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MOLECULAR DYNAMICS SIMULATION AND REVIEW OF SOME SPECTRAL PROPERTIES OF LIQUID METHYL IODIDE

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ABSTRACT

The molecular dynamics of liquid methyl iodide have been simulated with a 5 x 5 site-site model potential and the results compared with a variety of spectral data. A review of the results indicates that non pair-additive collision induction is an important factor affecting the spectral features in liquid CH_3I. This is seen most clearly in the far infra-red. The computer simulation can therefore only be partially effective for CH_3I because it is based on pair-additivity and excludes polarisability effects. Nevertheless the numerical method reveals some details of the molecular motion that cannot be obtained otherwise. These are exemplified by rotation-translation coupling.

INTRODUCTION

The various spectral properties of liquid methyl iodide may be used to investigate the molecular dynamics and interactions in the liquid phase

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provided a general theory is available to relate the statistical correlations in the molecular liquid to frequency-dependent absorption, scattering, dispersion etc. The molecular dynamics computer simulation method has now advanced to the stage where it can begin to deal with polyatomic molecules the size of methyl iodide. From a working model of the pair potential we can produce a variety of auto-correlation functions self-consistently.

In this paper we use a 5 x 5 site-site model of the pair potential for this purpose and compare our results with a variety of literature data. We begin with a short review of the literature of the last decade on the spectroscopy and bandshape analysis of liquid methyl iodide.

INFRA-RED, RAMAN AND RAYLEIGH SCATTERING

Goldberg et al [1] point out that methyl iodide has nine vibrational modes, each of which may be used to provide information on rotovibrational diffusion. There are three totally symmetric modes, of symmetry species A_1 and three doubly degenerate E modes. All are both infra-red and Raman active. A correct analysis of rotation-vibration coupling is necessary before accurate information can be obtained on rotational diffusion and its anisotropy. If we are to use classical dynamics these bands must be symmetrical. If there is no rotation/vibration coupling then all the infra-red and Raman A_1 bands must give the same rotational correlation function. This must also be true of the infra-red E bands, which contain information both about spinning and tumbling (motions around and of the C_{3v} symmetry axis). These authors find that the A_1 bands are symmetrical but the half-width of the ν_1 band is greater than those of the ν_2 and ν_3 bands, which are roughly the same [2]. Rotovibrational effects are present therefore in the A_1 modes. Coriolis forces introduce strong vibration/rotation effects into the E type modes because of the double degeneracy. The Coriolis force may also be transferred from an E mode to an

A_1 type. The E bands are asymmetric, so that quantum effects are important because of spinning about the C_{3v} axis. The moment of inertia of the symmetry axis is about 20 times smaller than that about any perpendicular axis through the centre of mass and the free-rotational velocity is nearly five times that for motion of the C_{3v} axis - the dipole axis. The ν_4 (E) band is the least affected by the Coriolis force. Goldberg et al. conclude that because of rotation/vibration coupling, not all bands of a given substance are equally amenable to simple analysis, and only by a study of as many as possible can a reasonable result be expected from infra-red and Raman spectroscopy. The results of several early investigations are summarised by Goldberg et al. and we have incoporated these into table (1) as relaxation times.

This argument is extended by Hyde-Campbell et al. [3] who investigated a combination of ν_3 (A_1) and 2_D relaxation times. These authors report a large effect of density on the molecular motion of methyl iodide. Using 2_D and spin-lattice NMR relaxation times they obtained diffusion coefficients for spinning and tumbling. As the density changes, however, the rotation of the methyl group about the C_{3v} axis remains largely unaffected, and the authors point out that any "serious" attempt to characterise the molecular dynamics in a liquid must involve data taken under hydrostatic pressure. They suggest that the true effects of temperature show up only at constant density and use the method of Nafie et al. [4] to separate the orientational and vibrational contributions to their Raman bandshapes. There is considerable uncertainty in the literature as to how to go about this correctly [5,6], and here a computer simulation can be valuable in fixing a dependable rotational autocorrelation function. Hyde-Campbell et al. provide orientational (second-rank) and angular momentum relaxation times which we list in table 1 (at 1bar and 2 kbar, 303 K).

Using the ν_4 (E) band Doege et al. [7] provide a Raman correlation time (table 1) for spinning at 293 K using a relatively simple model for the band-

TABLE 1

Some Relaxation Times for Liquid Methyl Iodide

Technique	Measured Relaxation Time (/ps)	Computed Autocorrelation Time (/ps) at 293 K
Dielectric	i) 3.6_5 (pure liquid [45])	$\tau_1(\underline{\ell}_3) = 1.5$
	ii) 2.5 (infinite dilution in Cl_4 [64])	$\tau_1(\underline{\ell}_3) = 1.5$
N.M.R. Relaxation	i) 0.27 ± 0.07 (weighted mean second-rank, pure [44])	$\tau_2(\underline{\ell}_3) = 0.5$
	ii) 0.50, as above [45]	$\tau_2(\underline{\ell}_1) = 0.05$
	iii) 1.42 (of C_{3v} axis at 1bar, 303 K, [3])	$\tau_2(\underline{\ell}_3) = 0.5$
	3.30 (of C_{3v} axis at 3kbar, 303 K, [3])	
	0.10 ($\perp$ to C_{3v} axis at 303 K, at both 1bar and 2kbar)	$\tau_2(\underline{\ell}_1) = 0.05$
	iv) Angular momentum correlation time, lab. frame [3]	
	$\tau_J = 0.03_2$ at 1bar, 303 K	$\tau_J = 0.01$
	$\tau_J = 0.01_3$ at 2kbar, 303 K	
	v) 1.4 (NMR dipole relaxation [52])	$\tau_2(\underline{\ell}_3) = 0.5$
	vi) 1.4 (Debye-Stokes theory [65])	$\tau_2(\underline{\ell}_3) = 0.5$
	vii) 1.6 (of C_{3v} axis at 1bar [53])	$\tau_2(\underline{\ell}_3) = 0.5$
	0.07 to 0.08 ($\perp$ C_{3v} axis at 1bar [53])	$\tau_2(\underline{\ell}_1) = 0.05$

