PROPOSALS FOR A EUROPEAN COLLABORATIVE PROJECT ON THE CONSISTENT EVALUATION OF MOLECULAR DYNAMICS IN LIQUIDS

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## I. INTRODUCTION

At the most fundamental level, molecules react with one another because they collide and interpenetrate. Furthermore, the vast majority of chemically important reactions are carried out in the liquid phase - usually in a 'suitable' (sometimes interacting) solvent. In order to investigate, therefore, the most fundamental aspects of chemical reactivity it is crucially important to promote a good understanding of the dynamics and interactions of molecules in the liquid state. Even a cursory glance at the vast literature which has been generated (R1-R10) (even over only the last 20 years) will serve to confirm that such an understanding is notoriously difficult to achieve. With the exception of a few liquid noble gas systems, it is remarkably crude. We still know very little, for example, about the nature of a 'collision' in the liquid phase, while only very recently have theoreticians used anything much more sophisticated than 'hard sphere' (purely repulsive) interactions in their attempts to simulate the static and dynamic properties of molecular liquids. Nevertheless, the last 10-15 years have seen the rapid development of a variety of both experimental and theoretical 'tools' which allow us to tackle the 'liquid' problem with greater confidence. These include a wide range of spectroscopic techniques including infrared, Raman and Resonance Raman, photon and neutron scattering, far-infrared/microwave, n.m.r. and e.s.r., fluorescence depolarisation etc.; thus giving information over a very wide range in both frequency and time domains. But, equally important, with the advent of large computers, have come new and more sophisticated algorithms for the generation of liquid properties. These mainly involve the use of more realistic intermolecular potentials (1-4) (with attractive as well as repulsive forces and with allowance for the effects of polarisability and induced dipoles). There has also been a great deal of activity by theoreticians (R6, R9, R10) using analytical (rather than simulation) techniques. Attempts have been made (R12) to develop theories which include, for example, vibrational/ rotational/translational coupling, the effects of finite intermolecular torques on molecular rotation, and the allowance which needs to be made for strong dipole-dipole or dipole-induced dipole interaction (section II and III). One might expect that work in the field would be rapidly progressing and even that a 'breakthrough' might be imminent. Unfortunately, relatively little has been achieved for any particular molecular liquid in the last 10 years (although much has been partially done on a very wide range of molecules from diatomics through to pigments and biopolymers (R14)). The main reason for this is, of course, that each experimental or theoretical group works on their own molecule (or algorithm or theory) under their own (accessible and convenient) set of physical conditions

using their own (available) technique. The result is a massive collection of (useful?) data and computations which casts only partial light on the problem as a whole (since extrapolation from one molecule to another is virtually impossible for most purposes).

The investigation of molecular dynamics in the liquid state of matter has thus reached the stage where coordination and collaboration are essential before further incisive advances can be made. There are three major areas for investigation which ought to be included.

(i)   The study of spectral bandshapes, which, on Fourier transformation, give experimental correlation functions. These may be either cross-correlation functions or auto-correlation functions dependeing on circumstances and technique (see below).

(ii)  The development of analytical theories, which are dependent on the methods of statistical mechanics, designed to reduce the number of dynamical variables involved from Avogadro's number order of magnitude to not more than two cr three thermodynamic averages.

(iii) The simulation of the individual trajectories of about $10^2$ to $10^3$ model potentials using Newton's equations. This requires a great deal of computer time but, within the framework of assumptions used, provides essentially a complete bank of data which can be used to build up both static and dynamic properties of the system. These may be compared with spectral (or other) data in an attempt to test the viability of the assumed inter-molecular potentials.

The third area has been expanding steadily since its inception in the early 1950's. With the increase in computer power now available, it is possible to simulate the motion and interaction of increasingly more complicated and presumably more "realistic" model potentials. For the first time it is becoming possible to simulate dipolar molecules (1-5) such as the substitutea methanes.

The time is therefore ripe for the initiation of a simultaneous programme of study (within these three areas) for a selected system(s) under identical conditions of pressure and temperature over the whole of the liquid range. With this purpose in mind several laboratories have already agreed to coordinate their research for the three molecules, $CH_3F$, $CH_3I$ and $CH_2Cl_2$ with the following major objectives.

(i)   To study these dipolar fluids by a wide range of spectroscopic techniques at thermodynamic conditions agreed upon by each laboratory. The end result will be a collection of spectral profiles and correlation functions which can be analysed for the information they contain about molecular motions and interactions.

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(ii)  To simulate these same band shapes by the technique of molecular dynamics
       under the same thermodynamic conditions.  A number of different model
       potentials is to be used to test (by direct comparison) the sensitivity of
       the simulated spectral features to changes in interaction potential.
(iii) To measure second virial coefficients (and related quantities) needed as an
       aid in the choice of intermolecular potential for computer simulations.
(iv)  To develop analytical models which attempt to describe the data obtained
       from spectroscopic (and other) techniques.
It is hoped that the combined efforts can be discussed at a conference (or
conferences) to be organised in 2 or 3 years time.

     The purpose of this article is primarily to provide a review of the reasons
why such a project is necessary, and to provide a source of reference concerning
the present conditions under which the investigations are planned.  We hope that
it will help to stimulate collaborative efforts between readers in this area.
The review is set out as follows:

     In section II we highlight the problem of achieving consistency of interpre-
tation among results obtained using different techniques.  We then present basic
outlines (section III) of the experimental spectroscopic and theoretical methods
available for the proposed studies.  In section IV we describe in more detail the
need for intercomparison of data from different sources.  This is followed by a
survey (in section V) of published data on each of the three molecules proposed
for collaborative study.  These accounts emphasise the lack of consistency in
conditions of study which have reduced the effectiveness of the results obtained
so far.  Finally, section VI gives a list of properties of the molecules with
which we are concerned and makes specific proposals for the physical conditions
to be used by all participating groups.


II.  SURVEY OF THE PROBLEM OF CONSISTENCY

     Hildebrand (6) has recently produced a number of criteria to be borne in mind
when dealing with a problem which is as complex as that of explaining the properties
of the liquid state in molecular terms.  In particular he emphasises that:-

(1) One should avoid concepts which are inconsistent with each other and with the pertinent facts. These include (7) "holes, cells, clusters, cages, lattices, scaled particles, fluidised vacancies, hypernetted chains and molecules with solid-like degrees of freedom". This reflects the comparative failure of analytical modelling of the liquid state even at the stage where molecular dynamics are not considered. Computer simulations are not based on so many conflicting preconceptions.

(2) "A model should be regarded as suspect if it yields inferences in serious conflict with any of the pertinent properties of a system, regardless of how closely it can be made to agree with some, especially if there are adjustable parameters. A model that is consistent with all properties even if only approximately, can probably be made more precise, but if it is in irreconcilable conflict with any part of the evidence, it is destined to be discarded, and predictions and extrapolations based upon it should be unreliable." (Quoted from ref. (6).)

(3) Any valid theory must not disagree with experimental findings such as

(a) The entropy of vaporization of all 'simple' liquids to the same concentration of vapour is the same. It is larger for 'associated' liquids, hence simple liquids are usually assumed to be in a state of maximum disorder and have no structure. (Notice, however, the evidence (R4) for microscopic 'order' in some simple systems obtained by the study of concentration fluctuations.)

(b) Simple liquids flow freely when expanded by only a few percent over their intrinsic volume. There is no room for "holes" or "lattices" or jumps greater than a small fraction of the molecular diameter. Self-diffusion occurs because thermal motion prevents any molecule from remaining in the same spot.

(c) For volumes smaller than the molar volume, $V_t$, (that at which soft (i.e. non-hard sphere) molecules begin to be sufficiently separated between collisions to acquire fractions of their momentum in free space) molecules are in fields of force not appropriately described by pair-potentials. The role of temperature is only to determine volume. Values of $V_t$ depend upon the capacity of a molecular species to absorb collision momentum by bending, vibrating or rotating.

Bearing in mind these criteria, it is clear that there has been a tendency for the analytical theoreticians to model the molecular dynamics with simplistic and subjective ideas. Even when an idea is complicated it often does not stand up to simple experimental facts (criterion 1). We are faced with a problem to which there are many apparent solutions. It is therefore unlikely that progress can be made using complicated and over-parameterised molecular models which, nevertheless, greatly over-simplify the problem and, in consequence, are subjective in nature.

I. OUTLINE OF BASIC APPROACHES TO THE PROBLEM

) Experimental Spectroscopic Methods

The study of molecular dynamics in polar liquids is usually tackled by
tempting to calculate from combined experimental data (R1-R6, R11) the vibrational
d rotational correlation functions,

$$
_{ib}(t) = <\sum_{i,j}[\underline{Q}_{\nu i}(o).\underline{Q}_{\nu j}(t)]> = <\sum_{i}[\underline{Q}_{\nu i}(o).\underline{Q}_{\nu i}(t)]>
$$

$$
+ <\sum_{i \neq j}[\underline{Q}_{\nu i}(o).\underline{Q}_{\nu j}(t)]> \tag{1}
$$

$$
d\ C_{\ell R}(t) = <\sum_{i,j}P_{\ell}[\underline{u}_{i}(o).\underline{u}_{j}(t)]> = <\sum_{i}P_{\ell}[\underline{u}_{i}(o).\underline{u}_{i}(t)]>
$$

$$
+ <\sum_{i \neq j}P_{\ell}[\underline{u}_{i}(o).\underline{u}_{j}(t)]> \tag{2}
$$

.ich contain all the information we can obtain about the relevant band broadening
ocesses. In these equations $\underline{Q}_{\nu i}$ is the normal coordinate of the $\nu$th vibration
the ith molecule, $\underline{u}$ is a unit vector along the direction of the molecular
pole ($\underline{\mu}$), polarisability tensor ($\underline{\underline{\alpha}}$) or transition dipole ($\underline{\mu}'$), etc, and $P_{\ell}$ is
e $\ell$th order Legendre Polynomial (R1).

The relationship between these functions and the various experimental spectral
atures mentioned above are summarised below.

(a) Infrared

$$
_{IR}(\nu)\exp(i\omega t)d\omega \varpropto <[\underline{Q}_{\nu i}(o).\underline{Q}_{\nu i}(t)]_{IR}.P_{1}[\underline{\mu}_{1}'(o).\underline{\mu}_{i}'(t)]> \tag{3}
$$

$$
\approx\ C_{vib}^{IR}(t)C_{1R}^{sp}(t) \tag{3a}
$$

ere $I_{IR}(\omega)\varpropto\epsilon''(\omega)/[1-\exp(-h\omega/kT)]\quad\varpropto\dfrac{n(\omega)\alpha(\omega)c}{\omega_{o}}$  for $h\omega \gg kT$

d $\epsilon''(\omega)$ is the imaginary part of the complex permittivity.

