0 kHz), $\tau_\omega = 0.025 \text{ ps}$, all at 297K. In agreement with Schwartz [40] they give an "effective" second-order orientational correlation time, $\tau_{\text{eff}}^{(2)}$, of 0.38 ps. We will simulate these results by computing the areas beneath the relevant moving frame angular momentum a.c.f.'s and second-rank Legendre a.c.f. $P_2(\cos \theta)$ [1]. Schwartz [40] also provides an effective lab. frame angular momentum correlation time of 0.093 ps by NMR spin-lattice (^{13}C) relaxation.

Breulliard-Alliot et al [9] have reported infra-red correlation times for liquid acetonitrile for motion parallel (i.e. around) and perpendicular to the C_{3v} symmetry axis. Using Fourier transforms of the raw data from all eight fundamentals produces eight different correlation functions. Vibrational

relaxation makes the c.f. from ν_1 decay much more rapidly than those from ν_2 or ν_4 , which are similar. The ν_5 , ν_7 and ν_8 correlation functions are all different because of Coriolis coupling [38]. These authors report a first rank orientational infra-red correlation time of 0.09 ps for motion around the C_{3v} symmetry axis, and 5.7 ps (the area beneath the dipole auto-correlation function), the motion of the C_{3v} axis itself. The correlation time of 0.09 ps is the area beneath the relevant first rank Legendre orientational auto-correlation function. These compare with the equivalent secondrank correlation time of 0.38 ps [38, 40] and 1.5 ps for tumbling motion from the Raman symmetric A_1 vibration [36].

It is generally accepted that correlation times from infra-red, Raman and NMR relaxation are single particle in origin (i.e. from auto-correlation functions). On the other hand the Rayleigh correlation time (τ_{LS}) is a many molecule property, and there have been numerous papers [e.g. 12-14, 20, 22] devoted to a comparison of Rayleigh and Raman correlation times. These attempts have been aptly summarised by Tiffon et al [41] who plot single particle ^{14}N N.M.R. relaxation times (τ_s) vs η/T for neat CH_3CN , and dilute CCl_4 solutions of CH_3CN . Here η is the bulk viscosity and T the absolute temperature. For neat CH_3CN , and for 0.0182 and 0.0037 m.f. solutions in CCl_4 these plots are linear, having nearly the same intercept as $\eta/T \rightarrow 0$ of $\tau_0 = 0.29$ ps or 0.23 ps, depending on the value taken for the nuclear quadrupole coupling constant. This is in complete contradiction to the results of Whittenberg and Wang [20], who find a zero intercept assuming $\tau_s = \tau_{\text{Ram}}$, the effective Raman-derived correlation time. The τ_0 value of Tiffon et al is almost the same as the free rotor correlation time of the major axis of CH_2CN (0.33 ps at 295K). The existence of the positive intercept has been discussed by Hynes et al [42].

Tiffon et al quote the single particle, Raman, (ν_1), relaxation time of Patterson and Griffiths [12], $\tau_s = 0.9$ ps. These authors also report a Rayleigh correlation time τ_{LS} of 1.8 ps. Whittenberg and Wang [20] also report $\tau_{LS} = 1.8$ ps, but, using the ν_2 Raman band, deduce $\tau_\delta = 1.5$ ps.

Whittenberg and Wang find that both τ_{LS} and τ_s are independent of concentration in CCl_4 , and $\tau_s = \tau_{LS}$ at infinite dilution. They ascribe any discrepancy between τ_{LS} and τ_s to isotropic relaxation mechanisms affecting the Raman band. This conclusion is contested by Versmold [22], who reports τ_{LS} for CH_3CN and CH_3CN in CCl_4 and τ_s from ^{13}C NMR. He relates a monotonic increase of τ_s with dilution directly related to the shear viscosity. He concludes that the increase in τ_{LS} however is not related to the shear viscosity, and discusses τ_{LS}/τ_s in terms of a decrease in orientational correlations.

From ^{14}N NMR relaxation, Tiffon et al [41] report $\tau_s = 1.29$ ps (Solid State NQC) or $\tau_s = 1.01$ ps (gas state NQC), as limits between which the effective second rank single particle orientational correlation time may be defined at 295K in pure liquid acetonitrile. They point out that the results of Whittenberg and Wang and of Versmold are contradictory. They show that the linear dependence of τ_s on viscosity is true only at high CH_3CN concentrations due to association between CH_3CN molecules which disappears at roughly 0.2 mole fraction CH_3CN when the single particle correlation times dramatically decrease. This is consistent with the far infra-red results of Knoesinger et al [43] who find that CH_3CN clusters remain in CCl_4 down to 0.2 m.f. Fini et al [15] have come to the same conclusion by studying the weak, high frequency anisotropic components in the totally symmetric Raman vibrational bands of CH_3CN . They have identified cluster vibration using isotropic and anisotropic Raman scattering of the shoulders on the ν_2 and ν_4 fundamentals.

Amarim da Costa et al [14] conclude that energy transfer from excited vibrational states to rotational motion affects the Raman bandwidths so severely in liquid acetonitrile as to hide any interpretation of the difference between Raman and Rayleigh bandwidths. Yarwood et al [32] also emphasize the difficulty of effectively separating out vibrational effects in the ν_1 and ν_3 infra-red and Raman bands of CH_3CN in dilute CCl_4 solution. In another paper Yarwood et al [21] conclude from a study of the ν_1 , ν_3 and

$2\nu_3$ bands that the second rank (Raman) reorientational correlation times (ν_3 band) do not agree with the literature values from other bands even though the ν_2 and ν_3 times are self-consistent.