Infra-red Bandshape Analysis	i) 3.6 (pure liquid [13])	$\tau_1(\underline{\ell}_3) = 1.5$
	ii) 3.1 (pure liquid [20])	$\tau_1(\underline{\ell}_3) = 1.5$
	iii) 3.2 ± 0.1 (20% mole fraction in CCl_4 [19])	$\tau_1(\underline{\ell}_3) = 1.5$
	2.0 ± 0.1 (20% mole fraction in hexane [19])	$\tau_1(\underline{\ell}_3) = 1.5$
Raman Bandshape Analysis	i) 0.8 (ν_1 [1])	
	1.1 (ν_2 [1])	$\tau_2(\underline{\ell}_3) = 0.5$
	1.4 (ν_3 [1])	
	1.4 (ν_2 [19])	
	1.5 (ν_3 [19])	$\tau_2(\underline{\ell}_3) = 0.5$
	1.7 (ν_3 [20])	
	ii) 1.3 ± 0.1 (20% mole fraction in CCl_4 [19]) 0.8 ± 0.1 (20% mole fraction in hexane [19])	$\tau_2(\underline{\ell}_3) = 0.5$
	iii) 1.6 (ν_3 Raman and ^2D NMR spin-relaxation [53])	$\tau_2(\underline{\ell}_3) = 0.5$
	0.07 to 0.08 (⊥ to C_{3v} axis, ν_3 + ^2D NMR [53])	$\tau_2(\underline{\ell}_1) = 0.05$
	iv) 0.05 (ν_4, ⊥ to C_{3v} axis [31])	$\tau_2(\underline{\ell}_1) = 0.05$
	1.6 ± 0.2 (mean value from sources in ref.[9])	$\tau_2(\underline{\ell}_3) = 0.5$
	In the range: 1.18 to 1.36 (ν_3, depending on wing cut-off frequency [40])	$\tau_2(\underline{\ell}_3) = 0.5$

Technique	Measured Relaxation Time (/ps)	Computed Autocorrelation Time (/ps) at 293 K
Depolarised Rayleigh Scattering	0.94 (pure liquid, [21])	$\tau_2(\underline{\ell}_1)$ = 0.05 $\tau_2(\underline{\ell}_3)$ = 0.5
	3.1 (pure liquid, [16])	$\tau_2(\underline{\ell}_1)$ = 0.05
	1.8 ± 0.2 (infinite dilution in 46:54 isopentane:CCl_4 [16])	$\tau_2(\underline{\ell}_3)$ = 0.5
	2.2 (pure liquid [18])	A mean of three times as above.
	1.0 (pure liquid [19])	A mean of three times as above.
Far Infra-red and Second Rayleigh Moment	$\bar{\nu}_{max} = 60 \pm 2\ cm^{-1}$ (100% v/v CH_3I in decalin [58]), T_q = 1980 gm [58]	See fig. (2).
	$\bar{\nu}_{max} = 100\ cm^{-1}$ (pure liquid, this work).	See fig. (2).
Rayleigh Second Moment Analysis	$R(\bar{\nu}) = \bar{\nu}^2 I(\bar{\nu})$ $= 64\ cm^{-1}$ (pure CH_3I [42]) $= 58\ cm^{-1}$ (pure CD_3I [42])	Compares with a far infra-red peak frequency of $100\ cm^{-1}$ in the pure liquid (this work).
Incoherent Neutron Scattering	Studied in the gaseous, liquid and solid states [54-57]. Qualitative result [54] that there is "freedom of translational motions" in the pure liquid.	Computer Simulation (this work) provides quantitative evidence for rotation-translation coupling Raman and infra-red work provides evidence for rotation-vibration coupling.

Coherent Anti-Stokes Raman Scattering (CARS)	Correlation time from all sources of 0.85 ± 0.2 [39]	
Vibrational Relaxation	2.73 (ν_1, isotropic at 287 K [30]) 2.81 (ν_2 [30]) 2.77 (ν_3 [30])	

shape. Arndt et al. [8] extend the analysis to the overtones involved with 0→1 and 0→2 transitions. The effect of the intermolecular potential and therefore the observed rate of vibrational relaxation, depends on the normal coordinates of the mode concerned. It is therefore imperative to develop a workable theory of rotation-vibration coupling. The work on liquid methyl iodide in these fields has been ably summarised by Steele [9] and again by Evans et al. [10]. Steele shows various correlation functions calculated from the ν_3 band of CH_3I in the far infra-red. They change appreciably as various corrections are applied to the data. He compares the unmodified results of Rothschild [11] with the correction made by Fulton [12] for refractive index variability, hot bands and isotopes, and with the results of Favelukes et al. [13] corrected by Crawford et al. [14] for the frequency dependence of the local susceptibility. These results were originally reported by van Konynenberg and Steele [15] who covered methyl iodide liquid with infra-red absorption and depolarised Rayleigh scattering. By using CCl_4 solutions of CH_3I they proved the inaapplicability of the rotational diffusion model. They used the ν_3 Raman band to extract a second-rank orientational correlation time of 1.5 ± 0.2 ps at room temperature. The equivalent for CD_3I is about

10% longer. The first and second rank orientational correlation times derived by these authors are summarised in table 1.

Cheung et al. [16] provide single particle (Raman) and multi-particle (Rayleigh) correlation times of CH_3I and constant viscosity solutions of CH_3I. The infinite dilution intercept of the Rayleigh correlation times is 1.8 ± 0.2 ps, roughly comparable with the Raman correlation times from totally symmetric stretching. They compare their results with the Raman correlation times of 1.6 ps given by Wright et al. [17] and 2.2 ps by Patterson et al. [18]

Several other groups [19-21] have studied liquid methyl iodide by infra-red, Raman or Rayleigh spectroscopy. We have reduced their data to correlation times, and these are summarised in table 1. Dill et al. [21] derive angular position and angular velocity auto-correlation functions which we shall compare with the computer simulation. These authors point out that in CH_3I the major axis of the rotational diffusion tensor coincides with that of the polarisability tensor, and that in this liquid depolarised Rayleigh scattering will measure an average reorientational time only. The simulation provides all three components (table 1) of this average. Constant et al. [19] list correlation times for solutions of CH_3I. In 20% mole fraction CCl_4 the first rank correlation time (infra-red) is 3.2 ± 0.1 ps; in hexane it is 2.0 ± 0.1 ps The equivalent second-rank (Raman) times are 1.3 ± 0.1 ps and 0.8 ± 0.1 ps respectively.

Shermatov et al. [22] have studied the ν_3 mode of methyl iodide to 150 cm^{-1}. At high $\Delta\nu$ a weak maximum of absorption is observed due to collision induction which would dominate the second moment spectrum [10]. More recently, Kluk et al. [23] have developed a method of relating angular velocity correlation functions to angular position correlation functions from Raman scattering for methyl iodide at 300 K. This is potentially an important method of linking spectroscopic results to computer simulation through the intermediacy of the angular velocity correlation function.