(b) Far-Infrared and Microwave

$$
_{FIR}(\omega)\exp(i\omega t)d\omega \varpropto <\sum_{i,j}P_{1}[\underline{\mu}_{1}(o).\underline{\mu}_{j}(t)]> \tag{4}
$$

$$
\approx\ C_{1R}^{sp}(t) + C_{1R}^{d}(t) \tag{4a}
$$

ere $I_{FIR} \equiv \dfrac{\epsilon''(\nu)}{\left[1-\exp\left(\dfrac{-h\nu}{kT}\right)\right]} = \dfrac{\alpha(\nu)n(\nu)}{\omega c[1-\exp(-h\omega/kT)]}$

(c) Isotropic Raman

$$\int I_{iso}(\omega)\exp(i\omega t)d\omega \; \propto \; <\underline{Q}_{\nu i}(o).\underline{Q}_{\nu i}(t)>_{iso} \tag{5}$$

$$= \; c_{vib}^{iso}(t) \tag{5a}$$

where $I_{iso}(\omega) = I_{VV}(\omega) - \frac{4}{3}I_{VH}(\omega)$

and $I_{VV}(\omega)$ and $I_{VH}(\omega)$ are the polarised and depolarised Raman band profiles.

(d) Anisotropic Raman

$$\int I_{aniso}(\omega)\exp(i\omega t)d\omega \; \propto \; <[\underline{Q}_{\nu i}(o).\underline{Q}_{\nu i}(t)].P_2[\beta_i'(o).\beta_i'(t)]> \tag{6}$$

$$\approx \; c_{vib}^{aniso}(t).c_{2R}^{sp}(t) \tag{6a}$$

where $I_{aniso}(\omega) = I_{VH}(\omega)$

(e) Depolarised Rayleigh

$$\int I_{DP}(\omega)\exp(i\omega t)d\omega \; \propto \; <\sum_{i,j} P_2[\beta_i(o).\beta_j(t)]> \tag{7}$$

$$\approx \; c_{2R}^{sp}(t) + c_{2R}^{(d)}(t) \tag{7a}$$

(f) Incoherent neutron scattering (by protons)

If rotation and translation are decoupled, then:

$$\int S_{inc}(\underline{Q}',\omega)\exp(i\omega t)d\omega \; \propto \; I_{rot}(\underline{Q}',t)I_{trans}(\underline{Q}',t) \tag{8}$$

where $I(\underline{Q}',t) = \sum_{\ell=o}^{\infty} (2\ell + 1)j_\ell^2(\underline{Q}'d)f_\ell(t)$

and $f_\ell(t) \equiv <P_\ell(\cos\theta_{ij}(t))>$

The $S_{inc}(\underline{Q}',\omega)$ is related to the incoherent scattering cross section and is a function of momentum ($Q'$) and energy ($h\omega$) transfer. In equations 3-8 the intergration is over as wide a frequency range as is practicable.

Thus, in principle, it is possible to determine both 'self' (sp) and 'distinct' (d) parts of the correlation functions in equations (1) and (2) at least for $\ell=1$ and $\ell=2$. In practice, however, there are a number of restrictions imposed mainly by the assumptions involved in making these formulations (which a discussed in detail below). One severe problem arises because it has been

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demonstrated (8) that if intermolecular coupling (via strong molecular interactions) is significant the $C_{vib}^{IR}(t) \neq C_{vib}^{iso}(t) \neq C_{vib}^{aniso}(t)$. There are also severe problems connected with the validity of the separation of rotational and vibrational corre- lation functions (for example, in eqns. 3 and 6) since, the two (or more) dynamic processes are unlikely to be statistically independent, especially if their respective correlation times are very similar (as they usually are for small molecules in liquids). The effects of vibration-rotation coupling in liquids have only recently received any serious attention (see below) while the effects of coupling of the various processes (both elastic and inelastic) leading to vibrational relaxation have been virtually ignored.

The spectroscopic techniques referred to above have been used separately in the past to look at molecular dynamics from different angles. They have only very rarely been used in combination with each other, and there have been few attempts to compare the results from more than one technique. (This has been attempted, however, by Brier and Perry (for $CH_2Cl_2$) (R8) and by Steele (R1) (for $CH_3I$).) Clearly, it is pointless to increase the complexity of liquid state theory without inter-technique or multi-technique consistency.

(b)  Theoretical Methods and Problems

Within the framework of the project there is available a variety of molecular dynamics algorithms each of which needs to be tested as thoroughly as possible with the thermodynamic and spectral data. By using the simulation method (which cannot yet be regarded as incisive for dipolar liquids as it is for other types) we can nevertheless use a much more realistic form for the intermolecular potential than can a model of the liquid state such as the itinerant oscillator (R9). Using a combination of algorithms it is possible to increase gradually the complexity of the potential under consideration from an atom-atom, Lennard-Jones basis, for example, gradually adding polarisability, multipole-multipole interaction, intramolecular vibrational effects and non-pair-additivity. Pair interaction is an assumption which is involved even in computer simulation. There is only one type of algorithm which does not use this, and which at the same time takes into account the effect of polarisability on molecular interactions and vice-versa (that of the Birkbeck College group (3) - see below). Significant evidence of non-pair-additivity has already been obtained.

The problem of the reaction field (1) is beginning to be tackled using molecular dynamics, especially in the context of $H_2O$. The algorithms written for this purpose can be adopted for use with $CH_2Cl_2$ because the symmetry is the same. The newly developed non-equilibrium methods of molecular dynamics (9) can be used to great advantage in order to build up multi-particle (cross) correlation functions observable with certain techniques. The equivalent autocorrelation functions are observable with other types of spectroscopy (section IIIa) and the analytical macro-micro theorems (R12) linking the two types can be directly tested.

There are also fundamental problems in trying to extend some of the concepts of the theory of Brownian motion to the case of the asymmetric rather than spherical top. For example, deciding what is the correct frame in which to diagonalise the friction tensor, when this is different from the frame defining principal axes of inertia. One has to consider how to evaluate separately the components of the grand friction matrix (10) of rotation-translation when using the Einstein relation between friction and diffusion and Langevin's idea of the molecular dynamics. There are well-known inconsistencies (11-13) in·the latter equation which balance force or torque with a strong combination of stochastic and hydrodynamic terms. The velocity or angular velocity of the Langevin equation has no time derivative, which is incompatible with the fact that probability hypotheses are imposed (i.e. relations are assumed between the stochastic force and the velocity). These inconsistencies, instead of leading to the rejection of the Langevin equation, have led to discoveries such as the Ito-Stratonovitch calculi (14, 15), and more lately to the use of Wiener processes (16) in the analysis (17). These problems have probably been most completely investigated (R12) in connection with spectroscopic measurements (R6) made in the 0-THz region (i.e. covering all frequencies from zero up to about $10^{12}$ Hz). Such work has been going on since it was realised (18) that the Debye model (successfully employed in the $10^7-10^{10}$ Hz region) cannot predict the observed far infrared spectral features. In the 1970s we have seen attempts to use the projection operator technique (19-25) of Kubo, Zwanzig, Mori and many others to reproduce (usually with adjustable parameters) the spectroscopic broad-band data up to and including the far infrared. The Mori continued fraction approach (25) has proven useful here but only in an empirical fashion because of the use of a truncation procedure (R6). It is still not known whether the fraction converges or if taken to infinity, is physically meaningful. On the one hand it is possible to give such truncations physical meaning by unravelling the implied equations of motion, but Scaife has criticised many of the basic assumptions made in this field (26). The evolution of the friction into a memory function is therefore providing us both with solutions and problems. There has been almost no attempt to see if the memory function makes simultaneous sense of results from different spectroscopic fields. There is a basic reason for this in that the relation between the angular velocity autocorrelation function $(C_{\underline{\omega}}(t))$ and the orientational autocorrelation function $(C_{\underline{u}}(t))$ in all but the simplest and most uninformative models based on Brownian motion theory is exceedingly intricate (27). The only reasonable 'stop-gap' at present is to consider the orientational dynamics of the symmetric top with an embedded dipole (orientation) vector $\underline{u}$ constrained to move in a plane (28). This leads to models such as the itinerant librator which are rigorously founded and capable of describing semi-quantitatively the far infrared as well as the low frequency part

of the zero-THz electromagnetic absorption and dispersion profiles. For planar
libration of the asymmetric top dipole there is a closed relation between $C_\omega(t)$,
and $C_u(t)$ and also higher Legendre polynomials of the orientational autocorrelation
function. This means that the results from different branches of spectroscopy
can be inter-related on the same basis. When the planar constraint is removed
there is no closed relation between $C_\omega(t)$ and $C_u(t)$, even in the case of diffusion
of the hypothetical dipole embedded in the spherical top (29). This is, of course,
the model originally considered by Debye, but <u>without</u> inertial and memory effects.
Fig. (1) illustrates the behaviour of the Debye model in the far infrared when
three dimensional diffusion is considered analytically. The only case where it
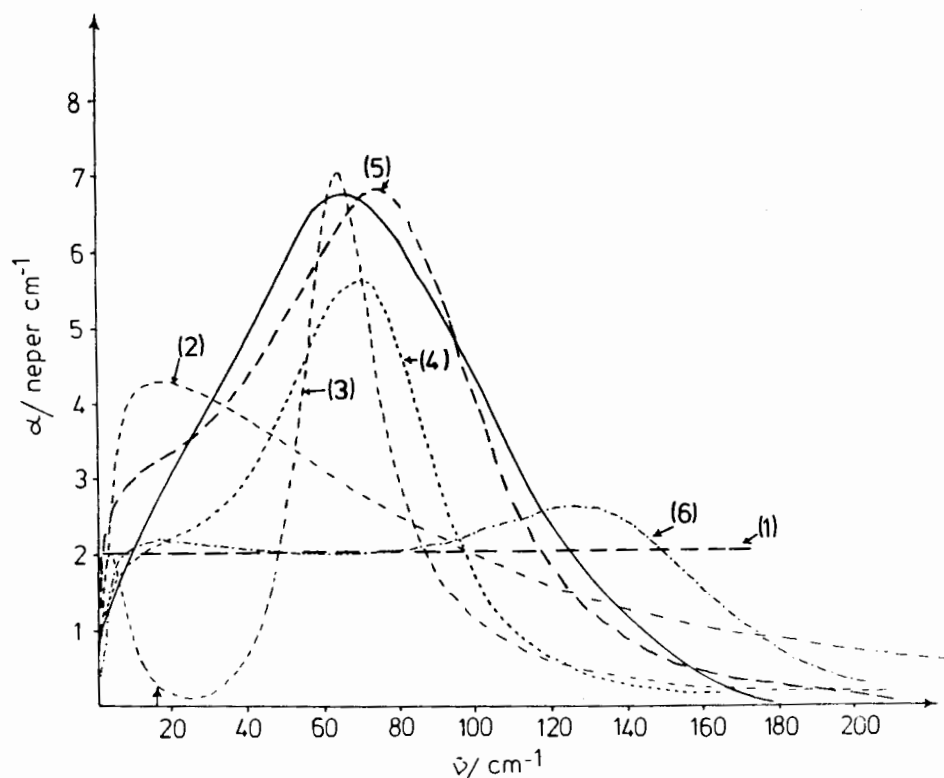