The overall conclusion from the papers is therefore far from clear, and various authors rely on results from other fields to get as far as they do. A computer simulation is appropriate therefore to try to clear up the uncertainties, especially that surrounding [16] the separation of vibrational dephasing from rotational loss of correlation.

N.M.R. Relaxation

Some of the earliest experimental work available on the anisotropy of rotational diffusion in pure liquid acetonitrile comes from N.M.R. relaxation [44, 45]. The rotational motion of acetonitrile is very anisotropic, it diffuses about its C_{3v} axis about 10 times easier than about the mutually perpendicular axes of the principal moment of inertia frame. The Rayleigh and dielectric correlation times are therefore weighted averages [1, chapter 2] of three diffusion coefficients, one for each axis of the frame. The anisotropy of the rotational diffusion can be determined uniquely by using a combination, for example, of ^{14}N and ^2D relaxation times, using nuclear quadrupole relaxation. ^{13}C and ^1H N.M.R. relaxation can also be employed for this purpose, as demonstrated, for example, by Heatley [46] and Lyerla et al [47]. Heatley produces an effective (averaged) second-rank correlation time of 0.32 ± 0.06 ps with a ratio of 9.6 for diffusion constants for spinning of the C_{2v} axis to those governing tumbling around perpendicular axes. Leipert et al [48] have used ^{13}C spin-lattice relaxation times and nuclear Overhauser enhancement in the range 239K to 314K and concluded that dipole-dipole and spin-rotation effects are important. More recently other groups have extended the NMR relaxation work in other directions [49, 50]. However, almost all these papers use the theory of rotational diffusion [1] or, at best, M and J diffusion theory [39] in their data reduction. These models are oversimplified [1] and may lead to approximately correct correlation times

only. One of the strengths of the molecular dynamics simulation method is its ability to test these assumptions directly, and we aim to do this by producing the relevant orientational auto-correlation functions and angular momentum auto-correlation functions about all three axes of the principal moment of inertia frame.

Dielectric and Far Infra-red Spectroscopy

The information available from these techniques [1] may be used effectively to test out some advanced theories of the liquid state as discussed in ref. [29]. The equivalent "first rank" procedure to comparing Raman and Rayleigh correlation times is to compare infra-red and dielectric reorientational correlation times. The dielectric relaxation time of acetonitrile in CCl_4 (25% v./v.) has been measured by Eloranta et al [51] who also measured the far infra-red part of the frequency dependent loss. The relaxation time in benzene (25% v./v.) is 6.7 ps at 297K, decreasing to 3.1 ps at 333K. In carbon tetrachloride under the same conditions the relaxation times are 7.6 ps and 4.5 ps respectively. Eloranta et al [52] have also measured a dielectric relaxation time for pure acetonitrile at 303K of 3.3 ps, which compares with a relaxation time of 3.8 ps measured by Krishnaji et al [53]. These relaxation times happen to agree, fortuitously, with a reorientational first-rank correlation time of 3.2 ps measured by Rothschild [6] from the ν_4 band of neat acetonitrile. (The infra-red correlation time of Breulliard - Alliot et al [9] is 5.7 ps).

Therefore, the single particle (infra-red) and multi-particle (dielectric) correlation times seem to be roughly equal, but the independent evidence of Tiffon et al [41] and Fini et al [15] indicates that clustering in acetonitrile is an important phenomenon. This means that cross-correlations are important in acetonitrile over a short range. Eloranta et al [51,52] report that the dielectric relaxation times of acetonitrile increase on dilution (in CCl_4 or benzene) which indicates that the rotational clusters are at least as big in solution (25% v/v) as in the pure liquid.

There have been some recent papers on the far infra-red spectroscopy of liquid acetonitrile [29,43,54-49]. Knoesinger et al [43] ascribe a far infra-red band centred at 90 cm^{-1} to orientational motions within clusters at high concentrations. These exist down to 20 mole % in CCl_4 . At less than 20 mole % there is equilibrium between antiparallel dimers, with a peak frequency at 75 cm^{-1} , and monomer molecules which absorb at 65 cm^{-1} (the Poley peak). Delker et al [55] have discussed the complete far infra-red/low frequency curves in dilute solutions of acetonitrile in terms of three variable Mori theory, which does not succeed [29] in reproducing the band-shape accurately. It is significant, though, that if acetonitrile is investigated in sufficiently dilute solutions, for example, in n heptane [29], the far infra-red peak frequency falls to 42 cm^{-1} (from 90 cm^{-1} in the pure liquid) and the Debye relaxation time to 2.2 ps. This is more in accord with the results of our own computer simulation from which we extract a.c.f.'s only and neglect polarisability. In a solvent such as n-heptane cross-correlations and polarisability effects are removed. These effects echo those found by Tiffon et al [41] by ^{14}C N.M.R. relaxation in dilute solutions of CH_3CN .

In the computer simulation we shall aim to reproduce the rotational velocity correlation function, the Fourier transform of the far infra-red power absorption coefficient. Such an analysis will allow us to see whether computer simulation with our model potentials can describe the cluster behaviour reported by Knoesinger et al [43]. If so, then we might expect the computed and experimental correlation functions to decay similarly in the picosecond time range.

