

Spectral Studies of Rotational Diffusion[†]

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The winkers that had no choke-band,
The collar and the reins . . .
In Ealing Broadway, London Town
I name their several names

Until a world comes to life –
Morning, the silent bog,
And the God of imagination waking
In a Mucker fog.

Patrick Kavanagh

The dynamics of molecular motion in the liquid and disordered, but condensed, states of matter have been the subject of some of the most elegant theories in natural philosophy. Some of their originators¹⁻³ are justly famous, others unjustly neglected, but all have contributed to the understanding of a liquid's microscopic world.

It was known over a century ago that the problem must be one of statistics applied to temporal processes, i.e., motion in the time domain, the collective evolution of many individual trajectories. This was visible in the form of Brownian movement, and the young Einstein realized, by calculating the Avogadro number, how this phenomenon could be used to convince his peers of the existence of molecules. His unique instinct led him to use the correct averages to relate the large number of short-lived events of the molecular world to observable phenomena such as osmosis. It was quickly realized that the key to the problem lay in the use of probability. For example, if a molecule's angular momentum is $J(t)$ at an instant t , then how do we predict $J(t_1)$ on average? The answer was given in terms of the probability density function, whose diffusion in time is governed by statistically based equations of motion such as the Boltzmann equation, not deterministic, as in the case of Newton.

Debye⁴ was probably the first to adapt these ideas to describe the modulation of low-frequency radiation by a dipolar liquid, where each molecule is effectively a rotating antenna, capable of interacting differently with radiation of different frequencies. The radiation absorbed in the liquid may be expressed as dielectric loss, $\epsilon''(\omega)$, and a plot of $\epsilon''(\omega)$ vs. $\log \omega$, where ω is the angular frequency of the radiation, is known as a loss curve.

Debye produced a theory based on an idealization of individual molecular motion known as "rotational diffusion", which may be described in one way as angular displacements, infinitesimally small in magnitude,

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taking place infinitely rapidly. It produces the characteristic bell-shaped loss curve of Figure 1. This idealization held sway for far too long because of its success in describing the limited data available up to roughly the 1960s and 1970s, when the horizon opened out in many different ways. Two of the most important features to emerge were spectroscopy in the far-infrared⁵⁻⁷ and the construction by computer⁸⁻¹¹ of molecular trajectories in the liquid state.

A far-infrared spectrum¹²⁻¹⁴ is usually a plot of power absorption coefficient, $(\alpha(\bar{\nu})$ in neper cm^{-1}) against $\bar{\nu}$, the wavenumber at frequencies roughly in the range $\bar{\nu} = 1-250 \text{ cm}^{-1}$, both limits being chosen arbitrarily. We have $\omega = 2\pi\bar{\nu}c$. It is illustrated in Figure 2 along with the theoretical predictions of rotational diffusion.¹⁵ The lower frequency end of Figure 2 corresponds to the higher frequency part of Figure 1. The ordinate, $\alpha(\omega)$, of Figure 2 is related to the ordinate $\epsilon''(\omega)$ of Figure 1 by

$$\alpha(\omega) = \frac{\omega \epsilon''(\omega)}{n(\omega)c} \quad (1)$$

where $n(\omega)$ is the refractive index, almost constant in the far-infrared, and c the velocity of light. Clearly, the theory in Figure 1 and 2, looked at together, is successful at *low frequencies only* and the use of both α and ϵ'' , as opposed to ϵ'' only, provides us with new features of rotational molecular dynamics. The landscape is completed with the use of related spectroscopies such as light scattering,¹⁶ NMR relaxation,¹⁷ and

[†] This article is dedicated to the memory of Thomas Thomas, West Cross, Swansea.