Fig. 1. The far infrared spectrum of a 0.018 mf $CH_2CN$ solution in $CCl_4$ at 318 K.
The solid line represents the observed power absorption coefficient. Calculated
spectra are (1) the Debye rotational diffusion model, (2) the extended J diffusion
model, (3) the symmetric top itinerant oscillator model with $I_1 = 10I_2$, $\beta_2 = 5$ THz,
(4) the best fit to a second order Mori truncation with measured $\epsilon_0 - \epsilon_\infty$, (5) the
best fit to a 2nd order Mori truncation with variable $K^{(o)}(o)$ and $\epsilon_0 - \epsilon_\infty$, (6) the
3rd order Mori truncation with measured $\epsilon_0 - \epsilon_\infty$. [For further details see M.W. Evans,
G.J. Evans, J. Yarwood, P.L. James and R. Arndt, Mol. Phys., 1979, 38, 699-716.]

is possible to relate $C_\omega(t)$ and $C_u(t)$ in a simple way is that which produces this unrealistic result. The classical theory of the Brownian motion is therefore an obstacle to progress rather than an aid. There are, of course, several well-known methods of relating $C_m(t)$ to $C_u(t)$ based on "collisonal" models such as those involving M and J diffusion (R7). Lately, methods using projection operators, have been developed to deal with two or three molecule interactions in the presence of N others (30, 31).

The above analytical considerations leave aside completely, of course, the electrodynamical problem of the internal field (32), or multipole-multipole interaction, beginning with dipole-dipole interaction (33, 34). Coffey and co-workers (35, R13) are now beginning to take account of the latter in relation to the far infrared absorption (R6, R12). However, there is a danger that these elaborate theories will lose touch with experimental findings. The use of molecular dynamics simulation, as a source of reference for thermodynamic averages not easily accessible experimentally, is therefore expected to be crucially important.

Hydrodynamical equations of energy, momentum and particle density conservation have always been of use in dealing with light-scattering. The linearised Navier-Stokes equations have recently been modified (24) with significant results such as the theoretical prediction and subsequent simulation of long-time 'tails' in various molecular autocorrelation functions, and the successful description of the Rytov dip (36). The modification has been used on the mixing of hydrodynamic modes within the overall framework developed by Mori and others. In this area of research there are different ideas of mode/mode coupling which lead to the same spectral result (see section IV) (i.e. the analytical frequency dependence of the intensity of polarised or depolarised scattered light), so that there is scope for resolving the issue (a) by computer simulation; (b) by exploring the implications of the mode-mode theory in the various branches of spectroscopy (microwave, far I.R., neutron scattering, N.M.R. etc.). Scant consideration has been given to the high frequency wings of light scattered from a molecular liquid where the available theories run into the type of trouble mentioned already in connection with Debye theory of dipolar relaxation (i.e. an inability to define the second spectral moment because of certain model assumptions). A typical example is the use of Lorentzian band profiles (R1-R5). Furthermore, there has been a tendency in the treatment of light scattering spectra to mix "molecular" and "hydrodynamic" ideas, so that the final result might be correct in some respects (e.g. in predicting the Rytov dip) but it is not clear why.

The study of molecular dynamics by infrared and Raman bandshapes analysis is, of course, well established (R1-R5, R11). For example, about 70 papers have been published on $CH_2Cl_2$ and about 50 on $CH_3I$. In theory, bandshape analysis provides information on the autocorrelation function of the transition dipole

involved (section IIIA). This necessitates consideration of rotation/vibration mixing. It is clear that it is not possible, in general, to factorise the relevant autocorrelation function into a vibrational a.c.f. multiplied by a rotational a.c.f. (as implied by eqns. 3 or 6). This has been made clear for $CH_2Cl_2$ liquid in papers by van Woerkom et al. (37,38). Unfortunately, the factorisation has been made a priori in many papers (R1-R5) and the conclusions may not, therefore, be meaningful. The problem of vibration - rotation coupling is difficult to tackle analytically, especially when memory effects are to be taken into account, so that this is a field which is acutely in need of some aid from computer simulations, providing as they do multi-particle and single-particle correlation functions for a well-defined intermolecular potential.

There are many papers for all three molecules considered here which report molecular dynamics studies using N.M.R. relaxation of different atoms in the molecule (see section V). For $CH_2Cl_2$, for example, it is possible to look at the movement of the carbon, hydrogen and chlorine atoms separately and evaluate the anisotropy of the reorientational motion. Despite some quite surprising inconsistencies between N.M.R. data from different laboratories, Brier and Perry (R8) attempted to use the N.M.R. infrared and Raman data as an aid for evaluating their neutron scattering experiment on liquid $CH_2Cl_2$. Table II of Brier and Perry is a summary of the N.M.R., depolarised Rayleigh and infrared work, and is reproduced in this article as Table 1. The construction of this table involved many scaling assumptions because the literature results were obtained at different temperatures. Brier and Perry (R8) did not attempt an analysis beyond the stage of the M and J diffusion models (R7) which are unrealistic in the far infrared. They shed light on the confusion which results from the application of different models to the N.M.R. spin-spin and spin-rotation relaxation data. By considering (in isolation) the various N.M.R. correlation times it was not easily possible to even distinguish between alternative models. Brier and Perry run into the fundamental difficulty already mentioned that there is no way of extending the concept of a spherical top diffusing against a hydrodynamical friction to the case of the asymmetric top ($CH_2Cl_2$) or even the symmetric tops ($CH_3F$ and $CH_3I$) without introducing too many phenomenological parameters. Accordingly, one of the first aims of the molecular dynamics simulations would be to produce their N.M.R. correlation times and to compare these with a freshly measured set in precisely the same thermodynamic states. These should then be compared with the infrared, Raman and Rayleigh correlation data remeasured under the same conditions. Brier and Perry emphasize that at present, the infrared and N.M.R. data provide an almost diametrically conflicting picture of the anisotropy of the molecular motion in $CH_2Cl_2$. Which is the more nearly correct should be answerable with molecular dynamics simulations. Concepts such as 'mean time between collisions' or 'mean size of angular jumps' are almost meaningless. Their use will (as Hildebrand

TABLE 1

Experimental Angular Correlation Times for $CH_2Cl_2$

(Reproduced by permission from Reference R8)

| Method | Molecular Vector involved; $(\eta, \xi)$ | Correln. Time | Symmetric Top Correln. Time | Correlation Times/$10^{-12}$ s (1) | | |
|---|---|---|---|---|---|---|
| | | | | (i) | (ii) | (iii) |
| $2\nu_8$, infrared[2] | b-axis;$(\pi/2,0)$ | $\tau_1$ (b) | $\tau_{1,1}$ | $0.51\pm0.06$ | 0.47 | 0.42 |
| $\nu_2+\nu_7$, infrared | c-axis;$(\pi/2;\pi/2)$ | $\tau_1$ (c) | $\tau_{1,1}$ | $0.56\pm0.10$ | 0.50 | 0.48 |
| $\nu_8$, infrared | | | | $1.11\pm0.15$ | 1.70 | 0.93 |
| $\nu_9-\nu_4$, infrared | a-axis;$(0,0)$ | $\tau_1$ (a) | $\tau_{1,0}$ | | 0.76 | 0.41 |
| $\nu_2+\nu_8$, infrared | | | | | 0.83 | 0.56 |
| neutron scattering | centre of mass- $^1$H $(\pi/2, \pm 33°)$ | $\tau_1$ (n.s.) | $\tau_{1,1}$ | $0.57\pm0.10$ | 0.56 | 0.47 |
| depol. Rayleigh[3] | a-axis (approx) $(0,0)$ | $\tau_2$ (a) | $\tau_{2,0}$ | $\gtrsim 1.85$ | | |
| n.m.r.($^1$H,intra)[4] | H-H vector; $(\pi/2,\pi/2)$ | $\tau_2$ (c) | | $0.53\pm0.06$ | | |
| n.m.r.($^2$H,quad) | C-D vectors; $(\pi/2 \pm 56°)$ | | $(\tau_{2,0}+3\tau_{2,2})/4$ | $0.80\pm0.10$ | | |
| n.m.r.($^{13}$C-H;dipolar) | C-H vectors $(\pi/2 \pm 56°)$ | | | $0.70\pm0.07$ | | |
| n.m.r.($^{35}$Cl,quad) | C-Cl vectors $(\pm 34°, 0)$ | | $0.282\,\tau_{2,0}+0.645\,\tau_{2,1}+0.073\,\tau_{2,2}$ | $1.20\pm0.10$ | | |

(1) Adjusted to the common temperature of 300 K. See text for detailed discussion of individual results.
   (i)   zeroth moment of the angular correlation function (A.C.F.)
   (ii)  time required for A.C.F. to fall to $e^{-1}$
   (iii) inverse rate constant of the exponential portion of the A.C.F.

(2) From Ref. 34 of section Va. We quote here only those results for which the calculated A.C.F.'s had approximately the correct second moment.

(3) From reference 78 of section Va.     (4) From references 10, 11, 12 and 33 of reference R8.

remarks) lead only to the likelihood of conflict rather than harmony, especially when the ideas are used with more than one technique. For example, almost totally opposing conclusions (based on consideration of these quantities) were reached by Dardy et al. (39) (Rayleigh scattering) and Larkin (40) (zero-THz spectroscopy) (for $CH_2Cl_2$), despite the fact that these techniques measure, in principle, closely complementary multi-particle correlation functions. All this points us away from analytical modelling towards its much more comprehensive (and comprehensible) counterpart, computer simulation.

Where does this leave neutron scattering from liquids? The interpretative problems with this technique are acute, if not overwhelming, for molecular systems. For example, translation, rotation and vibration motions are widely assumed (R8) to be uncoupled (in the sense that the relevant correlation functions are factorised). This is a dubious procedure, which often results in the incorrect use of <u>different</u> models for each type of motion. The interpretation of neutron scattering data using the results from other spectroscopic techniques can only be acceptable if there is a extensive coordination and simulation back-up. The project therefore provides an unique opportunity to assess critically the idea of using neutron scattering as a probe into molecular dynamical behaviour in the liquid and condensed phases of matter.

It is important to take into account the rapidly developing non-linear electrooptic techniques (41) as well as the more established methods such as hyper- and ultra-sonic dispersion and Brillouin scattering (see section V). Sound dispersion has been used extensively on liquid $CH_2Cl_2$, but the interpretation of the results is often not incisive on the molecular scale. However, when used in combination with Brillouin scattering and molecular dynamics simulation of the correlation function of the relevant off-diagonal elements of the microscopic stress tensor it can provide a valuable viewpoint which complements the other spectroscopic data. It is, in principle, possible to simulate the correlation function at high frequencies with the new computer technique of "non-equilibrium molecular dynamics" (22).