Kerr Effect and Kerr Effect Relaxation

The Kerr effect is generally recognised as being the induction of birefringence with an electric or electromagnetic field. If these fields are applied as pulses, the birefringence is induced transiently:- rise transients as the field is switched on, fall transients after the field has been switched off. These contain information about the dynamic properties of molecules and have been investigated for acetonitrile by a

number of groups in the last decade [60 - 65]. Ho and Alfano [65] have developed the optical Kerr effect for use in the picosecond time interval. In principle this provides information on the non-linear refractive index of liquid acetonitrile, and contains all the non-linear contributions from electronic, vibrational and reorientational motions. This technique is potentially of great interest. Burnham and Gierke [63] have used results from the optical Kerr effect, Cotton-Mouton effect and light scattering to obtain orientational pair correlation functions for liquid acetonitrile from the theory of Ladanyi and Keyes [66]. Orientational pair correlation parameters for liquid acetonitrile were derived showing strong antiparallel alignment.

The optical Kerr effect developed by Beevers et al [61] has been used to investigate generalised Kirkwood factors for the liquid using electrically-induced birefringence. These are defined by:

$$\begin{aligned}
 g_1 &= 1 + \sum_{i \neq 1} \langle \cos \theta_{1i} \rangle \\
 g_2 &= 1 + \sum_{i \neq 1} \left\langle \frac{3}{2} \cos^2 \theta_{1i} - \frac{1}{2} \right\rangle \\
 g_3 &= \sum_{i \neq 1} \sum_{i \neq 1 \neq j} \left\langle \frac{3}{2} \cos \theta_{1i} \cos \theta_{1j} - \frac{1}{2} \cos \theta_{ij} \right\rangle
 \end{aligned}$$

where θ is the angle between the axis for neighbouring dipoles. The sum is over all molecules correlated to a reference molecule, and the statistical averages are taken in the absence of an applied field. Beevers et al point out that acetonitrile is a strongly dipolar and optically anisotropic molecule and the electrooptical Kerr effect can be traced to the orientation of dipole moments.

Inhomogenous Raman Broadening

George et al [67] have recently provided a first account of inhomogenous broadening of vibrational linewidths in non hydrogen-bonded liquids, including pure liquid acetonitrile. They combine the results of isotropic spontaneous Raman studies with picosecond coherent probing experiments to study both homogenous and inhomogenous broadening in terms of one theoretical vibrational correlation function. The results of George et al indicate that non-hydrogen-bonded liquids are not motionally narrowed,

"presumably because the liquid site relaxation times are much longer than earlier predictions". However, no simple correlation was found between the inhomogeneous broadening linewidths and the Kirkwood dipole correlation factor (denoted already by g_1), for eleven liquids, including acetonitrile. In addition, there was no simple correlation with the molecular dipole moment, Trouton's ratio, the hydrogen-bond parameter, or the molecular polarizability. However, the inhomogeneous broadening scales with the molecular shape anisotropy : the pseudospherical molecules are nearly homogenous and vice-versa; and there is also a correlation with the liquid's free volume, and therefore with the number of different environmental sites in the liquid.

Liquid Structure : Pair Distribution Functions

Some papers have appeared on the equilibrium structure of liquid acetonitrile [68-70]. Steinhauser et al [68] have computed a generalised pair correlation function for liquid acetonitrile by means of perturbation theory applying the Percus-Yerick approximation. The computer-generated non spherical pair correlation function of liquid CS_2 was used as reference. The expansion coefficients of the perturbation potential were chosen to give the scattering data and Kirkwood g factors. Kratochwill [69] determined the ^{13}C relaxation rate of the nitrile carbon and the self-diffusion coefficient of acetonitrile over a wide temperature range. The $^{13}C - ^1H$ intermolecular part of the total relaxation rate was determined by isotope substitution and dilution. Combined with the known intermolecular proton relaxation rate the orientation dependent molecular pair distribution function was determined. In the first coordination sphere the molecules are arranged antiparallel. Kratochwill provides atom-atom pair correlation for the methyl to nitrile carbon pair, and for the methyl to methyl pair of an acetonitrile molecule described by the rod $I - S - T$, $I = \text{Methyl}$; $S = \text{Carbon}$, $T = \text{Nitrogen}$. These are derived from X-ray measurements [71], and NMR measurements. Hsu et al [70] have used the X-ray scattering data of Kratochwill et al [69,71] in a RISM

calculation of molecular distribution functions. Hsu et al point out that the CH_3CN molecule has a large electric dipole moment, but conclude that dipole-dipole interactions are unimportant in determining the microscopic structure. (This could be checked in a computer simulation by carrying out runs with and without point charges located at the atomic sites.) Hsu et al make the point that dipole-dipole interactions are slowly varying and emphasize the inapplicability of a multipole expansion of the electrostatic field at short distances. For this reason the point-charge model is preferred in the present computer simulation.

Hsu et al [71] produce atom-atom pair distribution functions for liquid acetonitrile from the RISM equation with a hard-core model potential composed of fused spheres. These may be compared directly with results from our computer simulation, at the same temperature and pressure, 293 K, 1 bar.