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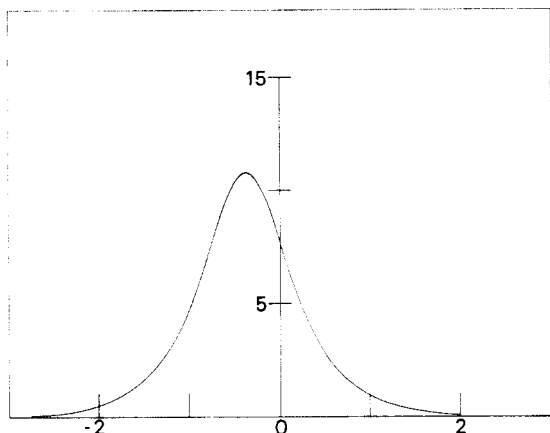


Figure 1. Loss curve for liquid 2-chloro-2-nitropropane at 293 K. (Reproduced with permission from ref 15. Copyright 1979, The Royal Society of Chemistry.)

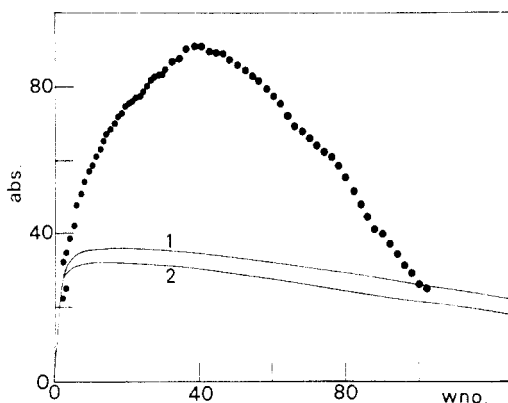


Figure 2. Absorption of 2-chloro-2-nitropropane (1) at 293 K: (1) spherical top Langevin equation; (2) asymmetric top Langevin equation. (Reproduced with permission from ref 15. Copyright 1979, The Royal Society of Chemistry.)

the new electrooptics^{18,19} with picosecond laser pulses, i.e., pulses of radiation on the "molecular" time scale.

Clearly we cannot hope to develop a "purely" analytical theory, enveloping such a variety of data sources, without involving the power of computer simulation,²⁰ where the liquid is represented by a group of maybe a thousand molecules moving according to Newton's laws and interacting with model potentials such as that of Lennard-Jones. In these terms the gap between Figure 1 and Figure 2 is immense, although they are only parts of the same spectrum expressed differently. The elegant and brilliant methods³ of Debye and his peers take us thus far (Figure 1) but not further (Figure 2). My co-workers and I have been concerned firstly with producing the experimental data²¹ represented by Figure 2, secondly with its analytical interpretation,²² and

increasingly with adapting for our needs the massive computer power now available.²³ There have been no "breakthroughs", rather a gradual evolution in our understanding.

Fourier Transform Interferometry¹³

Using a combination of far-infrared spectroscopy and computer simulation it is clear that the older theories, despite their beauty, are qualitatively inapplicable. For example, the equations of rotational diffusion as written by Debye imply that water would be opaque to visible frequency radiation.²⁴

The information which exposes this anomaly can be obtained by using Fourier transform interferometry, which was first developed by Gebbie and co-workers.²⁵ This is based on Michelson's interferometer and has the advantage of dispensing with the need for scanning the spectrum element by element (as with a grating or prism). This type of instrument is essential in the far-infrared, where Planck's law dictates that the power output of a conventional broad-band source is very low. Many varieties of interferometer are now available commercially, but the basic operating principle is to obtain an interferogram, a trace of the signal emerging from the Michelson interferometer as a function of mirror travel, i.e., of distance (in cm). The $\alpha(\bar{\nu})$ vs. $\bar{\nu}$ curve is then the Fourier transform of the interferogram, as sketched in Figure 2. We have adopted this instrument in our laboratory for use in many different configurations, suitable for gas-, liquid-, and solid-state spectra¹⁴ over a range of temperature and pressure.