Laubereau et al. [24] have examined the vibrational modes of methyl iodide in the electronic ground state with picosecond laser-pulse spectroscopy. The vibrations are excited with an intense laser pulse via stimulated Raman scattering or by resonant infra-red absorption. After the passage of the first pulse the excitation process rapidly terminates and free precessional decay of the vibrational system occurs. The instantaneous state of the excited system is monitored by a second "interrogating" pulse of variable time delay. This method allows us to look directly at the vibration-rotation coupling of methyl iodide at short and intermediate times, and awaits theoretical development for its proper interpretation. Gburski et al. [25] have provided a clear account of the problems involved in the interpretation of vibrational relaxation in picosecond laser-pulse experiments. There are basically two mechanisms which have been isolated. (a) Inelastic interactions which cause energy redistribution of the excited vibrational population among other degrees of freedom (the T_1 process of depopulation). (b) Quasi-elastic interactions which randomly modulate the vibrational phase (T_2 process or dephasing). Gburski et al. test the model of Fischer et al. [26] for liquid methyl iodide, a simple collisional model, but mention a number of physical processes which contribute to line-shapes in picosecond dephasing, - phase relaxation, rotational motion, isotope splitting, and inhomogenous broadening due to a distribution of molecules with different resonance frequencies according to environment. They mention the method of Nafie et al. [4] for eliminating rotational contributions. The rest is called the isotropic or vibrational part of the band-profile, and contains the other line-broadening factors. It is impossible, according to Gburski et al., to separate the different vibrational contributions by spontaneous spectroscopy (classical infra-red and Raman). The isotropic part of a spontaneous Raman line cannot be related to a single relaxation process. Other problems include the coupling of vibrational and rotational motion due to transition-dipole to transition-dipole coupling [27,28] and dephasing via vibrational anharmonicities not contained in the Laubereau-Fischer model [29]. Gburski et al. conclude that dephasing processes that involve no energy transfer between the ensemble of molecular oscillation and lattice usually dominate in the line-broadening process.

In our computer simulation we are interested only in the rotational autocorrelation functions of methyl iodide, which is treated as a rigid rotator. As long as the Raman, infra-red etc. can be used to extract reliable information on rotational a.c.f.'s we can attempt to apply our computer simulation method of interpretation. After extracting the rotational part of the molecular dynamics the remaining problems with interpreting the vibrational part of the overall motion have been discussed by Trisdale et al. [30]. These authors used polarised and depolarised Raman spectra of the ν_1 (2950 cm^{-1}), ν_2 (1150 cm^{-1}) and ν_3 (525 cm^{-1}) modes, calculating correlation functions only on the high frequency side of the bands. The Kubo lineshape theory was applied to describe the spectra in terms of relaxation through vibrational dephasing. This provides a bandshape of the form:

$$G_{iso}(t) = \exp \{ -M_{2v}(\tau_m^2(\ell^{-t/\tau_m} -1) + \tau_m t) \}$$

where M_{2v} is the vibrational second moment - the "average mean square perturbation". The modulation time τ_m is a measure of the decay time of the stochastic perturbation. $M_{2v}^{\frac{1}{2}}\tau_m$ determines the nature of the vibrational relaxation (i.e. either motionally narrowed or inhomogenous). Following the evaluation of M_{2v} by numerical integration, Trisdale et al. vary τ_m to obtain the best least squares fit to the experimental and theoretical isotropic functions. M_{2v} is almost temperature independent for ν_1 and ν_3, but decreses markedly with increasing temperature for C-H banding (ν_2). The area beneath $G_{iso}(t)$ gives the isotropic relaxation times, which increase with temperature for all three vibrations, but much more sharply for ν_2 than for the other two modes.

The modulation times from the work of Döge et al. [31] show a moderate temperature dependence, not observed by Trisdale et al. [30]. The difference between the two results arises from the method of calculation. The effect of dilution is to slow significantly the relaxation of the ν_2 mode, with the ν_1 band affected similarly by solution. This is put down to intermolecular dipole or resonant energy transfer effects.

Doege [32] and van Woerkom et al. [27] have shown that for a long-range dipole-dipole potential τ_m should be one half of the dipole reorientational correlation time obtained from "either dielectric or infra-red" spectroscopy. However, the predicted correlation times from Gillen et al. [33] have a far greater temperature dependence than the experimentally measured modulation times, and are a factor of 5 to 10 times longer. This implies [30] that dipolar coupling is a minor effect and that resonant energy exchange is a more consistent explanation. This seems to contradict diametrically the conclusion arrived at by Gburski et al. [25], i.e. that dephasing processes involving no energy trasnfer dominate in the line-broadening process.

Trisdale et al. discuss the Fischer/Laubereau model [26] for liquid methyl iodide. This assumes that vibrational dephasing results directly from binary hard-sphere collisions. These hard sphere collision times (τ_c) are compared with those derived by Hyde-Campbell et al. [3] from the Enskog model. Qualitative agreement is obtained, but recent studies of ν_1 in CH_3I liquid suggest that the principal decay mechanism of this mode is via population relaxation, and not via resonance energy transfer [34,35]; and that intermolecular energy exchange appears to dominate the relaxation of the ν_3 mode. Furthermore [30] if the primary mechanism of relaxation is by dephasing from short range repulsive forces, it is expected that both τ_c and τ_m will represent the time between collisions in the liquid. Yet the temperature trends [30] from these two are not in agreement, particularly for ν_3. Clearly, considerable confusion exists in the lietrature on vibrational relaxation in liquid CH_3I, and more data over a wide range of conditions are needed.

Theoretically speaking, much of the confusion is caused by the use of simple models, such as the Kubo oscillator [ref.10, chapter 2] which do not stand up to analysis with incisive methods such as far infra-red spectroscopy. If any one of a number of groups mentioned above had constructed a higher spectral moment [ref. 10, chapter 1] from their data the qualitative (let alone quantitative) shortcomings of these models would have been revealed. Grigolini et al. [ref. 10, chapters 9 and 10] have developed more powerful methods of interpretation involving no more adjustable parameters (generally only one) than the Kubo or Fischer/Laubereau models. Conclusions based on the fitting of these latter to Raman or infra-red bandshapes are at best approximate, at worst misleading.

There have been attempts [36,37] to use computer simulation to look at the vibrational dynamics of methyl iodide liquid in the presence of rotation. These were carried out, for example, by Maple et al. [36] using simple Lennard-Jones parameters and/or one dimensional arrays of CH_3I molecules to save computer time. Using this method, Maple et al. verified the "Gordon local-equilibrium conjecture" [38] that non-equilibrium fluctuations approach equilibrium faster than the average correlation function approaches equilibrium. In these papers, an artificially low vibrating frequency of the CH_3I band was used to conserve compueter time, with a classical harmonic or anharmonic expression for the vibrational motion. This promises to be a good method for looking at the details of rotation/vibration coupling in a polyatomic molecule such as methyl iodide. Riehl et al. [37] find that the vibrational correlation functions for their model of CH_3I were highly oscillating in the range up to 5.0 ps, whereas the normalised centre of mass velocity auto-correlation functions were not exponential (see fig.(6)) in their decay characteristics. The first rank orientational a.c.f.'s obtained by Maple et al

[36] are not oscillatory in the range up to 3.0 ps, and show the interesting characteristic that the function:

$$F(t) = [<[\underline{u}(0).\underline{u}(t)]^2> - <\underline{u}(0).\underline{u}(t)>^2]^{\frac{1}{2}}$$

reaches equilibrium faster than the a.c.f. $\langle \underline{u}(t).\underline{u}(0)\rangle$, where $\underline{u}$ is the dipole unit vector. The computer simulation method seems to be the only direct way of looking at "Gordon's conjecture" presently available. We note that the "Gordon equilibrium conjecture" is a way of stating that the transient statistics of reorientation are non-Gaussian [10].