Among the new electrooptical techniques now available is the dynamical Kerr effect, either with psec pulsed lasers or at lower frequencies (R16). The projected work on glasses should produce interest in the latter region in which Reid and Evans (42) have recently characterised the enormously broad band $(\alpha, \beta, \gamma)$ triad spectrum of $CH_2Cl_2$ dissolved in viscous and vitreous decalin. The interpretation of the data from the Kerr effect is not, of course, free from complications, not least because it is not strictly valid to use a theory of linear-response with transient responses dependent on pulsed electric fields (43). However Grigolini and Ferraro (43,44) have recently considered the problem in detail when intense laser pulses are used either to produce fluorescence or birefringence transients. There should be little technical difficulty in

simulating a psec pulse on the computer and directly testing linear response theory at a fundamental level. In fact, computer simulation runs are quenched into a 'glassy' state at present over ps periods (45).

The impulse methods developed by Małecki and others (46) have opened up the possibility of overcoming the heating effects caused by conductivity. There are now available, at low frequencies, non-linear dielectric transient measurements on aqueous systems. It is becoming possible to extend the study to the far infrared range using carcinotron or synchrotron radiation (or alternatively submillimetre laser radiation), ultra-short high voltage pulses and fast response pyroelectric and photoconductive detectors. It is possible to detect a minute of arc change in the plane of polarisation of the carcinotron beam which has passed simultaneously through the liquid and field pulse. This is the far infrared Kerr phenomenon recently described qualitatively by Evans et al. (47) in aniline using conventional interferometry. It is also possible to pursue the far infrared Faraday effect in the same way with powerful magnetic pulses. Leibler and Gerschel (48) are using eighteen carcinotron frequencies to cover the range 0.5 mm to 4 mm to pursue these experiments under the present conditions given in section VI. Kluk et al. (49) have employed low frequency Małecki impulse experiments in parallel with Raman, i.r., f.i.r., and (possibly) neutron scattering methods.

In dealing with electromagnetic absorptions, dispersion and scattering, consideration should always be given to collision induced absorption (R6,R9). One of the reasons for choosing $CH_2Cl_2$ and $CH_3F$ for the project is that the far infrared absorption intensities of these two molecules are high enough to counteract the induced absorption which always affects the bandshape whenever molecular interaction is present to any significant degree. Whenever there is absorption (or scattering) of electromagnetic radiation by a permanent dipole there is induced absorption or scattering due to temporary dipoles. This arises from the angular movement of the permanent dipole supplemented by temporary, collision-induced dipoles which fluctuate in both magnitude and direction with time. Baise (50) has shown that in liquid $N_2O$ the cross section is only approximately half due to the permanent dipole rotation. The remainder was induced absorption and it produced a significant high frequency distortion.

The simulation of the orientational correlation function of the permanent dipole will not therefore reproduce the observed bandshapes in general for any molecule without consideration of multi-body effects, polarisability and the induction of temporary dipoles. This poses an interesting problem for the techniques of molecular dynamics used in the project, especially for those with pair interaction assumptions built in.

In conclusion we may discern a trend away from analytical modelling of the spectroscopic bandshapes of molecular liquids towards the increased use of

molecular dynamics simulation. It is therefore necessary for the theoretical
work to develop in new, well defined directions. If the recent criticisms
of Scaife (26) are corroborated then the existing methods used by the theoreticians
(the various generalised Langevin equations for example) would be undermined.
Perhaps it might be possible to use a combination of simulated and experimental
data to rigorously test the fundamentals of liquid state theory. The chronic
unsolved problem of the study of polar liquids is that of the 'internal' reaction
field (32). An adequate solution to the problem of condensed phase molecular
dynamics must therefore be concerned with electrodynamics as well as with mechanics.
This is true on the microscopic scale and particularly so when dealing with the
relation between what is measured by zero-THz spectroscopy and what the theories
and simulations are able to supply. Whenever a solution describing a dynamic
ensemble situation is found at the microscopic level, the relation of the
measuring field to the displaced field in the dielectric medium must also be
predictable before the macroscopic spectral bandshapes can be calculated. The
most we can hope from this problem of the internal field is an approximate
solution based on some self-consistent technique such as molecular dynamics
simulation, or obtained by the analysis of set problems such as that of the
translationally invariant lattice of interacting dipoles. There are some cases
(such as that of water) where electrodynamic interaction is very strong, but only
one macroscopic relaxation time seems to appear. This suggests that in such cases
the concept of "microscopic relaxation time" is meaningless, and that we are
dealing with a cooperative process involving many molecules. Hydrogen-bonding
is, of course, an extreme example of dipole electrodynamic influences on the
system hamiltonian.

IV.   INTERCOMPARISON OF EXPERIMENTAL DATA FROM DIFFERENT SOURCES

The methods used to compare the insights obtained from these different
branches of spectroscopy in order to obtain a coherent view of the liquid state
involve the intercomparison of correlation functions. There are several articles
in the literature which deal with this, notably the review of Berne and Harp (R10).
It has, however, become clear that in their enthusiasm to develop one analytical
model for the interpretation of several types of spectroscopic data, some authors
in this field have overlooked the various assumptions involved in reducing what
is actually observed (say, by dielectric and far infrared spectroscopy) to
accessible autocorrelation functions. In this section we shall critically review
these assumptions for some of the experimental methods to be used in this project,
and indicate how the growing speed and power of computer simulation can be used to
build up a more realistic criterion of intercomparison of observable correlation
functions.

(a)   Dielectric and Far Infrared (or Zero-THz) Spectroscopy

In relating the microscopic (orientational) autocorrelation to the macroscopic

polarisation there are several unrealistic simplifications enshrined in the classical theory as described, for example, by Scaife (26). These are necessary for analytical progress in the face of the problem of relating the external measuring field used in the measurement of dielectric relaxation in liquids to the field actually present in the vicinity of a given molecule. The relationship between these fields (the internal field problem) is determined by the very molecular processes which we wish to investigate, and is an ever present problem also when we wish to consider the intensity of spectral features such as absorption in the infrared and Raman/Rayleigh scattering (51).

Typically (26), the resultant macroscopic dipole moment $\underset{\sim}{M}(t)$ induced in a dielectric body by an external field $\underset{\sim}{E}(t)$ may be calculated by means of:

$$\underset{\sim}{M}(t) \;=\; \int_{o}^{t} \underset{\sim}{E}(t-s)\frac{da(s)}{ds}ds \tag{9}$$

where $a(t)$ is the response of the molecule to a unit step-function and where it is assumed that $\underset{\sim}{E}(t) = \underset{\sim}{o}$ for $t < o$. For a dielectric sample $da/ds$ must be bounded and $\underset{\sim}{M}(t)$ cannot reach a finite value in an infinitesimally small time. We note that eqn. (9) is an expression of linear response of $\underset{\sim}{M}(t)$ to $\underset{\sim}{E}(t)$, i.e. terms in $E^2(t)$ etc. are neglected (41). Also the dipole moment $\underset{\sim}{M}(t)$ does not include the sum of extra, temporary dipoles induced on reference molecules by the presence of the other molecules in the sample. On the basis of eqn. (9) it is possible to derive the fluctuation-dissipation theorem linking the complex polarisability $\alpha^*(\omega)$ to the correlation function of $\underset{\sim}{M}(t)$:

$$\alpha^*(\omega) \;=\; \frac{1}{3kT}\left[ <\underset{\sim}{M}.\underset{\sim}{M}>_{o} \; - \; i\omega\int_{o}^{\infty} <\underset{\sim}{M}(t').\underset{\sim}{M}(t'+t)> \, e^{-i\omega t}dt\right] \tag{10}$$

known as the Kubo equation. Note that this equation links the complex macroscopic polarisability $\alpha^*(\omega)$ with the behaviour of the macroscopic resultant dipole moment $\underset{\sim}{M}$. However, the theoretical evaluation of $C_{\underset{\sim}{M}}(t)$ and $<\underset{\sim}{M}.\underset{\sim}{M}>$ allows us to obtain the observable $\alpha^*(\omega)$ only for a macroscopic spherical sample of dielectric, and from this point onwards the analytical theory of dielectric polarization and relaxation runs into the difficulties caused by the assumed shape of the cavity when considering the nature of the electrodynamic interaction of a molecule with its immediate surroundings. If we define $\underset{\sim}{u}$ as the unit vector along a molecular dipole, then the relation between $<\underset{\sim}{M}(t).\underset{\sim}{M}(o)>$ and $<\underset{\sim}{u}(t).\underset{\sim}{u}(o)>$ involves consideration of the displacement and orientational polarization, together with that of dipole-dipole interaction. Most analytical theories are constructed for $<\underset{\sim}{u}(t).\underset{\sim}{u}(o)>$ but the fact remains that only $<\underset{\sim}{M}(t).\underset{\sim}{M}(o)>$ is observable and, even then, only via $\alpha^*(\omega)$. A relation (32) such as that of Clausius and Mosotti linking

$\alpha^*(\omega)$ to the complex permittivity $\epsilon^*(\omega)$ is not independent of several assumptions usually involving cavities.

Accordingly an important aim of this project would be to maximise the use of molecular dynamics algorithms which involve well defined mechanisms of molecular interaction and to calculate the four correlation functions:

$$C_{\underset{\sim}{M}}(t) \;=\; <\underset{\sim}{M}(t).\underset{\sim}{M}(o)> \;;\qquad C_u(t) \;=\; <\underset{\sim}{u}(t).\underset{\sim}{u}(o)> \;;$$

$$C_{\underset{\sim}{\dot{M}}}(t) \;=\; <\underset{\sim}{\dot{M}}(t).\underset{\sim}{\dot{M}}(o)> \;;\qquad C_{\dot{u}}(t) \;=\; <\underset{\sim}{\dot{u}}(t).\underset{\sim}{\dot{u}}(o)> \;;$$

the latter two being related to Fourier transform of the far infrared spectrum. The macro-micro correlation theorems in the literature (24,52) can therefore be directly tested. For example, if $<\underset{\sim}{u}(t).\underset{\sim}{u}(o)>$ is constructed as a sum of complex exponentials, then it is possible to discern analytically that $<\underset{\sim}{M}(t).\underset{\sim}{M}(o)>$ will take the same basic mathematical form. There are promising signs that the computer technique can be used (for example by Brot and Darmon (53)) to directly test cavity theory (54) using molecular dynamics and, interestingly, without the use of periodic boundary conditions (64). Part of the aim of the experimentalists in the project would be to produce far infrared/dielectric data over a wide enough range of liquid density and temperature to serve as a reference set for comparison with different kinds of simulation, each involving specific aspects of the complete dielectric problem.