At the lower frequency end of this spectrum the detection apparatus must be helium cooled and the interferometer developed with the polarizing design of Martin et al.²⁶ This has allowed us to extend our measurements over the range 250–2 cm⁻¹ (60 GHz) in one sweep (with G. J. Davies,²⁷ Telecom U.K.). In the 60-GHz range we overlap with the older but valuable klystron spot frequency apparatus. Our range is extended to still lower frequencies by using sweep frequency and bridge techniques. The total therefore extends from hertz (radio) frequencies (s⁻¹) to terahertz (10¹² s⁻¹), which are in the far-infrared. The sweep is one of about 12 decades. The infrared range from, for example, 100–10 000 cm⁻¹ covers just 2 decades. The THz frequency results can be checked with submillimeter laser apparatus²⁸ and with carcinotrons.

The range of other techniques having some bearing on molecular diffusion is increasing very rapidly. Information about molecular motion and interaction can be obtained by an analysis of the way in which electromagnetic or neutron radiation is scattered from a liquid²⁹ by using the shape of infrared and Raman

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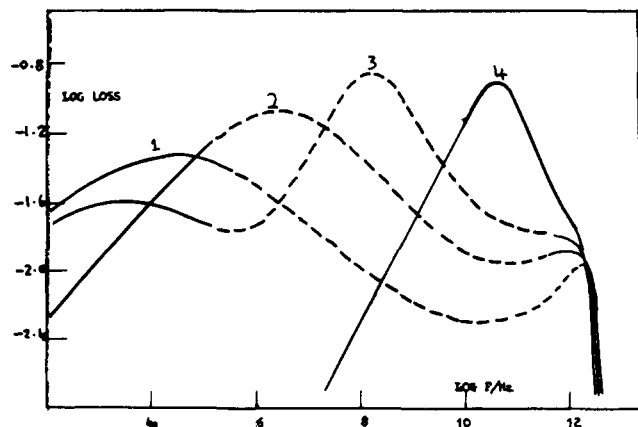


Figure 3. Zero to THz loss spectra for 10% v/v fluorobenzene in decalin: (1) 77 K (β and γ processes); (2) 110 K (β and γ processes); (3) 143 K (α , β , and γ process); (4) 293 K (liquid). Curves 1 and 2 are in vitreous decalin solvent, and curve 3 is in supercooled decalin solvent.

bands,³⁰ nuclear magnetic resonance,³¹ the features of transiently induced birefringence³² (e.g., the Kerr effect and Faraday effect), and a number of other sources.³³ These should ideally be used together to draw as complete a picture of the liquid as is possible in spectral (i.e., temporal) colours. This produces the required entity for theoretical analysis and computer simulation.

Types of Molecular Diffusion

The problem is that of solving a statistical equation of motion for interacting, polarizable, bodies. The liquid (and adjacent) states of matter absorb and disperse radiation as a broad band up to and including THz frequencies. The resulting features can reflect molecular motion on a picosecond timescale (as in a gas³⁴) to one of hours and longer (as in a glass). The overall aim has been to analyze these various phenomena starting from the same statistically based equations of motion,³⁵ i.e., to use the laws of probability to reduce the large number of molecular variables (such as position and momentum) to a much smaller set of accessible thermodynamic averages. Our primary concern has been with the high-frequency end of the enormous Hz to THz range.

The diffusion of rotating molecules takes place in a variety of ways. One of the most striking pieces of evidence³⁶ for motion very different from Debye's model is that of HBr in liquid SF_6 . The $\Delta J = 1$ rotational peaks of the gas can be observed as well in the far-infrared spectrum of the liquid mixture. The rotational freedom must therefore be far greater than that envisaged with the infinitesimally small angular displacements of Debye's rotational diffusion. At the other extreme, the dynamical evolution in the highly viscous environment of supercooled liquids and glasses can be

represented by a continuous and immensely broad dielectric loss curve as in Figure 3. This is very much broader than Debye's curve of Figure 1 and sometimes peaks *three* times (α , β , and γ losses). On a log (frequency) scale the far-infrared (γ) part, discovered recently by Reid and Evans,³⁷ occupies a small but theoretically important slot at the highest frequency end of the plot. It is crucial to realize that the complete broad band represents in a temporal context an *evolutionary* process based on picosecond fluctuations gradually making themselves felt on a time scale *up to a million million* (10^{12}) times slower.