Roland et al. [39] have employed coherent anti-Stokes Raman scattering (CARS) to investigate polarised and depolarised bands for the symmetric stretch of liquid CH_3I at 526 cm^{-1}. This has an appreciable hot-band intensity overlapping the fundamental. They quote a value of 1.6 ± 0.2 ps from an analysis of the spontaneous Raman bands of the review by Steele [9]. The experimental CARS time (including all effects) is 0.85 ± 0.2 ps.

Finally in this section on the infra-red, Raman and Rayleigh we mention a paper by Bansal et al. [40] on the ν_3 (A_1) band profile of liquid methyl iodide at 296 K. These authors emphasize the importance of looking well out into the wings of the spectrum. There is a marked disagreement between their results (out to 175 cm^{-1}) and those of other sources. This is put down to truncation error and incorrect data reduction. Their second-rank orientational relaxation times vary from 1.36 ps to 1.18 ps according to where the band is truncated. These results are all markedly shorter than that quoted above by Steele et al. [9,39], i.e. 1.6 ± 0.2 ps.

In summary, there is considerable disagreement between the various literature sources when their results are reduced to first or second rank correlation times as the case may be. It is clear that few groups have taken the advice of Goldberg et al. [1], i.e. to look at all the nine vibrational modes available to them, or alternatively the advice of Hyde-Campbell et al. [3]: to look at the liquid under hydrostatic pressure over a temperature range. The resulting spread of uncertainty in the reorientational correlation times is therefore very wide. The mechanisms governing vibrational relaxation are not known with any certainty, the principal reason being that almost no attempt has been made to produce the appropriate higher spectral moments. This procedure immediately reveals the inapplicability of models such as J diffusion or Kubo oscillator, and has been developed for the far infra-red (librational) absorption by Evans et al. [41]. Far infra-red power absorption provides automatically the second spectral moment of the dielectric loss spectrum [10, chapters 1 and 4] and in this field, moment analysis is standard procedure. With relatively complicated techniques such as picosecond dephasing [24,26,34,35] or CARS spectroscopy [39] the information about rotational motion is masked by experimental and theoretical uncertainty, their only advantage over far infra-red/ dielectric spectroscopy being their ability to probe auto-correlation functions as opposed to cross-correlation functions.

As an example of moment analysis we mention the work of Nielson et al. [42] on the depolarised Rayleigh wing spectrum of liquid methyl iodide ($I(\bar{\nu})$). The higher moment $R(\bar{\nu}) = \bar{\nu}^2 I(\bar{\nu})$ was calculated from the experimental data. $R(\bar{\nu})$ peaks at about 64 cm^{-1} for CH_3I and about 58 cm^{-1} for CD_3I. This shift in frequency was compared with a corresponding far infra-red frequency shift of ~ 6 cm^{-1}. The Kubo model would produce a plateau in $R(\bar{\nu})$ [ref.[10], chapters 1, 2 and 4], i.e. would leave the higher moment undefined. The J diffusion model [ref.[10], chapters 2 and 3] would not follow the observable shifts in the peak of $R(\bar{\nu})$ with density or temperature. Grigolini [ref.[10], chapters 9 and 10] has developed the theory necessary to interpret pico-second or CARS experiments, or those on spontaneous Raman and infra-red spectroscopy, and an algorithm is being produced to enable easy comparison of the theoretical formalism with experimental data [43].

NMR RELAXATION

Schwartz [44] points out that the effective reorientational correlation time from ^{13}C NMR relaxation in liquid methyl iodide is an outcome of spin-rotation and dipolar coupling, the dominant mechnaims. This is 0.27 ± 0.07 ps at 301 K, a weighted mean of second rank orientational correlation times (table 1) about all three principal moment of inertia axes. This was obtained by Schwartz using Overhauser enhancement on natural abundance $^{13}CH_3I$ with a $180^{\circ}-\tau-90^{\circ}$ pulse sequence. Not surprisingly, Schwartz finds that the extended diffusion models cannot characterise the reorientational dynamics. Using the techniques of far infra-red spectroscopy, this result has been clear for almost a decade [10]. Some of the NMR relaxation work on CH_3I liquid has been reviewed by Evans et al. [ref. [10], chapters 6 and 12]. This has been pursued by a number of groups [45-52]. The earlier work has been summarised by Goldberg et al. [1] and correlation times are tabulated in table 1. Hyde-Campbell et al. [3] have produced ^{2}D relaxation times over a range of density and temperature and derive a resultant molecular angular momentum correlation time (in the lab. frame) of τ_J = 0.03 ps at 1bar, 303 K and 0.01 ps at 2 kbar, 303 K. τ_J increases with temperature at constant density. We aim to compare the 1bar, 303 K result with that from our computer simulation of the complete angular momentum a.c.f. in both the laboratory and moving frames of reference (the latter being defined in the principal moment of inertia frame).

Heatley [45] produces a mean second-rank orientational correlation time of τ_2 = 0.50 ps, which compares with 0.27 ± 0.07 ps from Schwartz's work [44]. Heatley also quotes a dielectric correlation time of 3.65 ps. This is not, however, directly comparable with the NMR time because the latter is single particle, second-rank in nature, and the former a multi-particle, first-rank orientational correlation time of the dipole unit vector.

Griffiths [53] combines ^2D NMR and diffusion coefficents parallel and perpendicular to the C_{2v} symmetry axis in CH_3I. The reorientational dynamics are highly anisotropic. These diffusion coefficients have been converted to relaxation times and are tabulated in table 1.

Steele [9] summarises the early work in this field on nuclear quadrupole relaxation, ^{13}C spin-rotation and $^{13}C-^1H$ spin-spin relaxation. Unequivocal NMR relaxation times cannot be calculated because of the uncertainties in the Raman times (vide supra). However, a combination of NMR, infra-red and Raman data shows conclusively that the motion of CH_3I cannot be described by rotational diffusion. The motion around C_{3v} axis seems to be very free. These conclusions can be treated directly with our computer simulation method (e.g. fig.(3)).