For example, Kohler and Bellemans (56) have used the molecular dynamics method to isolate the effect of dipole-dipole interaction on the dielectric response function by simulating weakly interacting dipoles on a rigid lattice. The approach to equilibrium of an assembly of dipoles as a lattice is a direct case of application of the fluctuation-dissipation theorem. The first point that emerges is that a weak interaction involving only two dipoles cannot drive the system to equilibrium. The time equilibrium state is only attained by means of processes involving at least three interacting dipoles. This illustrates the difficulty of using analytical theories with only pairs of interacting dipoles. A molecular dynamics simulation in two dimensions by Kohler and Bellemans corroborates this point. The same type of molecular dynamics simulation may be used to obtain the following information concerning the dielectric response function.

(a) The form of the dielectric response function is strongly related to the nature of the orientational (shape dependent) interaction between the molecules.

(b) If this interaction is purely dipolar in nature the response function is not very different from its limiting form at zero coupling (free rotation) even if dipolar interaction is quite strong.

(c) The long range part of the dipolar interactions seems to play a very limited role in the response function. (Notice however that the zero-THz work of Gerschel et al. (57,58) on liquid $CH_3F$ has shown that long range fluctuations are not unimportant in dipolar fluids.)

These conclusions were reached in a simulation (by Bellemans and Kohler (56)) of the total moment $\underset{\sim}{M}(t)$ of dipoles located in a plane on the sites of a rigid square lattice involving 101, 193 and 421 dipoles respectively. In this simulation the usual central forces (van der Waals) do not appear in the Hamiltonian since the molecules are translationally fixed. The correlation function $\underset{\sim}{C_M}(t)$ was calculated using running time averages and not phase space averages (i.e. by assuming that the system is ergodic). The error caused by this is of the order $N^{-1}$ where N is the number of molecules (i.e. the difference between the microcanonial and canonical ensembles (22)). Starting from randomly oriented dipoles (with random angular momenta) correlations grow within the system so that its potential energy becomes slightly negative with respect to the starting level. The simulated dipole-dipole interaction are not capable of producing an exponentially decaying response function, instead they have a tendency to make it oscillate.

The far infrared region is rich in information concerning electrodynamics. The most extreme case is that of water (59) and in liquids where electrodynamic forces are relatively important, such as $CH_3F$ and $CH_2Cl_2$ there is a large shift away on dilution from the neat liquid value of the far infrared power absorption coefficient. The anisotropy of the total intermolecular potential strongly depends on the contribution of electrodynamic interactions. Another sign of electrodynamic influence is a weak density dependence of the r.m.s. torque (58), coming from the fact that the dipole interactions are long-ranged, and not sensitive in consequence to the mean intermolecular separation.

To obtain unambiguous information on the mean squared torque, the relationship between $\underset{\sim}{C_M}(t)$ and the autocorrelation function, and between $\underset{\sim}{C_M}(t)$ and the observables in zero-THz spectroscopy (the power absorption coefficient, $\alpha(\omega)$, and the dielectric loss, $\varepsilon''(\omega)$) must also be defined unambiguously. To try to achieve this aim the following scheme of simulating $\alpha(\omega)$ and $\varepsilon''(\omega)$ is suggested for the project participants.

Gerschel et al. (58) have put the problem of the internal field (with attendant cavity theory complications) into the far infrared context. Despite the fact that there is a considerable amplitude of dispersion and absorption in these compounds there is little appreciable difference between the cavity corrections used. What follows is therefore designed to produce microscopic correlation functions by computer simulation using various models for the intermolecular interaction. The problem of relating these to the polarisation and then to the observables comes in at a later stage.

(i)    A simulation for the four correlation functions already mentioned should be carried out using only dipole-interactions in three dimensions - extending the work of Kohler and Bellemans (56) to the $CH_3F$, $CH_3I$ and $CH_2Cl_2$ dipoles. This would isolate the dipole-dipole contribution to the far infrared spectrum, and the dependence of the far infrared spectrum on the dipole-dipole strength. In this and following simulations the simplest kind of procedure should be used to relate the calculable response function to the power absorption coefficient. We suggest the Lorenz-Lorentz procedure or more accurately, that developed by Gerschel et al. (57,58) specifically for the far infrared.

(ii)   The second simulation is intended to look at the far infrared/dielectric region with pairwise atom-atom interactions (55). It is particularly important to see whether this kind of 5 x 5 (or 3 x 3) atom-atom interaction can reproduce the major features of zero-THz spectra along, for example, the gas-liquid coexistence curves, where the far infrared peak (in $\alpha$) shows considerable shifts.

(iii)  Several algorithms are available which can be adapted easily for $CH_2Cl_2$ simulations using charge-charge interactions along the lines of Rahman and Stillinger (60) for water. These are apparently fairly successful for simulating the spectral data for water but, in all probability their limitations have not yet been exposed by joint spectroscopic effort. The Rahman/Stillinger algorithm would probably fail to describe the far infrared spectrum of water even in the most qualitative manner because of the two-body interaction assumption built into the algorithms.

(iv)   The restriction of pairwise additivity has been lifted by Finney and coworkers (61) using polarisability considerations which might also allow the simulation of collision induced absorption to be carried out on a non-pairwise basis. This is clearly the case experimentally, since the cross sections of infrared and far infrared induced absorptions cease to vary as the square of the molecular number density as the liquid densities are approached (62). Strong evidence for multi-body effects have already been found in $CH_3F$ (liquid) using this simulation algorithm.

(v)    It is clear that the simulation of collision induced absorption cannot proceed without the inclusion of molecular polarisability. The only simulation along these lines so far seems to be that of Buontempo et al. (63) on $N_2$.

(vi)   A "hybrid potential" consisting of atom-atom interaction + multipole-multipole forces could be used to evaluate the extra effect of electro-dynamic forces on the zero-THz spectrum.

(vii)  In some cases the effect of removal of boundary conditions (Brot et al. (64)) could be evaluated.

(viii) Semi-stochastic methods (Ciccotti et al. (65)) and non-equilibrium molecular dynamics (9) should be used whenever possible to save computer time when evaluating $<\underset{\sim}{M}(t).\underset{\sim}{M}(o)>$ with complicated intermolecular potentials.

(ix) Attempts should be made (Evans et al. (66)) to produce an intermolecular potential for $CH_3F$ from molecular orbital theory, and to investigate the H-bonding in $CH_2Cl_2$ and $CH_3F$ by molecular orbital (ab initio and INDO/CNDO) methods.

The microscopic response functions or correlation function from all these techniques should be compared with each other in both time and frequency domains before introducing macroscopic cavity theories of any kind to relate the orientational correlation functions to loss and power absorption coefficient (Brot has discussed the relations in detail (20)).

Finally, we mention that it is important that the simulations produce the angular momentum autocorrelation function ($C_\omega(t)$) to provide analytical theoreticians with a reference set of results for testing ways of relating this a.c.f. to the orientational a.c.f. for the symmetric and asymmetric tops in 3-D space. This particular analytical problem is one of the most difficult ones confronting theoreticians involved in the Langevin and Fokker-Planck approach to molecular motion in the condensed phases of matter.

(b) Infrared and Raman Spectroscopy

In attempting to extract the molecular vibrational and reorientational correlation functions (of equations (1) and (2)) it has been found necessary to use approximate equations such as (3a) and (6a) in order to achieve the required separation. However, it has been known for some time (38) that the coupling of vibrational and rotational processes is important in molecular liquids and, as implied by equations 3 and 6, that they are not statistically independent. Further problems are encountered (as mentioned previously) if the resonant (i.e. distinct) parts of the correlation functions are significant. In this case the infrared correlation function $\Phi_{IR}(t)$ (eqn. 3b) includes the effects of cross correlations. Thus if

$$\Phi_{IR}(t) = \frac{1}{2}<[\underset{\sim}{M},\underset{\sim}{M}(t)]_+>$$

$$= \frac{1}{2}\frac{<[\underset{\sim}{M},\underset{\sim}{M}]_+>\int_{-\infty}^{\infty}\coth\left(\frac{1}{2}\frac{h\omega}{kT}\right)n(\omega)k(\omega)\cos\omega t d\omega}{\int_{-\infty}^{\infty}\coth\left(\frac{1}{2}\frac{h\omega}{kT}\right)n(\omega)k(\omega)d\omega}$$

(where $\underset{\sim}{M}$ is the total dipole moment of the system and $n(\omega)$ and $k(\omega)$ are the real and imaginary parts of the complex refractive index) then it is assumed that the microscopic transition dipole moments which contribute to the total electric moment are mutually uncorrelated if localised on different molecules. Presumably what is meant by this is that the quantity $\frac{1}{2}<[\underset{\sim}{M},\underset{\sim}{M}(t)]_+>$ may be replaced by

autocorrelation functions. However, if $\underset{\sim}{M}$ is a property of the whole system, then cross-correlations, as for the far infrared $\underset{\sim}{M}$ (eqn. 4a), must be taken into account. One of the major contributions to the theoretical investigation of these effects has been made by Lynden-Bell (67). She has also given a convenient general formalism for expressing the band shape of a particular experiment as a function of angular frequency ($\omega$). In general, this is the real part of,

$$I(\omega) = (S|[-i(L-\omega)-K]^{-1}|S)$$

S is the operator corresponding to the observation of the vibrational system and L and K are super-operators describing the propagation and relaxation of the system. S depends on the experiment involved. For infrared absorption the observed quantity is the total electric moment of the sample induced by the electromagnetic field; for Raman scattering it is the total induced electric moment, which, at each point, is proportional to the isotropic or anisotropic parts of the molecular polarisability (equations 5 and 6). In each experiment, S is a sum over all the molecules in the system.

An important result is that, even excluding reorientational effects, the vibrational widths of the isotropic and anisotropic scattering may differ. The principal mode of interaction of vibrations with intermolecular forces are (a) very short-range repulsive overlap; (b) van der Waals or dispersion forces; (c) multipole forces (which we have also termed, more accurately, 'electrodynamic') exemplified by dipole-dipole interactions. All these can be expressed in a convenient form for the interaction between two molecules (1 and 2):

$$U_{12} = \sum_\gamma F_\gamma R_\gamma(r_{12}) \left[ \sum_{m_1 m_2} \begin{pmatrix} L & \ell_1 & \ell_2 \\ M & m_1 & m_2 \end{pmatrix} \right.$$

$$\left. \times \; D^{(\ell_1)}_{\nu_1 m_1}(\Omega) D^{(\ell_2)}_{\nu_2 m_2}(\Omega_2) D^{L}_{OM}(\Omega r) \right]$$

where the Wigner rotation matrix elements relate the angles of molecules 1, 2 and the intermolecular vector $\underset{\sim}{r}$ to the laboratory frame respectively, R is a function of the intermolecular separation, r, only, and $F_\gamma$ is a property of the pair of molecules, independent of their separation and transforming like spherical tensors. $\gamma$ enumerates the interaction. For dipole-dipole interaction F is the product of the molecular dipole moments and R is proportional to $r^{-3}$. Coupling of the vibrational system to the bath of translational degrees of freedom occurs because these F's vary with nuclear displacements. Changing the density of the liquid by changing the pressure affects the time correlation functions of the relative molecular position, but not the F operators. Within the assumptions of slow

molecular reorientation (i.e. in the rapid modulation regime) and independent translational diffusion the correlation times for the intermolecular potentials are inversely proportional to the translational diffusion constant D (it should be noted that modulation of intermolecular forces by reorientational motion is neglected).