Electrodynamics and Kinematics: Collision-Induced Absorption

When considering the motion and interaction of molecules we are dealing with polarizable entities which may be described for the sake of argument in terms of multipole moments.³⁸ The movement and interaction of these molecular moments may be termed electrodynamics. Sometimes molecules may be described by impenetrable surfaces which collide more or less elastically. The motion of such objects may be termed kinematics. This separation is arbitrary in general, but electrodynamic interactions are responsible in the far-infrared for the collision induction³⁹ of temporary dipoles in otherwise nondipolar molecular liquids such as CCl_4 . This type of absorption is a multimolecular phenomenon in the liquid state and is reducible to a two-body process only in the dilute gas.

When dealing with this theoretically the electrodynamic part of the potential is more effective usually in producing the spectral features than the hard repulsive cores. As the gas is compressed toward the liquid state, a given interacting pair of molecules is influenced to an increasing extent by others in its immediate vicinity so that in the liquid state one molecule is at an instant of time influenced by the field of nearest and less proximate neighbors. The mutual interaction of all these fields leads to a much less intense induced far-infrared absorption than in the dilute gas,⁴⁰ where pair interaction allows the one molecule to exert the fullest influence on its solitary and temporary neighbour. The integrated intensity of the absorption band per molecular number density squared (A/N^2) is much less in the liquid because of the effect of symmetry. In the ideal molecular crystal the induced absorption would cancel completely if the symmetry were right. It would be informative to simulate this behavior with computer molecular dynamics because it is unrealistic to attempt to describe this type of phenomenon, which occurs universally and in addition to absorption or scattering, without consideration of polarizability and without dispensing with pair additivity, the usual theoretical approximation.

For the more dipolar or polarizable molecules, the dipole will interact with its neighbors in a complicated non-pair-additive manner. Water is the case where the electrodynamic network extends via H bonding throughout the sample. The meaning of a single mol-

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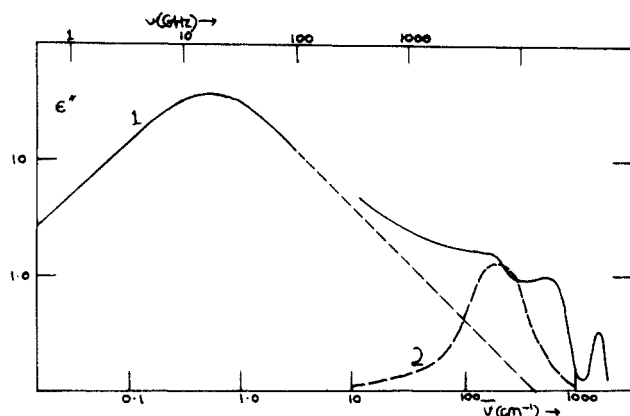


Figure 4. Loss curve of (1) pure liquid water and (2) of water molecules free of hydrogen bonding. The second curve peaks almost in the mid-infrared, the former in the microwave.

ecule relaxation process (such as envisaged by Debye) is now obscured, but by using the far-infrared spectrum of very dilute solutions of water in organic solvents such as cyclohexane²⁴ and by matching the spectrum theoretically, the dynamics of individual water molecules can be seen plainly to be gas like, in stark contrast to the case in pure liquid water (Figure 4).

Mean Square Torque and Volume of Rotation

A variety of theoretical methods has been developed (based on the work of Mori, Kubo, Zwanzig, Berne, and many others)¹⁴⁻¹⁶ to deal with the broad-band spectral features in the static to THz range.