INELASTIC NEUTRON SCATTERING

Methyl iodide has been studied by neutron scattering in the gaseous, liquid and crystalline solid states [54-57]. Fischer [55,57] has measured the neutron scattering cross-section (in barn/proton) for methyl iodide. This increases with increase in neutron wavelength in the range 4 Å to 17 Å. The cross section for CH_3I at 17 Å is 254 barn/proton and the slope (in barn/Å) of σ vs neutron wavelength is 13.9. The latter is related to rotational "barriers" and decreases smoothly with increase of the NMR rotational relaxation times. The latter is related to rotational barriers and decreases smoothly with increase, for example, of NMR rotational relaxation times. The neutron method shows some advantages, according to Fischer, for the separation of internal molecular rotations from reorientations of the whole molecule.

A molecular dynamics study by the neutron inelastic scattering method has been made by Janik et al. [54]. The lattice molecular dynamics of solid and liquid CH_3I were studied by the inelastic neutron scattering method. The spectrum obtained for solid CH_3I was caused by lattice vibrations (below 120 cm^{-1})

and by intramolecular vibrations of the CH_3I molecules (above ~500 cm^{-1}). Peaks obtained in the intermediate region were higher harmonics of the torsional vibrations. The spectrum obtained for liquid CH_3I was regarded as proof of the "freedom of translational motions" in the liquid phase. Apart from this semi-qualitative result, little insight to the molecular dynamics of CH_3I liquid has been obtained by neutron scattering.

DIELECTRIC AND FAR INFRA-RED SPECTROSCOPY

Used in combination [10] these two techniques still provide by far the most penetrating insight to the rototranslational dynamics of dipolar and (via induced absorption) non-dipolar, molecules. Reid et al. [58] have reported and analysed the far infra-red spectrum of a 10% solution of iodomethane in decalin. This peaks at 60 cm^{-1}, with a maximum intensity of 6.5 neper cm^{-1}. The Evans/Reid torque factor is 1980 g. The integrated intensity of the far infra-red band may be described by the Gordon/Brot sum rule which falls only 15% short of the observed intensity. For this paper we have measured the far infra-red absorption of pure liquid methyl iodide by interferometric and laser spectroscopy, and this is discussed in the results section. Heatley [45] has quoted a dielectric relaxation time of 3.6(5) ps for pure liquid methyl iodide, and in our simulation we hope to see to what extent this is affected by cross-correlations by comparison with the auto-correlation function of the dipole unit vector from the computer.

INHOMOGENEOUS RAMAN BROADENING

George et al. [59] have recently provided a first account of inhomogeneous broadening of vibrational linewidths in non hydrogen-bonded liquids including pure liquid methyl iodide. They combine the results of isotropic spontaneous

Raman studies with picosecond coherent probing experiments to study both homogeneous and inhomogeneous broadening in terms of one theoretical vibrational correlation function. These results indicate that non-hydrogen-bonded liquids are not motionally narrowed, because the liquid site relaxation times are much longer than earlier predictions. However, for eleven liquids, including methyl iodide, no simple correlation was found between the inhomogeneous broadening linewidths and Kirkwood dipole correlation factor (denoted by g). There was no simple correlation with the molecular dipole moment, Trouton's ratio, the hydrogen-bond parameter, or the molecular polarisability. However, inhomogeneous broadening tends to scale with the molecular shape anisotropy: the pseudo-spherical molecules are nearly homogeneous 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. The dynamics of the band-shapes observed were again treated by George et al. employing the relatively simple Kubo theory, to cover both the slow and fast processes observable.

In conclusion, the various spectroscopic methods used to investigate the molecular diffusion of methyl iodide in the liquid state have not produced a clear and consistent picture of the dynamics and interactions. A computer simulation is therefore appropriate as a convenient means of producing a number of related autocorrelation functions self-consistently from a given model of the pair interaction potential.

COMPUTER SIMULATION METHOD

The rototranslational and translational equation of motion are integrated with basically the same numerical method, which we have described more fully elsewhere [60]. The interaction between two methyl iodide molecules is modelled with a 5 x 5 Lennard-Jones atom-atom "core" with point charges localised at each site. Mutlipole-multipole terms are therefore represented with charge-charge interactions. The complete set of parameters are as follows.

$\varepsilon/k(\text{H-H}) = 13.4$ K, $\sigma(\text{H-H}) = 2.60$ Å; $\varepsilon/k(\text{C-C}) = 51.0$ K, $\sigma(\text{C-C}) = 3.20$ Å;

$\varepsilon/k(\text{I-I}) = 314.0$ K, $\sigma(\text{I-I}) = 4.10$ Å.

The cross terms were evaluated with the Lorentz-Berthelot combining rules. The carbon and hydrogen parameters are identical with those used for parallel simulations on CH_2Cl_2, $CHCl_3$, $CHBr_3$, tert-butyl chloride and bromoform, and we adhere to our method of using interchangeable Lennard-Jones parameters. This will eventually allow us to see whether a general theory of "simple" (non-associated) liquids can be developed using site-site models of this type. The I-I parameters were obtained using molecular crystal data [61]. This intermolecular pair potential may be refined, but this would require 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. The electrostatic interactions in methyl iodide were represented by point charges, calculated using bond moments and bond distances [62]. This provides:

$q_H = 0.055|\ell|$; $q_C = -0.043|\ell|$; $q_I = -0.122|\ell|$.

Charge-charge interactions are long-ranged, but their relatively small magnitude in this case means that periodic boundary conditions can be used with our 108 molecules.

The simulation run was initiated at 293 K, with a molar volume of 62.2 cm^3 at 1bar. The 108 methyl iodide potentials were arranged initially on a face-centred cubic lattice in a cube of half-side 11.17 Å, the potential cut-off distance. This is over twice the longest Lennard-Jones σ used. According to Bossis et al. [63] who have developed a method of computer simulation with no periodic boundary conditions medium range correlations even in intensely dipolar molecules disappear at about 10 Å from a given molecule.

Different minimum image criteria were employed for Lennard-Jones and charge-charge interactions. In the former case atomic sites were considered independently of what 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 25 contributions for each pair of molecules.

A time-step of 2.5×10^{-15} sec was employed initially to melt the lattice to the liquid state. Thereafter this could be doubled, the total energy being conserved to well within 0.5%. Autocorrelation functions were evaluated by running-time averaging from disk on the CDC 7600 computer of U.M.R.C.C., using standard procedures [10, chapter 1].

EXPERIMENTAL

The far infra-red power absorption of liquid methyl iodide was measured in CCl_4 and decalin solutions using interferometry and submillimetre laser spectroscopy [10, chapter 6]. VC-01 and VT-01 variable path-length sample cells were used to minimise the uncertainty on the ordinate scale (power absorption coefficient). Good agreement was obtained between the laser and interferometer results.