If three-body correlations are neglected the line-width is also inversely proportional to the number density of oscillators. Therefore, whatever the method by which the intermolecular potential couples to the vibrational system of the bath, the vibrational line-width and dephasing rate should decrease quickly with temperature at constant density (motional narrowing), and increase rapidly with density. The temperature and pressure effects should be the same for all normal modes of the same molecule. However, this has not been the indication of completed experiments to date (8,68).

In real liquids three-body correlations may be important. Simulation by Finney et al. (61) have already shown that non-pair additivity is important (e.g. for $CH_3F$). According to Lynden-Bell such contributions give a term in the line-width proportional to density squared. If the molecules are not taken merely as hard spheres, the effective distance of closest approach decreases with increasing temperature.

The relative importance of the various contributions and the total line-width depend on the particular normal mode being excited. Considering the methyl halides, the C-X (X = F or I) stretching motion affects both the polarisability and the dipole moment to a considerable extent so that intermolecular contributions from both dispersion and dipolar interactions should appear. If dipolar relaxation dominates and self and exchange terms are comparable the symmetric Raman spectra of the methyl halide stretching bands may be narrower than the corresponding depolarised vibrational Raman line-widths even in the absence of vibration-rotation coupling. If dispersion induced relaxation dominates, then according to this model the reverse is likely to be true.

Another prediction which can be made theoretically and tested by the project is that, assuming negligible changes in the molecular dynamics and intermolecular potentials, isotopic substitution should change the line-width by a factor proportional to the square of the ratio of reduced molecular masses.

Several other theoretical predictions can be found by reference to Lynden-Bell's original papers (67) which investigate both Raman and infrared vibrational band widths in liquids. The width is caused by interaction of molecular vibrations with translations and rotations by rapidly varying terms in the intermolecular potential dependent on both internal and external coordinates. The vibrational dephasing is assumed to be slow compared with the timescale of decay of inter-molecular correlation. Bratos et al. (69) have considered the opposite (slow modulation) extreme.

It would be a task for the analytical theoreticians attached to the project to use methods such as those of Lynden-Bell to develop predictions as described above for pressure, temperature, isotopic dilution etc. via the same types of intermolecular potential being used by the molecular dynamics simulators. In this kind of way it might become possible to use the information coming from molecular dynamics simulations to predict what kind of experimental changes should occur in the infrared and Raman spectra. The experimental evidence obtained so far (8,68, R4,R5) seems to point to a rather more complex pattern of behaviour than has so far been predicted.

Vibrational dephasing has often been assumed to be decoupled from rotational relaxation, allowing a basis for the deconvolution of the isotropic Raman spectrum from the infrared or depolarised Raman spectrum to obtain a "pure" reorientational line shape. Lynden-Bell points out that secular terms (i.e. terms arising from zero frequency components) in the fluctuating vibrational hamiltonian are normally responsible for dephasing. These come from the second derivative of the inter-molecular potential with normal coordinate (and also from the first derivative if the vibration is anharmonic). These may be divided into 'self' and 'exchange' (or resonant energy transfer) terms (eqns. 1 and 2), the latter being important in neat liquids. Efficient dephasing comes from those parts of $\delta^2 V/\delta Q^2$ which have a large amplitude and vary slowly (but still rapidly compared with the dephasing time). Coupling of vibrational and reorientational dephasing occurs when these parts depend on the orientation of the observed molecule. Orientation-dependent intermolecular interactions are affected by relative molecular translation and by reorientation. Traditionally the translational motion would be related to neutron scattering data, the reorientational motion to zero-THz, N.M.R., Kerr effect data.

It would be preferable, however, to use the technique of molecular dynamics in an attempt to avoid any ad hoc assumptions about rotation/vibration interaction. The method of taking orientational autocorrelation functions from infrared and Raman data is obviously fraught with difficulties. "Comparison of techniques" should mean the generation of spectra by some means (such as computer simulation) whereby specific forms of molecular interaction are used from the beginning. To use correlation functions from a technique in the analysis of data from another very often compounds uncertainty, leading to discord when considering the totality of work on a specific molecular liquid. It seems much more satisfactory to take a particular model of the liquid, develop it on the computer and then produce a variety of bandshapes corresponding to the different techniques available. In this way, even if the simulation algorithm is not able to incl de molecular vibrations, it will be possible to construct in a sensible way the rotational contribution to the infrared and Raman band shapes.

Some difficulties with earlier approaches may be illustrated as follows.

Firstly vibrational relaxation is not in general temperature independent and may be strongly affected by the reorientational motions of the molecules. This fact normally invalidates an approach developed by Rakov (70) and extended by Bartoli and Litovitz (39) in which the temperature independence of the vibrational relaxation is assumed. From the infrared bandshape at low temperatures, the intrinsic vibrational linewidth is then used to determine the reorientational linewidth at higher temperatures by subtracting from the whole bandwidth the intrinsic width at a given temperature. This method is applicable in any case only if the band-shape is Lorentzian (or nearly so) over a large temperature range. Another incorrect procedure in the literature assumes the independence of rotational and vibrational relaxation. Using this method the vibrational lineshape is obtained from Raman scattering data. Therefore the applicability of the method is confined to IR active vibrations which are also Raman active. Fourier transformation of Raman bands yields information about the correlation functions for the elements of the polarisability tensor. The correlation function of the isotropic part of the polarisability tensor obtained in this way is assumed to be the vibrational corre-lation function for both the infrared correlation function (overall) and that of the anisotropic part of the polarisability tensor correlation function. The vibrational correlation function is then used to extract from the infrared corre-lation function the "reorientational" correlation function. This method is valid only if rotational and vibrational relaxation are independent of each other and if vibrational relaxation affects infrared and Raman bands in exactly the same way. The procedure has been found to be invalid in at least one instance (8).

(c) Neutron Scattering Spectroscopy

In view of the assumptions which have to be made in obtaining orientational autocorrelation functions from infrared and Raman spectroscopy it seems clear that the use of these functions in the analysis of neutron scattering data merely adds to the confusion without added insight such as can now be provided by molecular dynamics simulation. Sears' method (71) of expanding the van Hove correlation function in terms of orientation functions was specifically designed to allow easy comparison with infrared and Raman functions, but the theory is available only for spherical or symmetric top symmetry and only for incoherent scattering. Accordingly it is better to redefine the criterion for inter-technique comparison when dealing with inelastic scattering of thermal neutrons from liquids. In the present context this means specifically that molecular dynamics simulation should be the common denominator.

If the system under discussion is classical and all nuclei are equivalent then essentially what the simulations should supply is the self and distinct van Hove functions for each atom in the molecule under consideration. The fundamental equations linking these to the spectral observables (such as time-of-flight variation) should then be utilised without any further analytical assumptions

concerning the factorisation or separation of rotational translational and
vibrational motions.

In view of the uncertainties surrounding Sears' method of relating these
functions to orientational correlation functions it is preferable to simulate
these probabilities directly by constructing histograms in the molecular dynamics
run and to build up the experimentally observed scattering law directly.

Brier and Perry have discussed the theoretical problems of treating the neutron
scattering from a rotationally diffusing asymmetric top. Careful quantitative
studies of molecular liquids by neutron scattering are extremely limited in both
kind and number. In particular, no liquid of non-spherical molecules had been
systematically investigated prior to $CH_2Cl_2$.

The first incorrect assumption made in the attempt to develop a theory for
the intermediate scattering function $I(\underset{\sim}{k},t)$ is factorising it into a translational
and rotational part. Berne and Montgomery (72) have shown to what extent this is
(dynamically) misleading, even for rough hard spheres. Vibrations contribute a
further Debye-Waller factor to the final expressions but apparently with a value
close to unity for the range of momentum transfers covered in a slow neutron
scattering experiment. The Sears expansion of $I(\underset{\sim}{k},t)$ is therefore not useful in
practice because of rotation/translation coupling.

It seems therefore that the only realistic method of treating experimental
incoherent neutron scattering must be based on the ability of very large computers
to handle the complexity of the data. The phenomenological theory, based on a
generalised Mori theory, and that of classical Brownian theory, is immediately
in trouble when dealing with neutron scattering. For example, the memory function
is a rotation-translation supermatrix whose elements are themselves matrices each
with nine scalar elements. The situation is over parameterised, while the basic
concept is still very much over simplified as regards definition of the molecular
potential. Models such as the M and J diffusion of Gordon (R7) cannot be developed
exactly for the asymmetric top because the free rotor autocorrelation function
for such molecules is not known analytically in a closed form. It would be
fruitful, however, to adapt the ideas of the statistical theory for use with
computer simulation, as in the "semi-stochastic" approach now under development.
Other problems in need of attention are concerned with the removal of pairwise
interaction and boundary conditions. There is no purpose in trying to use only
phenomenological theories, with the computer power now available.

(d)  N.M.R. Relaxation

Several N.M.R. investigations of $CH_2Cl_2$ have been reported, and very carefully
analysed by Brier and Perry (R8), upon whose work this section is largely based.
Such analysis typifies the problems of intertechnique consistency and, for this
reason, we comment on it here in some detail.

O'Reilly et al. (73) measured the intramolecular $^1$H, $^2$H and $^{35}$Cl relaxation

rates over a range of temperature. An activation energy $\sim 7.5$ kJmole$^{-1}$ was found for all three relaxation processes and at 300 K the quoted correlation times are $\tau_2(^1H) = 0.64 \pm 0.06$ ps (9 mole percent solution in $CD_2Cl_2$), $\tau_2(^2H) = 0.82 \pm 0.04$ ps; $\tau_2(^{35}Cl) = 1.20 \pm 0.10$ ps. These correlation times refer to the orientation of the C-H, C-D and C-Cl vectors respectively. Rothschild (74) has also reported proton $\tau_1$ measurements for $CH_2Cl_2$ in various dilutions in $CD_2Cl_2$ at the single temperature of 311 K. These were extrapolated to infinite dilution giving $\tau_2(^1H) = 0.66$ ps. Adjusting this result to 300 K using the activation energies determined by O'Reilly et al., Brier and Perry find $\tau_2 \sim 0.73$ ps. On the other hand, decreasing the value of $\tau_2(^1H)$ of O'Reilly et al. by $\sim 5$ percent as an estimate of the infinite dilution value gives $\tau_2 = 0.61$ ps. The two measurements, therefore, are not in particularly good agreement. Independently, Brier and Perry have estimated from the published $T_1$ data of O'Reilly et al. that at 300 K, 9 mole percent solution, $T_1^{-1} \sim 0.21$ ps, giving $\tau_2(^1H) = 0.77$ ps, which, when adjusted to infinite dilution gives, $\tau_2(^1H) \sim 0.73$ ps, in agreement with the temperature adjusted result of Rothschild. This change from the published result of O'Reilly et al. has its origin in an error in the H-H distance used by these authors in calculating $\tau_2$ from $T_1^{-1}$.