The most characteristic and discriminating feature of a spectrum such as that in Figure 1 and 2 is the shift in frequency of the α and ϵ'' peaks with pressure, temperature, viscosity, etc. It is difficult and interesting to match these combined features theoretically. To start with, using both ϵ'' and α data we have to produce the respective peak frequencies ω_1 and ω_2 at which

$$\left[\frac{d\epsilon''}{d\omega} \right]_{\omega_1} = 0 \quad (2)$$

$$\left[\frac{d\alpha}{d\omega} \right]_{\omega_2} = 0 \quad (3)$$

with equations of motion on the molecular scale.

At the same time the measured band shape must also be reproduced theoretically with the same equations. It is frequently the case that with the far-infrared data produced by our interferometer we are able to define the spectra $\omega^2\alpha(\omega)$ vs. ω , and more rarely $\omega^4\alpha(\omega)$ vs. ω , together with the peak frequencies ω_3 and ω_4 , respectively. As far as I know, there exists no analytical technique (including computer simulation) which can deal with this kind of moment analysis in detail. My colleague C. J. Reid and myself have accordingly developed a series of semiempirical equations designed^{21,41} to deal with just ϵ'' and α in terms of the Reid/Evans torque factor

$$T_q \propto I_r \omega_2^2 \quad (4)$$

which is an approximate but useful measure of the molecular mean square torque. Here I_r is an average moment of inertia. Although eq (4) looks very simple and limited in scope, it is as well to remember that

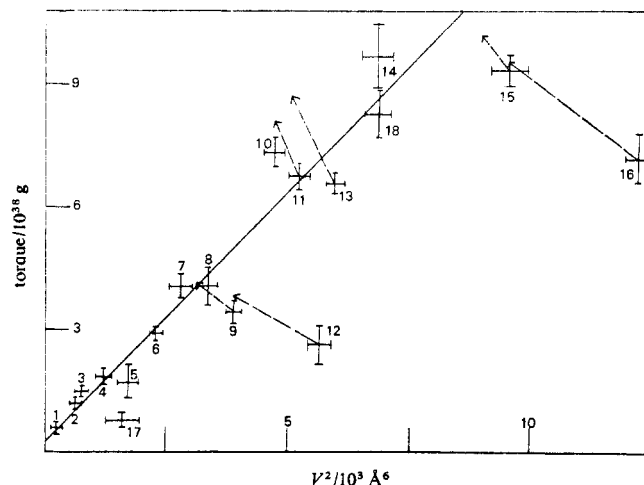


Figure 5. Plot of V^2 (10^3 \AA^3) against torque ($\times 10^{38} \text{ G}$) for the following solutes in decalin at 293 K: (1) CH_2Cl_2 ; (2) chloroform; (3) furan; (4) pyridine; (5) tetrahydrofuran; (6) fluorobenzene; (7) α -picoline; (8) pentafluorobenzene; (9) chlorobenzene; (10) toluene; (11) benzonitrile; (12) bromobenzene; (13) nitrobenzene; (14) *o*-xylene; (15) 1-chloronaphthalene; (16) 1-bromonaphthalene; (17) *tert*-butyl chloride. (Bottom panel) As for top in decalin glass at 110 K. (Reproduced by permission from ref 21b. Copyright 1980 The Royal Society of Chemistry.)

models incorporating elastic collisions such as the extended diffusion models of Gordon⁴² leave the frequency ω_2 essentially undefined. Equation 4 is derived on the basis of a theory³⁵ published in 1976. Whatever its drawbacks, this has the advantage of rationalizing shifts in ω_1 and ω_2 in terms of T_q and the relation between this and the square of a molecular volume of rotation V . Thus:

$$T_q \propto V^2 \quad (5)$$

This is illustrated for about 20 solutes in decalin Figure 5. The volume V can be constructed from the individual molecular geometry and is not empirical. On the whole, the correlation in Figure 5 is good. We can rationalize anomalies in terms of mechanisms such as rotation/translation coupling, which we consider using only the facts of molecular geometry.