RESULTS AND DISCUSSION

The computed and experimental correlation times are collected in table 1. On the whole, the computed times are shorter than their experimental counterparts In view of figs.(1) to (2) this is not surprising, because the far infra-red absorption cross-section of these figures is clearly <u>non-linear</u> in the number density of CH_3I molecules in, for example, decalin solvent. This means that

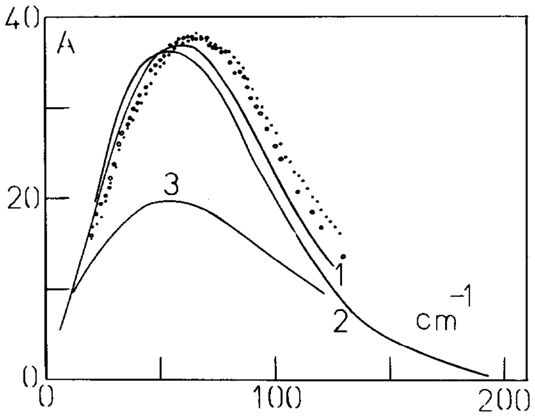

Figure (1)

Power absorption of CH_3I solutions in the far infra-red. 1) 100% CH_3I (v/v); 2) 75% (v/v) CH_3I; 3) 50% (v/v) CH_3I; 4) 25% (v/v) CH_3I.

Ordinate: power absorption coefficient: $\alpha(\bar{\nu})$ / neper cm^{-1}.

Abscissa: $\bar{\nu}$/cm^{-1}.

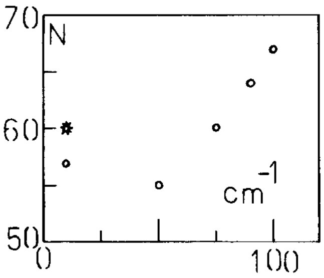

Figure (2)

Plot of far infra-red integrated intensity (A) against number density (N in molecules/cm^3) for the solutions of CH_3I in figure (1).

Ordinate: Integrated intensity (neper cm^{-2}).

Abscissa: Number density (molecules cm^{-3}).

the spectral properties of pure liquid methyl iodide (table 1) are heavily dependent on induced effects which are not pair-additive in the first approximation. The computer simulation method is, of course, pair-additive in nature and can therefore only provide an approximate idea of the orientational dynamics in pure CH_3I. Therefore it might be more appropriate to compare the results of the simulation with spectral results for CH_3I in dilute solution (table 1). In this case the experimental and theoretical results agree more closely, but the measured correlation times remain longer. For example, the dielectric relaxation time at infinite dilution is 2.5 ps [64], compared with a simulated auto-correlation time of 1.5 ps for the relevant first rank orientational a.c.f. The infra-red relaxation time in 20% m.f. hexane [19] is 2.0 ± 0.1 ps, compared with the computed time of 1.5 ps.

Raman, second-rank, orientational correlation times from various sources range from 0.8 ps [1] to 1.7 ps [20], and compare with a simulated time of 0.5 ps. In 20% m.f. hexane solution there is a reported Raman time of 0.8 ± 0.1 ps [19]. Similarly, the literature multi-particle second-rank Rayleigh correlation times range from 0.9 ps [21] to 3.1 ps [16] for the pure liquid. These are weighted averages of correlation times about each of the three principal axes in CH_3I as listed in the table.

By using a combination of Raman and NMR relaxation some authors have obtained estimates of second-rank correlation times for motion about the C_{3v} axis - the "spinning" of CH_3I as opposed to the "tumbling" observable by dielectric spectroscopy. These range from 0.05 ps [31] to 0.08 ps [53] for the pure liquid at lbar and ambient temperature. This compares with the equivalent computer simulated correlation time (see fig.(3)) of 0.05 ps. We can see from fig.(3) that 70 to 90% of the decay of these spinning a.c.f.'s is completed before they become exponential, so that the CH_3I potential used in the computer simulation allows the molecule to spin quite easily. This also seems to be the picture we obtain spectroscopically [9,31,53]. Again we emphasize that our fresh far infra-red results (figs.(1) and (2)) show that liquid CH_3I is heavily influenced in the spectroscopic sense by induction effects. Our computer simulation cannot take account of these non pair-additive effects (which stem from the influence of polarisability). We therefore draw the conclusion that the spinning motion of CH_3I is relatively unaffected by polarisability and induction effects and that the tumbling motion is heavily affected by collision induction in the pure liquid, less so in dilute solution.

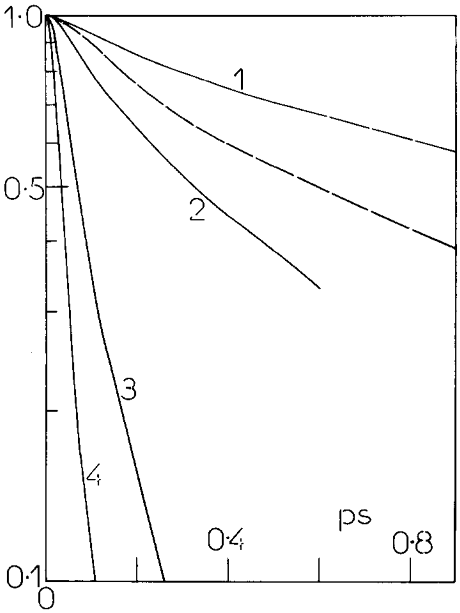

Figure (3)

Computer simulated first (P_1) and second (P_2) rank orientational autocorrelation functions for tumbling ($\underline{\ell}_3$ vector) and spinning ($\underline{\ell}_1$ vector) in CH_3I at 293 K, 1bar.

1) $P_1(\underline{\ell}_3)$; 2) $P_2(\underline{\ell}_3)$; 3) $P_1(\underline{\ell}_1)$; 4) $P_2(\underline{\ell}_1)$.

– – – – $P_2(\underline{\ell}_3)$ from ref.[40].

Abscissa: time/ps.

Dill et al. [21] have obtained an angular velocity correlation function for pure liquid methyl iodide from Raman and Rayleigh scattering. This is compared with the simulated angular velocity auto-correlation function $<\underline{\omega}(t).\underline{\omega}(0)>/<\omega^2(0)>$ in fig.(4). The latter is distinctly non-exponential, the influence of the spinning motion on the tumbling manifests itself through the oscillations superimposed on the basic structure of the a.c.f. This supports Steele's conclusion [9] that rotational diffusion theory cannot describe the

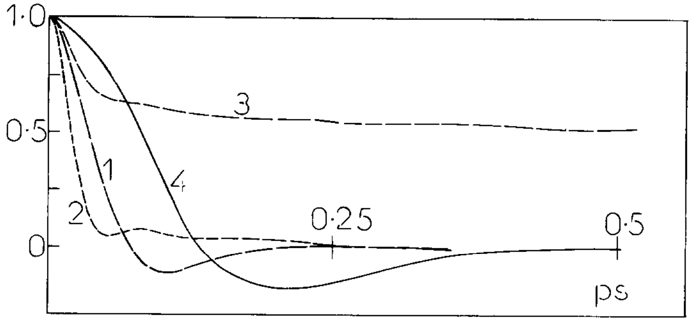

Figure (4)

Normalised angular velocity and angular momentum a.c.f.s from the computer simulation.