Hsu et al point out that scattering experiments such as those of Kratochwill et al [71] can probe linear combinations of the Fourier transforms of these pair distribution functions and can be used to determine the structure factor. The simple RISM theory of Hsu et al describes the experimental results of Kratochwill et al [71] (X-ray scattering) and Bertagnolli et al [72] (neutron scattering) to within the uncertainty in the data.

From a detailed analysis of their atom-atom distribution functions, Hsu et al point out the interesting fact that when two CH_3 groups come into contact, the hydrogen atoms must interlock and there are two well-resolved intermolecular H - H lengths associated with the same pair of neighbouring molecules. Even though dipolar interactions are apparently of "little importance" (sic) there are strong pair correlations between neighbouring acetonitrile molecules. The most probable location of a neighbouring CH_3CN molecule is at right angles between 3.5\AA and 4.5\AA away. There is a "mild tendency" for the angle between the principal axes (C_{3v} axes) to lie between 60° and 120° . The most preferred orientation is near $\theta = 0^\circ$ or $\theta = 180^\circ$ (i.e. parallel alignments), but relatively few pairs of molecules are close enough for this to be the case. There are slightly more than twelve

RISM neighbours in the first coordination shell. The coupling of orientational and translational coordinates is negligible outside the first coordination shell, but inside (i.e. at short range) it is fairly strong. We test this RISM result below in a dynamical context by constructing for single molecules mixed linear/angular momentum correlation functions in the moving frame of reference (the principal moment of inertia frame). The RISM results indicate that noticeable pair correlations must be washed-out in a short distance.

Hsu et al do not discuss the independent evidence available to test their results from spectroscopic data. We have already reviewed this in detail, and some of it supports the RISM indications and some of it directly contradicts the fundamental assumptions of RISM theory. The fact that Raman and Rayleigh (or infra-red and dielectric) correlation times seem to be similar in neat liquid acetonitrile supports the RISM indication of washing out of pair correlation inside the first coordination shell, so that orientational cross - correlations are similar in their time dependence to orientational auto-correlations. However there is independent evidence from dielectric relaxation, where the correlation time increases on dilution in CCl_4 [51,52], that clusters of CH_3CN molecules persist in dilute solution. This cannot be explained in the absence of strong electrodynamic forces, which we approximate in our simulation with point charges. We have described, also, the new results of Tiffon et al [41], (not available to Hsu et al) which corroborate the existence of strong association in CH_3CN and in solutions of CH_3CN . We have described the Raman results of Fini et al [14] where cluster vibrations are assigned. They are also assigned in the far infra-red work of Knoesinger et al [43]. Results from the Kerr effect [61-66] point to electro-dynamic sources of molecule-molecule correlation in acetonitrile. The interesting effect of an applied external electric field on the Raman spectrum seems to indicate that the electrodynamic interactions can be transmitted and enhanced over a macroscopic distance. As a basic description, the RISM theory remains very useful, despite these reservations, reservations which

are mentioned by Hsu et al themselves [70].

Description of the Molecular Dynamics Algorithm

The equations of motion for 108 interacting CH_3CN molecules were solved with an algorithm which integrates the translational and rotational parts of the motion with basically the same numerical technique.

The potential of interaction between two CH_3CN molecules was modelled with a 6 x 6 atom-atom representation in the spirit of the RISM theory of Hsu et al. The repulsive and dispersive forces were dealt with using Lennard-Jone parameters, and the electrodynamical forces with point charges localised at each atomic site. For consistency we have used the parameters already available in the literature, and utilised in parallel simulations of acetone, CH_2Cl_2 , CHCl_3 , CHBr_3 and t butyl chloride liquid and rotator phases [73]. These are $\sigma(\text{H} - \text{H}) = 2.75\text{\AA}$; $\sigma(\text{C} - \text{C}) = 3.20\text{\AA}$; $\sigma(\text{N} - \text{N}) = 3.31\text{\AA}$; $\epsilon/k(\text{H} - \text{H}) = 13.4\text{K}$; $\epsilon/k(\text{C} - \text{C}) = 51.0\text{K}$; $\epsilon/k(\text{N} - \text{N}) = 37.3\text{K}$. The point charges for CH_3CN were estimated in two ways. Firstly we used the direct calculation of the dipole and quadrupole moments of Stucky et al [74], who implemented experimental results from X-ray and neutron diffraction on the electron density distribution of acetonitrile. From the observed 1s binding-energy shifts they produce: $q_{\text{C}_1} = 0.01|e|$; $q_{\text{C}_2} = 0.16|e|$; $q_{\text{N}} = -0.20|e|$ and $q_{\text{H}} = 0.01|e|$; where C_1 is the methyl and C_2 the nitrile carbon atom. Secondly we used the CNDO $\bar{2}$ /2 calculation of Pople et al [75] which produces: $q_{\text{C}_1} = -0.02|e|$; $q_{\text{C}_2} = 0.09|e|$; $q_{\text{N}} = -0.16|e|$; $q_{\text{H}} = 0.03|e|$. The actual values used in the simulation were averages from both sources.

The standard methods of m.d. simulation were then employed, first to equilibrate the sample from an f.c.c. array and then to compute correlation functions by running-time averaging at equilibrium. A time-step of 2.5×10^{-15} s helped to conserve the total energy to within $\pm 0.1\%$. Runs were made with and without charges. An atom to atom minimum image criterion was employed, because of the shape anisotropy of CH_3CN , with a potential cut-off distance of 10.54\AA .