The low viscosity (single particle) theory which produces eq 4, and therefore eq 5, is not valid at high viscosities such as those encountered in supercooled and vitreous decalin solvent. Nonetheless, the relation $T_q \propto V^2$ still holds true for a large number of solutes (Figure 6) while the ϵ'' and α spectra are, of course, spread over the decades of Figure 3. The limitations of the theory are brought out the most clearly when we extend our consideration to ω_3 and the spectrum $\omega^2\alpha(\omega)$. If we consider ω_4 as well then the theory produces a plateau in much the same way as Debye's theory does in α itself.

Molecular Dynamics Simulation

The simulation runs in our laboratory have been designed to complement both the theoretical and experimental work described briefly above. The technique was used to Raman⁴³ in 1964 for 864 interacting atoms and since then has been developed for use with, for example, ions, rotator phases, liquid crystals, surfaces, and molecular liquids.⁹ It allows us to use in the

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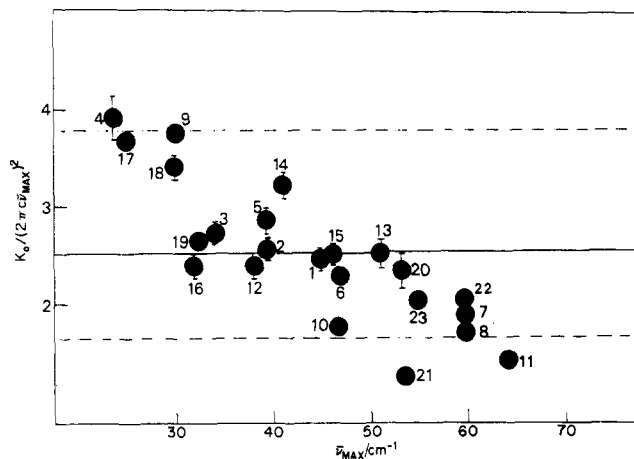


Figure 6. Ratio of Mori/Evans mean-square torque to far-infrared peak frequency squared for 23 solutes in decalin solvent at 293 K. If the theory were not approximate this would be a constant, i.e., the peak frequency is also determined by higher derivatives of the mean-square torque in general. (Reproduced from ref 21a. Copyright 1980, Taylor and Francis.) (1) Pyridine; (2) fluorobenzene; (3) chlorobenzene; (4) bromobenzene; (5) nitrobenzene; (6) benzonitrile; (7) α -picoline; (8) toluene; (9) pentafluorobenzene; (10) chloronaphthalene; (11) aniline; (12) bromonaphthalene; (13) furan; (14) tetrahydropyran; (15) thiazole; (16) chlorocyclohexane; (17) *tert*-butyl chloride; (18) chloroform; (19) 2-chloro-2-nitropropane; (20) methylene chloride; (21) acetone; (22) methyl iodide; (23) methylene bromide.

equations of motion models of the intermolecular potential energy based on experimental data from independent sources. There is, of course, a great deal of literature available on the problem of defining the potential-energy contours of the isolated molecule,⁴⁴ and the major problem facing the dynamicists is that of incorporating this knowledge in the dynamical context of molecular interaction.

We have space here for one illustration of the technique in Figure 7. In this diagram we have simulated the Langevin function for the orientation in space of an assembly of 108 C_{2v} triatomics, interacting via a 3×3 Lennard-Jones atom-atom potential. The Langevin function describes the statistical response of a liquid to an external perturbation and is the backbone of dielectric spectroscopy.^{7,18} It was first derived for magnetic dipoles by Langevin⁴⁵ in 1905, and Figure 7 represents the first attempt⁴⁶ at simulating this function by taking the 108 molecules and perturbing their motion with an externally applied force, incorporated into the molecular dynamics algorithm. The great advantage of being able to do this is that the severe mathematical problems of solving Kramers/Fokker/Planck statistical equations such as that of Nordio et al.⁴⁷ for liquid crystals⁴⁸ can be bypassed.