1) $<\underline{J}(t).\underline{J}(0)>/<J^2(0)>$; $\underline{J}$ = molecular angular momentum, lab. frame.

2) $<\underline{\omega}(t).\underline{\omega}(0)>/<\omega^2(0)>$; $\underline{\omega}$ = molecular angular velocity, lab. frame.

3) $<\underline{J}(t).\underline{J}(t)\underline{J}(0).\underline{J}(0)>/<J^4(0)>$

———— Normalised angular velocity a.c.f. from the work of Dill et al.[21].

Abscissa: ps.

molecular motion in liquid CH_3I. It is clear from fig.(4) that the simulated a.c.f. decays much more rapidly than the function derived by Dill et al. Kluk et al. [23] have also derived an angular velocity correlation function from the 525 cm^{-1} Raman (ν_3) band of the pure liquid, but this has an even deeper negative overshoot than the Dill et al. version, and cuts the time axis at about 0.2 ps.

We note that it is important to distinguish between the angular velocity and angular momentum a.c.f.'s $<\underline{J}(t).\underline{J}(0)>/<J^2(0)>$ for methyl iodide and in general for non-linear polyatomics. The simulation in fig.(4) shows clearly that these two functions do not have the same decay, and we explain why in the appendix. It is by no means clear that Dill et al. [21] or Kluk et al. [23] factorise out the inertial components in the same way. However, the major conclusion is that neither of these groups reports an <u>auto</u>-correlation function unaffected by polarisability effects on their original spectra. This is clear from our independent source of information in the far infra-red. Finally in fig.(4) our computed second moment a.c.f. $\langle \underline{J}(t).\underline{J}(t)\underline{J}(0).\underline{J}(0)\rangle/\langle J^4(0)\rangle$ is transiently non-Gaussian but finally reaches the equilibrium Gaussian level of about 0.5 for the C_{3v} symmetry of CH_3I. The angular velocity second-moment a.c.f. attains a final level of about 0.4, again the Gaussian result.

The rotational velocity autocorrelation functions for spinning and tumbling are shown in fig.(5). These are, respectively, $\langle \dot{\underline{\ell}}_1(t).\dot{\underline{\ell}}_1(0)\rangle/\langle \dot{\ell}_1^{\,2}(0)\rangle$ and $\langle \dot{\underline{\ell}}_3(t).\dot{\underline{\ell}}_3(0)\rangle/\langle \dot{\ell}_3^{\,2}(0)\rangle$ where $\underline{\ell}_3$ is a unit vector in the C_{3v} axis, and $\underline{\ell}_1$ a unit vector $\perp$ to this axis. In CH_3I the C_{3v} axis is also the dipole axis. According to classical adiabatic, fluctuation-dissipation theory [10, chapters

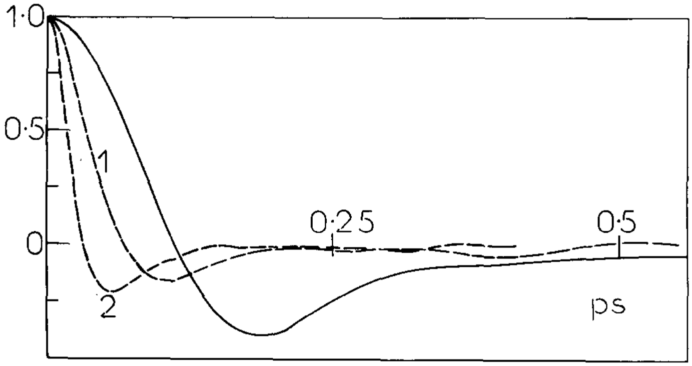

Figure (5)

Normalised rotational velocity a.c.f.s.

1) $\langle \dot{\underline{\ell}}_3(t).\dot{\underline{\ell}}_3(0)\rangle/\langle \dot{\ell}_3^2\rangle$;

2) $\langle \dot{\underline{\ell}}_1(t).\dot{\underline{\ell}}_1(0)\rangle/\langle \dot{\ell}_1^2\rangle$.

——— 3) Straight Fourier transform of the far infra-red power absorption of 10% CH_3I in decalin.

——— 4) As for 3) pure liquid CH_3I.

<u>Abscissa</u>: ps.

1-3] the rotational velocity a.c.f. of $\underline{\ell}_3$ may be related via a Fourier transform to the power absorption coefficient, $\alpha(\bar{\nu})$, (in neper cm^{-1}) of the far infra-red. (Lippert et al. [66] have recently extended this basic theory to the non-adiabatic case, with interesting results.) Straight Fourier transforms (no internal field corrections) of our far infra-red data are shown for comparison in fig.(5). In the pure liquid the Fourier transform of $\alpha(\bar{\nu})$ is a complicated multi-body correlation function, involving cross-correlations, correlations between induced-dipole moments [10, chapter 11] and internal field effects [10, chapter 3]. Some of these effects may be lessened or removed by dilution, and the Fourier transform of a 10% v./v. CH_3I/decalin solution [58] is shown for comparison in fig.(5).

Fig.(6) illustrates centre of mass linear velocity auto-correlation functions for CH_3I computed in both the usual laboratory frame of reference, and in a

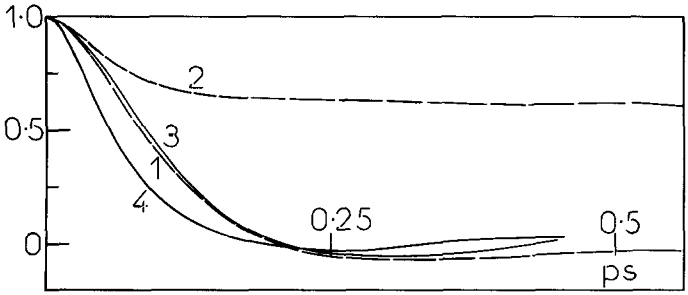

Figure (6)

Normalised linear centre of mass velocity a.c.f.s in the lab. and moving frames of reference.

1) $<\underline{v}(t).\underline{v}(0)>/<v^2(0)>$, lab. frame.

2) $<\underline{v}(t).\underline{v}(t)\underline{v}(0).\underline{v}(0)>/<v^4(0)>$, lab. frame.

3) $<v_C(t)v_C(0)>/<v_C^2(0)>$, moving frame (see appendix).