Frame-Transformation and Moving Frame A.c.f.'s

The moment of inertia of CH_3CN about the unique (C_{3v}) axis is about 18 times smaller than the other two (equal) principal moments of inertia. The anisotropy of the rotational motion is large, in consequence, and involves translation of the molecular centre of mass. In consequence, mixed correlation functions with linear and angular momentum components exist in a moving frame of reference fixed in the molecule [76]. For convenience this may be defined by the three principal moment of inertia axes. Vector quantities such as \underline{V} (the centre of mass velocity); \underline{J} (the angular momentum); \underline{F} (force) and \underline{T}_q (torque) may be defined either in the laboratory or moving frame. We denote the components of \underline{V} , for example, in the laboratory frame by V_x , V_y and V_z ; and in the moving frame by V_1 , V_2 and V_3 . If we define three unit vectors \underline{e}_1 , \underline{e}_2 and \underline{e}_3 with respect to the frame (1, 2, 3) the velocity components are then related by:

$$V_1 = V_x e_{1x} + V_y e_{1y} + V_z e_{1z}$$

$$V_2 = V_x e_{2x} + V_y e_{2y} + V_z e_{2z}$$

$$V_3 = V_x e_{3x} + V_y e_{3y} + V_z e_{3z}$$

In a symmetric top such as CH_3CN we have $|\underline{e}_1| = |\underline{e}_2|$, so that $V_1 = V_2$. In these relations e_{1x} is the x component of \underline{e}_1 in the laboratory frame etc.

Having made the transformation into the moving frame for each vector \underline{V} , \underline{J} , \underline{F} and \underline{T}_q we can simulate the various auto and mixed correlation functions of interest. These are

$$\text{i) } \langle \underline{V}(t) \underline{J}^T(o) \rangle / (\langle V_i^2(o) \rangle^{1/2} \langle J_j^2(o) \rangle^{1/2});$$

$$\text{ii) } \langle \underline{V}(t) \cdot \underline{V}(o) \rangle / \langle V^2(o) \rangle;$$

$$\text{iii) } \langle \underline{J}(t) \cdot \underline{J}(o) \rangle / \langle J^2 \rangle;$$

$$\text{iv) } \langle \underline{F}(t) \underline{T}_q^T(o) \rangle / (\langle F_i^2(o) \rangle^{1/2} \langle T_{qi}^2(o) \rangle^{1/2})$$

$$\text{v) } \langle \underline{F}(t) \cdot \underline{F}(o) \rangle / \langle F^2(o) \rangle; \text{ and}$$

$$\text{vi) } \langle \underline{T}_q(t) \cdot \underline{T}_q(o) \rangle / \langle T_q^2(o) \rangle. \text{ Here } \langle \rangle \text{ denotes a running-time average}$$

over vector components defined with respect to the moving frame of reference (1, 2, 3). These functions can be used to describe in detail the interaction

of rotation with translation in acetonitrile molecules in the liquid state.

By symmetry [76] all the elements of $\langle \underline{v}(t) \underline{J}(0)^T \rangle / (\langle v_i^2(0) \rangle^{\frac{1}{2}} \langle J_i^2(0) \rangle^{\frac{1}{2}})$ vanish except the (1,2) and (2,1) elements. Fig. (1) shows that these are mirror images of each other peaking at ± 0.23 and vanishing by symmetry at $t = 0$.

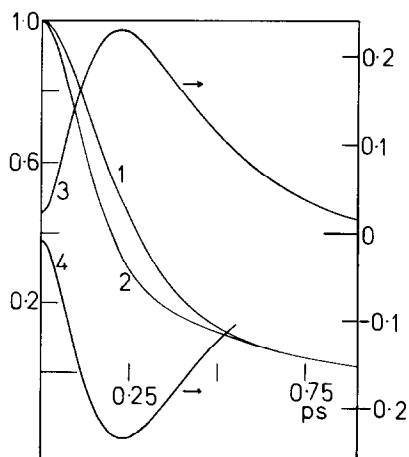


Figure (1)

Illustration of rotation/translation in liquid acetonitrile as simulated on a computer

- (1) Centre of mass velocity a.c.f. component $\langle V_3(t) V_3(0) \rangle / \langle V_3^2(0) \rangle$, in the moving frame of reference.
- (2) $\langle V_2(t) V_2(0) \rangle / \langle V_2^2(0) \rangle$, which is not isotropic with (1) in the moving frame.
- (3) $\langle V_2(t) J_1(0) \rangle / [\langle V_2^2 \rangle^{\frac{1}{2}} \langle J_1^2 \rangle^{\frac{1}{2}}]$, the (2,1) component of the mixed linear velocity/angular momentum (\underline{J}) correlation function in the moving frame of reference.
- (4) $\langle V_1(t) J_2(0) \rangle / [\langle V_1^2 \rangle^{\frac{1}{2}} \langle J_2^2 \rangle^{\frac{1}{2}}]$

[6 x 6 site-site pair potential without charges].

This result shows clearly that the rototranslational motion of CH_3CN molecule in the liquid state cannot be described adequately by theories based on exclusively rotational diffusion. The interpretation to date of the

spectroscopic results reviewed already is lacking in this essential feature. Before going on to a comparison of the molecular dynamics simulation with the available data we must therefore discuss the basic theoretical challenge of developing a statistical mechanical theory to deal with the new results illustrated in fig. (1).