Future Developments

The time is ripe to select molecules for a combined investigation using the methods described in this Account under stipulated conditions³³ of temperature and

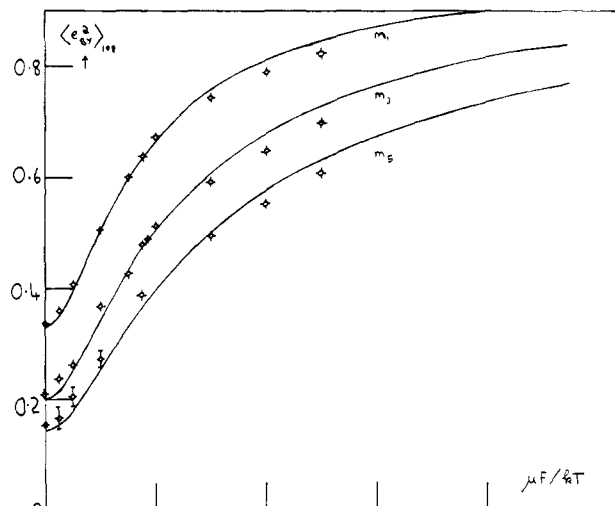


Figure 7. Langevin functions (vs. $\mu F/kT$) from the linear response region to saturation. (Stars) Points taken from a computer simulation; (unbroken line) theoretical curves, calculated using Boltzmann statistics (taken from M. W. Evans, *J. Chem. Phys.*, 1982, submitted for publication). m_1 , m_3 , and m_5 are the first, third, and fifth order Langevin functions.

pressure.⁴⁹ For example, if we choose substituted methanes such as CH_3F , CH_3I , and CH_2Cl_2 , we would expect to attain objectives such as (i) studies of these liquids at the same state points with all available spectroscopic techniques;³³ (ii) simulation of the results at these state points with different molecular dynamics algorithms; (iii) improvement of our theoretical methods to deal with these results; (iv) collection of the thermodynamic data where necessary; for example, pressure and dielectric virial coefficients.

The choice of CH_2Cl_2 , for example, is supported by the following considerations:

(1) It is dipolar asymmetric top (C_{2v}) which is a liquid at room temperature. It has been widely used in industry as a solvent, and many of its basic physical properties are known.

(2) It has a wide liquid range of almost 140 K from the melting point to the boiling point at 1 bar. Its critical temperature and pressure have been measured.

(3) The variation of solidification temperature with applied pressure is known, and so is that of the static permittivity. This facilitates measurements at constant volume over a temperature range.

(4) A comprehensive literature search³³ has shown that CH_2Cl_2 has been investigated with a variety of spectroscopies with an unacceptable degree of disagreement between interpretations.

(5) There are infrared-active vibrations with transition moment vectors parallel to any one of the axes of inertia so that the rotational moment of each axis may be studied by choosing an appropriate vibrational band.

(6) The liquid absorbs strongly in the zero to far-infrared frequency region (static to far-infrared) and is easy to study. The behavior of CH_2Cl_2 in vitreous and viscous environments is especially significant.

(7) It has a predominantly incoherent scattering cross section under cold neutron irradiation due to the presence of equivalent hydrogen atoms. There are no low-frequency vibrational inelastic features in a low-

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(49) Interested readers are invited to get in touch with the author for details of this project.

energy neutron scattering experiment. The far-infrared absorption is also free from this type of distortion on the high-frequency side.

(8) The C_{2v} symmetry of the molecule is that of water so that the available water algorithms of the molecular dynamics simulation can be adapted straightforwardly for CH_2Cl_2 , which is possibly "weakly H bonded" in the neat liquid state.

(9) For NMR spectroscopy the presence of C, H, D, and Cl nuclei is an advantage for probing motional anisotropy.

(10) The large amount of work completed already on acoustic relaxation in liquid CH_2Cl_2 means that it will be relatively straightforward to coordinate this technique with Brillouin and neutron scattering to inves-

tigate centre of mass motions and their relation to orientation.

(11) A number of simulation algorithms are already available which can now handle a molecule the size of CH_2Cl_2 .

(12) Finally, several nonlinear electrooptical methods (e.g., high-field birefringence induction) can be brought to bear on the molecular motion.

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