4) $<v_A(t)v_A(0)>/<v_A^2(0)>$, moving frame.

Abscissa: time/ps.

moving frame defined in the axes of the principal moment of inertia dyadic. Ciccotti et al. [67] have shown that the components of the velocity a.c.f. are no longer isotropic in a frame of reference which moves with the molecule, and fig.(6) corroborates this for CH_3I. The lab. frame a.c.f. has the characteristic long negative tail [10, chapter 5], and its second moment is again transiently non-Gaussian, but attains the Gaussian equilibrium level of 3/5.

ROTATION-TRANSLATION COUPLING

Ciccotti et al. [67] have shown that the angular momentum of a polyatomic molecule of C_{3v} symmetry is correlated statistically to its centre of mass linear velocity in a moving frame of reference. If we transform both J and v (the centre of mass linear velocity) into the moving frame of the three principal moment of inertia axes we can compute the auto-correlation matrix $\langle \underline{v}(0)\underline{J}^T(t)\rangle$. By symmetry [67] the (2,1) and (1,2) elements of this matrix exist and are illustrated in fig.(7), suitably normalised. Both elements should vanish by symmetry at t = 0 and this may be used as a test of the noise-level of the simulation. Fig.(7) shows that the noise is low near the time origin. Symmetry considerations again lead us to expect the (2,1) and (1,2) elements to be mirror images for C_{3v} molecules. This is indeed the case (fig.(7)) up to about 0.25 ps when the simulation becomes noisy. The (2,1) and (1,2) elements together show that the correlation of rotation with translation in CH_3I liquid is strong. Currently there are no theories available for the description of this effect, which can be discerned only by using the numerical method of molecular dynamics simulation. The most promising line of approach to these novel functions of molecular dynamics seems to be that of Grigolini et al. [68-74], using the synergetic philosophy (multi-disciplinary progress).

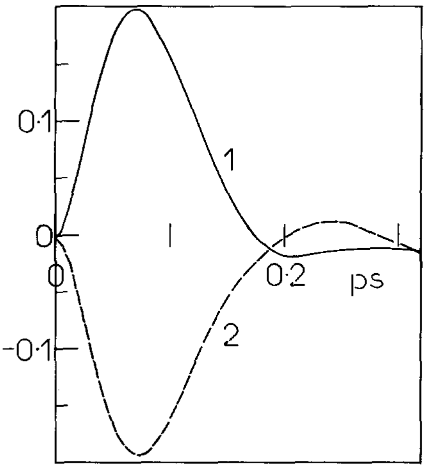

Figure (7)

Rotation-translation coupling in liquid methyl iodide, computer simulation.

$$1)\ \frac{\langle v_B(t)J_A(0)\rangle}{\langle v_B^2(0)\rangle^{\frac{1}{2}}\langle J_A^2(0)\rangle^{\frac{1}{2}}}\ ; \qquad 2)\ \frac{\langle v_A(t)J_B(0)\rangle}{\langle v_A^2(0)\rangle^{\frac{1}{2}}\langle J_B^2(0)\rangle^{\frac{1}{2}}}\ .$$

Function (1) is the (2,1) element of the moving frame matrix $\langle \underline{v}(t)\underline{J}^T(0)\rangle$ of the text, function (2) is the (1,2) element.

Abscissa: time/ps.

CONCLUSIONS

The spectral effects observable in pure liquid CH_3I are strongly affected by non pair-additive collision-induction, masking the observation of single molecule autocorrelation functions. The computer simulation is therefore an approximation to what is really going on in the pure liquid, but can, nonetheles produce insights which cannot be obtained yet in other ways. The clearest spectroscopic insight into the collision-induction process in pure liquid methyl iodide may be obtained using far infra-red absorption cross-sections as a function of CH_3I solute concentration.

APPENDIX: ANGULAR MOMENTUM AND ANGULAR VELOCITY OF METHYL IODIDE

One of the clearest ways of illustrating that the decay of the normalised angular velocity a.c.f. is not the same, in general, as that of the normalised angular momentum a.c.f. is as follows.

The components of the molecular angular momentum in the lab. frame (x, y, z) are defined as usual by:

$$\underline{J} = \underline{i}J_x \quad + \underline{j}J_y \quad + \underline{k}J_z \qquad \text{(A1)}$$

We may transform these into a frame of reference defined by the three unit vectors $\underline{\ell}_1$, $\underline{\ell}_2$ and $\underline{\ell}_3$ in the principal moment of inertia axes of the molecule. We shall denote these components by J_A, J_B and J_C.

$$\begin{aligned} J_A &= \ell_{1x} J_x + \ell_{1y} J_y + \ell_{1z} J_z \\ J_B &= \ell_{2x} J_x + \ell_{2y} J_y + \ell_{2z} J_z \\ J_C &= \ell_{3x} J_x + \ell_{3y} J_y + \ell_{3z} J_z \end{aligned} \qquad \text{(A2)}$$

In this frame the angular velocity components are:

$$\begin{aligned} \omega_A &= J_A/I_1 \\ \omega_B &= J_B/I_2 \\ \omega_C &= J_C/I_3 \end{aligned} \qquad \text{(A3)}$$

where I_1, I_2 and I_3 are the three principal moments of inertia about the axes defined by the directions of $\underline{\ell}_1$, $\underline{\ell}_2$ and $\underline{\ell}_3$. I_1, I_2 and I_3 are scalars, and therefore invariant under frame transformation.

We can transform ω_A, ω_B and ω_C back into the laboratory frame with the equations:

$$\omega_x = \omega_A \ell_{1x} + \omega_B \ell_{2x} + \omega_C \ell_{3x}$$

$$\omega_y = \omega_A \ell_{1y} + \omega_B \ell_{2y} + \omega_C \ell_{3y} \qquad \text{(A4)}$$

$$\omega_z = \omega_A \ell_{1z} + \omega_B \ell_{2z} + \omega_C \ell_{3z}$$

In this frame the decay of either the normalised angular velocity or momentum a.c.f. is the same (in an isotropic liquid) as that of any of its normalised components (sub. x, y or z). The decay of the $\cdot J_x$ component is $\langle J_x(t) J_x(0)\rangle / \langle J_x^2(0)\rangle$, whereas that of the ω_x component involves, from eqns. (A4) and (A2) all three components of $\underline{J}$ in the lab. frame and all three of the principal moments of inertia. The decay of $\langle \underline{J}(t).\underline{J}(0)\rangle / \langle J^2\rangle$ is not, therefore, the same as that of $\langle \underline{\omega}(t).\underline{\omega}(0)\rangle / \langle \omega^2\rangle$ in general. (The frame transformation (A2) has been used to construct the autocorrelation matrix $\langle \underline{v}(t)\underline{J}^T(0)\rangle$ of the text.)

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