In another investigation of the proton $T_1$ in $CH_2Cl_2$, Heatley (75) made measurements on the $^{13}C$ satellites. From a numerical solution of the coupled relaxation systems (which did involve the assumption of axial symmetry of the reorientational motion through assuming equal correlation times for the H-H and C-H vectors). Heatley estimates that the contribution of the spin-rotation relaxation is therefore considerable in $CH_2Cl_2$, and Heatley's revised estimate of $\tau_2(H)$ is $0.48 \pm 0.06$ ps at 308 K or $0.53 \pm 0.06$ ps at 300 K. Lyerla et al. (76) have reported $^{13}C$ spin-lattice relaxation times and C-H nuclear Overhauser enhancement factors from $CH_2Cl_2$. The latter allow the separation of this $^1H-^{13}C$ dipolar relaxation time from the measured $^{13}C$ $T_1$ time, giving a relaxation time $\tau_2$ for the reorientation of the C-H vector (which we will designate as $\tau_2(^{13}C)$) of $0.53 \pm 0.06$ ps at 310 K or $0.69 \pm 0.07$ ps at 300 K.

Heatley's revised value for $\tau_2(^1H)$ is a key result in Brier and Perry's discussion. If Heatley's measurements were analysed assuming a zero contribution from spin-rotation relaxation $(1/T_1(S-R) = 0)$ the correlation time $\tau_2(^1H)$ for the H-H vector is found to be 0.66 ps at 310 K, 0.73 ps at 300 K, in perfect agreement with the adjusted values of both O'Reilly et al. and Rothschild. Secondly, any non-zero value of $T_1^{-1}(S.R.)$ must lead to a smaller value of $\tau_2(^1H)$. Thirdly, the magnitude of $\tau_2(^1H)$ is not critically dependent on the original assumption that $\tau_2(H-H) = \tau_2(C-H)$.

Heatley analysed his values of $\tau_2(H)$ in terms of the small step rotational diffusion model for a symmetric top after noting that stochastic models for large angular steps are generally experimentally indistinguishable from small

step theory unless the angular steps are in excess of $30^{\circ}$. Separate estimates of $D_{//}$ and $D_{\perp}$, the components of the diffusion tensor, were derived on the basis of taking $CH_2Cl_2$ as a symmetric top. (It is an inertial asymmetric top.) The estimates were derived from $\tau_2(^1H)$ by utilising the infrared value for the ratio $D_{//}/D_{\perp}$. In view of the comments in IVb about vibration-rotation interaction, the use of infrared and Raman correlation times should be regarded with extreme caution. However, he was in this way able to obtain a value for the relevant relaxation time for comparison with, for example, dielectric data. A collection of such times is tabulated by Brier and Perry (their table 2) from various experimental sources. Their tables 1 and 2 represent the data before and after correction for numerical interpretative errors in original papers and before and after numerous adjustments forced on the reviewers by the fact that the original data were published under different conditions of temperature and/or pressure. There is an obvious need therefore to repeat the $CH_2Cl_2$ N.M.R. work under rigidly controlled conditions.

Table 2 of Brier and Perry shows a corrected analysis of the revised n.m.r. data in terms of the rotational diffusion model for $D_{//}/D_{\perp} = 3$ (the infrared and neutron result) and for $D_{//}/D_{\perp} = 9$ (the requirement for the J diffusion model to be formally identical with the rotational diffusion model in the Debye limit of the former). In contrast to the above analyses, O'Reilly et al. attempted to interpret their n.m.r. data in terms of models involving the idea that significant rotational motion occurs only during the period a molecule is excited to an "interstitial site" in the liquid "lattice" by a "hard" collision. It was then specifically assumed that, during this time, the anisotropy of the reorientational motion is determined entirely by the inertial properties of the molecule, i.e. that $<\theta_i^2> \sim I_i^{-1}$ where $<\theta_i^2>$ is the mean square angle of rotation about the i'th principal axis. The original data did not fit this model particularly well but they do with the correction applied by Brier and Perry to $\tau_2(^1H)$ (= 0.73 ps). The same model predicts also that the ratio $\tau_2(^{13}C)/\tau_2(D)$ for the C-H/C-D vectors in $CH_2Cl_2$ and $CD_2Cl_2$ should equal 0.87 ($CD_2Cl_2$ is also approximately a symmetric top rotor with $(I-I_z)/I_z \sim 6.7$). Brier and Perry find experimentally a value of $0.88 \pm 0.14$. However, within experimental error, the measured ratio also agrees with the predictions of stochastic models (ratio = 1) for which the correlation times are independent of the inertial changes produced by deuteration. This illustrates very well the problem of experimentally distinguishing between alternative models. This type of comparison is invalidated further by the incorrect procedures adopted in original papers. The infrared and Raman correlation times are uncorrected for vibration-rotation interaction and the n.m.r. data are interpreted with models which break down in the far-infrared region although they can apparently be made to fit the neutron scattering data (R8).

As Brier and Perry point out, the above considerations are over-shadowed by

the fact that with Heatley's value of $\tau_2(^1H)$ (= 0.53 ps), the available n.m.r. data do not support the assumption of axial symmetry of the angular motion about the a axis since $\tau_2(H-H) \neq \tau_2(C-H)$. Possibly it is more realistic to take the mean of $\tau_2(^2H)$ and $\tau_2(^{13}C)$ as the best estimate of $\tau_2$ for the C-H vectors. However it is not then possible to define what is meant by diffusion anisotropy as implied by the n.m.r. data ($\tau_2(H-H) = 0.53 \pm 0.06$ ps; $\tau_2(C-H) = 0.75 \pm 0.07$ ps and $\tau_2(C-Cl) = 1.2 \pm 0.10$ ps). The only simple model is small step rotational diffusion, which of course involves three adjustable parameters $D_{aa}$, $D_{bb}$ and $D_{cc}$, already too many for the available data. With correlation time data of modest precision, the anisotropy of the angular motion may be very poorly defined in certain circumstances. This is illustrated by Brier and Perry for a symmetric top where the anisotropy factor $D_{//}/D_\perp$ is seen to become an <u>insensitive</u> function of the ratio of two correlation times for different molecular vectors beyond $D_{//}/D_\perp \stackrel{\sim}{>} 2.5$. As an example, in the case of $CH_2Cl_2$, the available data only defines $D_{//}/D_\perp$ within the range $2 \stackrel{\sim}{<} D_{//}/D_\perp \stackrel{\sim}{<} 3$, centred on 2.3. Larger values of the anisotropy, $D_{//}/D_\perp$, will be even less closely defined for the same precision of the n.m.r. data. A similar problem will arise in trying to deduce quantitative results for the ratios $D_{aa}:D_{bb}:D_{cc}$ in the more general case of a completely anisotropic diffuser.

Using the formulae given by Woessner (77), Brier and Perry find that there is no single set of values ($D_{aa}$, $D_{bb}$, $D_{cc}$) which will reproduce the three n.m.r. data simultaneously. A value of $\tau_2(H-H)$ as low as 0.53 ps is incompatible with a value of $\tau_2(C-H)$ as large as 0.75 ps in this model. Taking account of the experimental uncertainties, the optimum compromise solution taken by Brier and Perry lies in a small region around $D_{aa}:D_{bb}:D_{cc} \sim 10:10:1$, or in absolute values. $D_{aa} \sim D_{bb} \sim 0.3$ ps$^{-1}$ and $D_{cc} \sim 0.03$ ps$^{-1}$. This tentative analysis of the n.m.r. data again corresponds to axial symmetry of the reorientational motion but this time with the c-axis being the unique axis, the motion about one axis being much more highly hindered than about the other two axes. Brier and Perry are able to rationalise this in that $D_{aa}$ will then be largely determined by the dipole effect, $D_{bb}$ by steric effect, and $D_{cc}$ by a combination of both of these. This is a completely different picture from that provided by infrared analysis. It should be possible to determine which of these pictures is the more correct by molecular dynamics simulation with and without electrodynamic interaction.

Brier and Perry consider the infrared and neutron scattering data in terms of the new model of angular anisotropy. This makes a great change in the picture of angular anisotropy compared with the original model, but when compared with the neutron scattering data turns out to have only the most approximate validity. This is not surprising when one considers what is known from the far infrared/dielectric data. It has been clearly demonstrated (R6) that the extended diffusion models are unable to shift the peak frequency of the far infrared absorption band since there is no definition of the mean square torque.

We have commented already in detail on the similar situation for $CH_3I$. This is typified in the next section by reference to a particular study.

(e) Comparison of Far Infrared and Rayleigh Wing Data in $CH_3I$

This has been carried out for several liquids, including $CH_3I$, in an interesting paper by Lund et al. (78). The study of the depolarised Rayleigh wing scattering which has been intensified in recent years but, as Lund et al. point out, without much attempt to compare the results with the corresponding far infrared bandshapes. An exception is the theory of Bartoli and Litovitz (79). These workers claim that collision induced far infrared absorption and depolarised Rayleigh wing scattering of dipolar anisotropic liquids are due to the same local fluctuation in the orientations of the individual molecule.

Lund et al. (78) do not compare the dipolar and polarizability correlation function directly as is often done, but instead construct a quantity $R(\omega)$ proportional to the energy absorbed in a scattering experiment. $R(\omega)$ is compared with the infrared power absorption $\alpha(\omega)$ to see if they show the maximum for the same value of the frequency. This will be the case if the dipolar and polarisability correlation functions have the same time dependence for times, studied in this paper, which are smaller than the rotational diffusion times i.e. $< 10^{-12}$ s. This procedure is chosen because the far infrared absorption maxima are very pronounced.

By direct comparison the frequency maxima for $R(\omega)$, together with reported values for the absorption maxima found in the far infrared are tabulated by Lund et al. The results show that for dipolar symmetric tops ($CHCl_3$, $CH_3I$, $CHBr_3$, $CH_3CCl_3$, $(CH_3)_3CCl$, $(CH_3)_3CBr$) the maximum for $R(\omega)$ and $\alpha(\omega)$ coincide in frequency. The discrepancy is largest for $CH_3CCl_3$ and $(CH_3)_3CCl$ this may be due to the fact that the convolution of the apparatus slit function and the "true" Rayleigh line due to molecular diffusion may contribute considerably at low frequency shifts ($< 20 \approx 25$ cm$^{-1}$). The discrepancy could also be caused by a strong variation of the refractive index for these compounds.