Analytical Theory

The theory is already there, of course, in the rotational and translational cases taken separately. Bien et al [36], for example, produce what are effectively angular momentum correlation times in the moving frame of reference. In our notation these would be the correlation times associated with $\langle J_3(t)J_3(o) \rangle / \langle J_3^2(o) \rangle$ and $\langle J_1(t)J_1(o) \rangle / \langle J_1^2(o) \rangle$ respectively. The computer simulation (fig. (2)) is in agreement with the results of Bien et al, which indicate that $\tau(J_3)$ is shorter than $\tau(J_1)$, in obvious notation. We remark that the components of $\langle \underline{v}(t) \cdot \underline{v}(o) \rangle / \langle \underline{v}^2(o) \rangle$ in the moving frame are also anisotropic (fig. (2)) due to the influence of their rotational motion on the translating CH_3CN molecules.

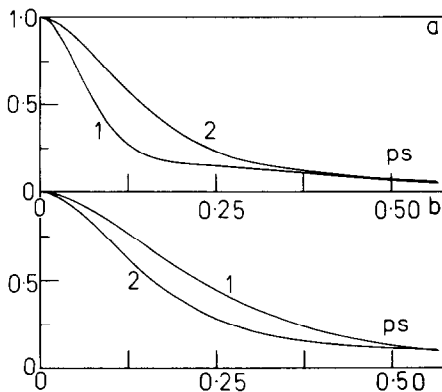


Figure (2)

A.c.f.'s in the moving frame of reference

$$(a) (1) \langle J_3(t)J_3(o) \rangle / \langle J_3^2 \rangle; \quad (2) \langle J_2(t)J_2(o) \rangle / \langle J_2^2 \rangle.$$

$$(b) (1) \langle V_3(t)V_3(o) \rangle / \langle V_3^2 \rangle; \quad (2) \langle V_2(t)V_2(o) \rangle / \langle V_2^2 \rangle.$$

Liquid acetonitrile at 293K, 1 bar.

Evans et al [77] have developed the Langevin equation and Fokker-Planck equation for use with rototranslation in either frame of reference, but Ferrario [78] has shown recently by stochastic simulation, that neither set of equations succeeds in producing non-vanishing elements such as those of fig. (1). The traditional phenomenological theory used by many groups to interpret the spectroscopic data reviewed above is therefore fundamentally defective.

Grigolini et al [79-84] have worked on the problem of integrating memory and rototranslational effects into a non-linear general approach to molecular diffusion in liquids. Essentially, this involves an attempt at modelling the intermolecular potential with a more realistic representation than that used in the Langevin equation, and is an extension of the recent work of Mori et al [85]. These new mathematical techniques may be linked with numerical methods of solution [82] to produce a more realistic theory of the liquid state. One of the major challenges of such a theory would be describing the indications of computer simulation, such as those in fig. (1). The efficiency of the computer simulation itself can be judged by comparison with a wide range of experimental data.

Results and Discussion

Some of the simulated correlation times are compared with some of the available experimentally derived correlation times in table 1. Some of the more obvious features of comparison are summarised below.

i) The N.M.R. times are similar to the simulated times, especially those from refs [36,38 and 40]. The correlation times from spin-lattice relaxation are shorter than the simulated counterparts (in both static and moving frames). The mean orientational correlation times from refs [38] and [40] are roughly similar to the computed times, but those from Tiffon et al [41] are longer. In the light of what follows it is worth recalling that Tiffon et al find their correlation times decrease "dramatically" (sic) at a concentration of CH_3CN in CCl_4 of less than 20% mole fraction. In its pure form and in dilute solution CH_3CN is a strongly associated liquid.

Table 1

Selected Correlation Times for Liquid Acetonitrile: Spectroscopic Data and
Computer Simulation.

Technique	Correlation Times	Computer Simulation (293K, 1 bar)	
Infra-red Absorption	Reorientation of C_{3v} axis, $\tau_1 = 3.2 \text{ ps}^6$ $\tau_1 = 5.7 \text{ ps}^9$	$\tau_1(e_3) = 0.7 \text{ ps}$	
	Reorientation about C_{3v} axis, $\tau_1 = 0.09 \text{ ps}^9$	$\tau_1(e_{-1}) = 0.3 \text{ ps}$	
Dielectric Relaxation	Pure acetonitrile at 303K ⁵² ;		
	Pure acetonitrile ⁵³ ,	$\tau_1 = 3.3 \text{ ps}$	
	25% v/v in benzene ⁵¹ ,	$\tau_1 = 3.8 \text{ ps}$	$\tau_1(e_3) = 0.7 \text{ ps}$
	25% v/v in CCl_4 ⁵¹ ,	$\tau_1 = 6.7 \text{ ps}$ $\tau_1 = 7.6 \text{ ps}$	
Raman Scattering	Reorientation of C_{3v} axis, $\tau_2 = 1.5 \text{ ps}^{36}$	$\tau_2(e_3) = 0.4 \text{ ps}$	
	Reorientation about C_{3v} axis, (symmetric A_1 vibration/rotation)	$\tau_2 = 0.38 \text{ ps}^{36}$	$\tau_2(e_{-1}) = 0.2 \text{ ps}$
	Reorientation of C_{3v} axis, ¹² (symmetric ν_1 stretch)	$\tau_2 = 0.9 \text{ ps}$	$\tau_2(e_3) = 0.4 \text{ ps}$
	Reorientation of C_{3v} axis, ²⁰ (symmetric ν_2 stretch)	$\tau_2 = 1.5 \text{ ps}$	$\tau_2(e_3) = 0.4 \text{ ps}$
Rayleigh Scattering	Reorientational correlation time ¹² ,	$\tau_2 = 1.8 \text{ ps}$	A weighted mean of:
	Reorientational correlation time ²⁰ ,	$\tau_2 = 1.8 \text{ ps}$	$\tau_2(e_2) = 0.4 \text{ ps};$ $\tau_2(e_2) = \tau_2(e_{-1}) =$ 0.2 ps
NMR Relaxation	Spin Lattice Relaxation ³⁸ , angular momentum correlation times in the principal moment of inertia frame (297K):		
	$\tau_w = 0.063 \text{ ps}$ (NQC ³⁸ = 172.5kHz)		0.19 ps Both a.c.f.!
	$\tau_w = 0.044 \text{ ps}$ (NQC ³⁸ = 160.0kHz)		0.12 ps non-exponential.
	$\tau_w = 0.025 \text{ ps}$		
	Spin-lattice Relaxation ⁴⁰ (¹³ C), effective lab. frame angular momentum correlation time, $\tau_J = 0.093 \text{ ps}$		0.15 ps (non-exponential a.c.f.)

Table 1 (continued)

Technique	Correlation Times	Computer Simulation (293K, 1 bar)
NMR Relaxation (continued)	^{14}N nuclear-quadrupole relaxation ⁴¹ , mean second rank orientational correlation time, $\tau_2 = 1.29$ ps (NQC ⁴¹ = solid state) $\tau_2 = 1.01$ ps (NQC ⁴¹ = gas)	Mean of $\tau_2(\underline{e}_3) = 0.4$ ps; $\tau_2(\underline{e}_2) = \tau_2(\underline{e}_1) = 0.2$ ps
	^{13}C to ^1H spin-spin relaxation ⁴⁶ , mean (i.e. isotropic) second-rank orientational correlation time, $\tau_2 = 0.43 \pm 0.06$ ps $\tau_2 = 0.38$ ps ⁴⁰ The molecule spins about 10 times easier than it tumbles.	Mean of $\tau_2(\underline{e}_3) = 0.4$ ps; $\tau_2(\underline{e}_2) = \tau_2(\underline{e}_1) = 0.2$ ps.

The N.M.R. relaxation times are true single particle correlation times, in the sense that auto-correlation functions can be used for their computation, as in our simulation. These times reflect the effect of strong cross-correlation in the pure liquid on the auto-correlation function.

ii) Turning our attention to the infra-red and Raman correlation times, the computed orientational auto-correlation functions of first and second rank are illustrated in fig. (3) for both tumbling and spinning. The simulated correlation times (the areas) are compared with their experimental equivalents in table 1 and are nearly always much shorter, in contrast to the N.M.R. results. The only exception is the first-rank spinning correlation time of ref. [9], which is shorter than the equivalent from the computer. The overall discrepancy is much more than in our parallel simulation [73] of molecules such as CH_2Cl_2 and acetone which are highly dipolar but not associated in solution. These simulations were carried out with the same atom-atom Lennard-Jones parameters using literature sources for point-charges and neglecting the effects of polarisability. However, polarisability and association in pure liquid acetonitrile should presumably affect the N.M.R. correlation times as well as the infra-red and Raman times, so the source of

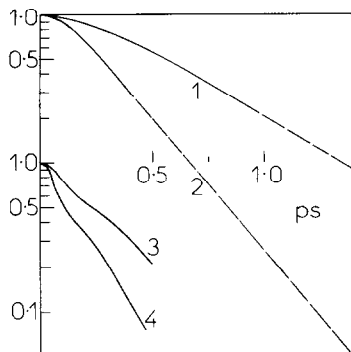


Figure (3)

Orientalional auto-correlation functions

- (1) First-rank, tumbling of the C_{3v} axis.
- (2) Second-rank, " " " " "
- (3) First-rank, of a vector \perp to the C_{3v} axis
- (4) Second-rank, " " " " " " "

Computer simulation, 293K, 1 bar.

the much greater discrepancy must be sought in the data-reduction of the infra-red and Raman methods themselves. Amorim da Costa et al [14] take the view that energy transfer from excited vibrational states to rotational motion (the motion we are attempting to simulate) affects the Raman bandwidth: so severely in liquid acetonitrile as to hide any interpretation of, for example, the difference between Raman and Rayleigh bandwidths. Taking again the infra-red results of refs [6] and [9] (see the entry in table 1) we note firstly that there is a considerable spread in the experimental times themselves (3.2 ps and 5.7 ps) and secondly that the experimental range of times straddles the computed range (0.09 ps to 5.7 ps as compared with 0.3 ps to 0.7 ps), as regards the anisotropy of the rotational motion. The Raman and infra-red data reduction seems, in conclusion, to be masked by a) rotation/vibration coupling (not present in the simulation); and b) polarisability effects due to strong association (e.g. Fini et al [15]). Effects a) and b) are mutually interdependent. Further work is needed on the

Raman and infra-red bandshapes of acetonitrile in very dilute solution [41]. Tiffon et al [41] have pointed out the pitfalls in the available literature on Raman/Rayleigh comparisons. In both the Rayleigh and dielectric cases the discrepancy between the experimental and simulated correlation times (table 1) is very large. In these cases (and in the far infra-red) the probe-radiation "sees" many thousands of molecules of acetonitrile and the bandshape in consequence must be described theoretically with statistical cross-correlations between different molecules. In a strongly associated liquid such as acetonitrile these cross-correlations are more of an influence on the dielectric and Rayleigh correlation times than the auto-correlations. Restrictions on computer power mean that we can only simulate the latter, so that a direct comparison of the areas in fig. (3) with the dielectric and Rayleigh data is not strictly valid. It would be more meaningful to extrapolate the available Rayleigh and dielectric relaxation times to infinite dilution in a solvent, such as CCl_4 , which does not produce a viscosity complex with the solute. We have mentioned already that the dielectric relaxation times of acetonitrile appear to increase in both CCl_4 and benzene and this is indicative of the need to use very dilute solutions [41] and solvents which do not "encourage" the association of acetonitrile in dilute solution.

For the purposes of comparison (fig. (4)) we have remeasured for this work the spectrum of pure acetonitrile and that of acetonitrile in dilute solution (2% v/v). There is a large change in the frequency of maximum absorption between the two cases, implying that the acetonitrile is less associated in dilute solution. We have Fourier transformed the far infra-red curve of the 2% v/v solution, and the result is compared with the computer simulated rotational velocity a.c.f. [1] in fig. (4). The latter decays more slowly, and does not account for statistical cross-correlations between acetonitrile molecules. Also in fig. (4) we illustrate the simulated angular momentum a.c.f.. The area of this is compared with the experimentally derived angular momentum correlation time [40] in the table.

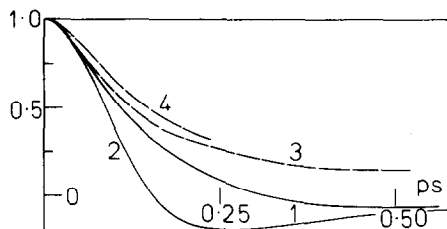


Figure (4)

- (1) Computer simulation of the rotational velocity a.c.f. of the C_{3v} (dipole) axis of CH_3CN .
- (2) Fourier transform of a 2% solution of CH_3CN in n. heptane.
- (3) Angular momentum a.c.f., lab. frame.
- (4) Centre of mass velocity a.c.f., lab. frame.

We note that the centre of mass velocity auto-correlation function (fig.(4)) decays in the laboratory frame on a similar scale to the angular momentum a.c.f. Both functions are transiently non-Gaussian,[83], but their second-moments eventually reach the Gaussian level at equilibrium ($t \rightarrow \infty$).

Atom-Atom Pair Distribution Functions

In fig. (5) we compare the simulated atom-atom p.d.f.'s for nitrogen-nitrogen, carbon-carbon and hydrogen-hydrogen. The overall shapes of these p.d.f.'s are roughly similar but it is clear that the RISM theory tends to overestimate the intensity of the first peak and underestimate the position. The best agreement is found in fig. 5(b) for the carbon-carbon p.d.f.'s. (We have computed a mean p.d.f. for both carbons of acetonitrile.) The worst mismatch is for the hydrogen-hydrogen p.d.f.'s, where the pronounced first-peak of RISM theory is reduced to a flat shoulder in the computer simulation.

The mismatch is not caused to a great degree by electrodynamic interactions, because the essential shape of the computed p.d.f.'s is retained when we remove the point charges and work with the Lennard-Jones atom-atom cores. It is clear that further work is needed to improve our basic knowledge of liquid structure at equilibrium.

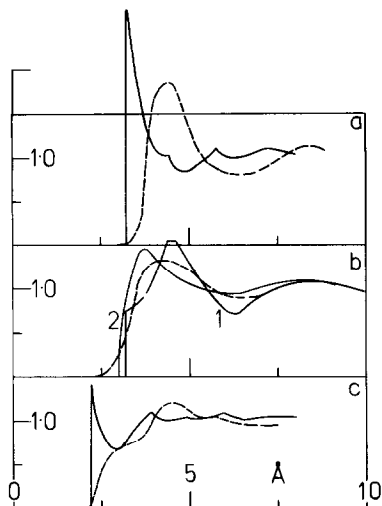


Figure (5)

Atom-atom probability density functions.

— RISM theory [70]

- - - Computer simulation

(a) Nitrogen-nitrogen; (b) carbon-carbon;

(1) nitrile carbon; (2) methyl carbon; (c) hydrogen-hydrogen.

Conclusions

We have reviewed most of the available literature on the dynamics and structure of liquid acetonitrile. These data have been compared with the results of a molecular dynamics simulation with a 6×6 site-site model potential. The best agreement is found in the fields of N.M.R. relaxation, the worst in infra-red and dielectric spectroscopy, where the effects of cross-correlations dominate the spectral bandshapes. The inter-experimental uncertainty in the infra-red and Raman fields implies that the effects of vibration-rotation coupling have not been analysed correctly. The substantial disagreement between the computer-simulated correlation times pertinent in these fields implies that the observed bands are more or less strongly affected by inter-molecular association effects.

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