Lund et al. also investigated the Rayleigh and far infrared spectra of the non-dipolar species $C_6H_6$, $C_6D_6$ and $CCl_4$, which are without a permanent dipole moment and show maxima in the $R(\omega)$ curves coinciding with the corresponding $\omega_{max}$ in the absorption spectra. The shift in the far infrared absorption maximum on going from $C_6H_6$ to $C_6D_6$ is reproduced in the $R(\omega)$ curves. The maximum in the $R(\omega)$ curve for the asymmetric tops $C_6H_5Cl$ and $C_6H_5Br$ is very close in frequency to the maximum in benzene, whereas the absorption maximum is at a lower frequency. An examination of the $R(\omega)$ curves for $C_6H_5Cl$ and $C_6H_5Br$ shows that these curves have an augmented intensity compared with the corresponding benzene curve on the low frequency side of the maximum. This is especially pronounced for $C_6H_5Br$. Lund et al. suggest that the $R(\omega)$ curves for $C_6H_5Cl$ and $C_6H_5Br$ are composed of two curves: one with a frequency maximum at ~75 cm$^{-1}$ and another showing a maximum in the far infrared, the latter curve being less intense than the former.

Finally, these authors mention that the $R(\omega)$ curve for $CCl_4$ is very similar to the far infrared spectrum with bands of very weak intensity at $\sim 95$ cm$^{-1}$ and $\sim 140$ cm$^{-1}$. The far infrared bands have been assigned as difference modes.

The similarity between the far infrared absorption and the "Raman absorption" $R(\omega)$ for dipolar symmetrical top molecules makes it plausible that the same component of the short time motion is responsible. The authors go on to propose a molecular mechanism involving molecular rotation around an axis perpendicular to the top axis. This will lead to a change both in the component of the permanent dipole moment in the direction of the field and of the static polarizability in the laboratory frame, whereas a rotation around the top axis cannot give rise to far infrared absorption in a slowly varying field.

The hypothesis that librations around axes perpendicular to the top axis are responsible for both the depolarised Rayleigh wing scattering and the far infrared absorption bands for symmetric top molecules with a permanent dipole moment could be tested if symmetric tops with the dipole moment perpendicular to the top axis existed. This is because librations around the top axis would give rise to a far infrared absorption while they would be Raman inactive and $\alpha(\omega)$ and $R(\omega)$ would not look alike. The asymmetric top molecules chlorobenzene and bromobenzene almost fulfil this condition. The far infrared and Rayleigh spectra of the spherical molecule carbon tetrachloride arise from induced dipole moments and distortions of the ellipsoid of polarisability respectively. The similarity of $R(\omega)$ and $\alpha(\omega)$ again make it plausible that the same librational motion is responsible.

Finally, we consider a paper on methyl iodide, produced by Claesson and Jones (80) in 1975, and see whether such an effort at coordination can be improved upon in the context of the project. These authors mention several experimental techniques used to study rotational motion in liquids composed of small molecules: N.M.R. spin-lattice relaxation measurements, Raman scattering and depolarised Rayleigh scattering. The latter are considered as concerning both single particle and pair correlation effects in the context of a theory by Kivelson and co-workers (81).

Depolarised Rayleigh scattering experiments have shown that for some molecules (e.g. benzene and toluene) the pair correlation effects are small while for other molecules (e.g. chloroform and nitrobenzene) the rotational relaxation time varies with solute concentration, suggesting that pair correlations are significant. For molecules with little pair correlation the depolarised Rayleigh rotational relaxation time varies linearly with viscosity at constant temperature and is independent of solute concentration. Even when pair-correlations do affect the depolarised Rayleigh results, the relaxation times still vary linearly with viscosity at constant concentration and temperature. Claesson and Jones test the linear relation between relaxation times; whether this varies linearly with

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viscosity at constant concentration and temperature. By studying pure liquids at different pressures, the viscosity (and density) can be varied over a wide range while keeping the chemical composition of the sample constant.

Results were presented for depolarised Rayleigh light scattered from four molecular liquids, including $CH_3I$ under kbar (or MPa) of applied pressure. High pressure Raman and N.M.R. data were available at this time for methyl iodide. By comparing the light scattering results with such data the effect of pair-correlations at high pressure can be studied. Alternatively the authors could examine the approximations used to obtain the Raman and N.M.R. relaxation times from the experimental results. A comparison of results was used to obtain light scattering relaxation times from the rather complex "Rayleigh wing" spectra. Unfortunately, the Kivelson theory of pair correlations based on rotational diffusion is used without refinement. If this theory were subjected to the same kind of treatment as in the paper by Lund et al., (78) in order to obtain direct comparison with the far infrared power absorption its weakness would be exposed immediately in the form of a Debye plateau.

However, for dilute solutions or cases where pair correlations are small the relaxation time measured by light scattering would be equal to the single particle relaxation time, always assuming that the internal field or vibration/rotation coupling effects can be treated in a reasonable way.

Both Raman light scattering and nuclear magnetic resonance techniques measure the single particle relaxation time; but as Claesson and Jones point out, in obtaining a relaxation time from Raman measurements one must assume that the vibration/rotation coupling prolbem is insignificant and also that non-orientational relaxation processes affect the isotropic and anisotropic Raman spectra in the same manner. Accordingly any conclusions about pair-correlations arrived at by comparing rotational "relaxation times" measured for pure liquids using depolarised Rayleigh light scattering and Raman scattering must be reinvestigated cautiously with the help of any available simulations.

In the rotational diffusion approximation, the single particle relaxation time for rotations perpendicular to the molecular symmetry axis, $\tau_2$, measured in depolarised Rayleigh, Raman or N.M.R. experiments, is related to the rotational diffusion coefficients of the symmetry axis, $\theta$, by $\tau_2 = (6\theta)^{-1}$. We have already seen how the rotational diffusion theory may be extended, in principle, to include the effects of memory and inertia. For spherical hydrodynamic particles in the limit of "stick" boundary conditions, the Stokes-Einstein relaxation predicts that the rotational diffusion coefficient is related to the viscosity of the medium, $\eta$, and the temperature, T, by

$$\theta = kT/(8\pi\eta a^3)$$

where a is the particle radius. Hu and Zwanzig (82) have extended the theory to

"slip" boundary conditions. Although the rotational diffusion model does not apply rigorously to a liquid composed of identical small molecules, the linear dependence of rotational relaxation time on $\eta/T$ seems fairly general. By plotting $\tau$ vs $\eta/T$ we can compare relaxation times for a given molecule measured under different conditions and by different techniques.

This paper also reports depolarised spectra recorded in all three polarisation configurations: VH, HV and HH. Linewidths for all three configurations were the same within experimental error as were the intensities of the VH and HV spectra. Values of correlation time $\tau_{LS}$ were obtained for each liquid. All four liquids showed a significant increase in $\tau_{LS}$ with pressure. For direct comparison with other data $\tau_{LS}$ was replotted as a function of $\eta/T$. In all cases the data fit well to a straight line: $\tau_{LS} = A\eta/T + \tau_o$, where $\tau_o$ is the zero viscosity (or infinite temperature) intercept.

Using interferometry Alms et al. (83) have measured $\tau_{LS}$ for benzene and toluene both in the pure liquid and as solutions in isotropic solvents. They found that for these two liquids the relaxation times varied only with viscosity and not with the molecular nature of the solvent. Their relaxation times for benzene were independent of concentration, suggesting that pair correlations in this liquid are small. The high pressure results of Claesson and Jones (80) substantiate this conclusion. Even at densities approaching the freezing point the relaxation time measured by depolarised Rayleigh scattering remains the same linear function of viscosity. They conclude that for benzene the measurements give single particle relaxation times.

Proton spin-lattice relaxation times have been measured for benzene at high pressure by Bull and Jonas (84). The reorientational relaxation time changed from 1.7 ps at 0.1 MPa to 1.8 ps at 50 MPa, thus showing little or no pressure dependence. The proton relaxation time is affected both by rotations parallel and perpendicular to the $C_2$ symmetry axis, whereas the $\tau_{LS}$ depends only on rotations perpendicular to the axis. Bull and Jonas point out that spinning of benzene about its axis is relatively free and should show little pressure dependence. This explanation of the n.m.r. results is in agreement with the conclusion that in benzene one measures the $\tau_2$ single particle relaxation time for rotation perpendicular to the symmetry axis.

Dill et al. (85) have reported values of $\tau_{LS}$ for benzene at high pressures with a grating spectrometer. However in discussing methyl iodide, Claesson and Jones point out limitations involved in measuring depolarised Rayleigh rotational relaxation using a grating spectrometer.

Part of the difficulty with light scattering data of intermediate accuracy is that they can be described by a single Lorentzian, making a more realistic analysis difficult. The $\tau_{LS}$ for toluene for example is a linear function of the viscosity and Alms et al. (82) have discussed the possible significance of the fact that

this asymmetric top molecule has a single relaxation time.  Pair correlation, if present, do not seem to influence the viscosity dependence of the single relaxation time.

Dill et al. (85) also studied the depolarised Rayleigh scattering of toluene at high pressures and detected the wavenumber dependent doublet features predicted by Stegemann and Stoicheff (86) at a pressure of 400 MPa.  Claesson and Jones found no evidence of the doublet at 205 MPa but the pressure dependence of the Rayleigh scattered radiation is certainly informative as to individual and collective molecular dynamics.

Claesson and Jones compared their high pressure depolarised Rayleigh relaxation times for methyl iodide measured using interferometry with high pressure Raman results by Campbell et al. (87) and high pressure depolarised Rayleigh results of Dill et al.  Again, according to Claesson and Jones, the Raman experiments should yield single particle relaxation times.  In comparing the $\tau_{LS}$ results and the $\tau_2$ (Raman) times Claesson and Jones find a situation similar to that for chloroform, i.e. pair correlations appearing to be significant at atmospheric pressure.  However the $\tau_{LS}$ of Claesson and Jones and of Dill et al. do not agree, the latter being significantly smaller.

This illustrates an experimental difficulty of depolarised Rayleigh scattering because the spectrum obtained using spectrometers consist of two prominent features: an intense narrow peak at the laser frequency and a broad Rayleigh-wing which extends for several hundred wavenumbers.  It is very important to realise that this Rayleigh-wing is precisely the most important feature as regards molecular dynamics and should not be subtracted out in any way.  It is exactly this wing that when converted to "Raman absorption" form  closely matches the far infrared spectrum.

It is clear from these remarks that Claesson and Jones, in subtracting out the wing by the use of interferometry, have also subtracted out the most interesting part of the spectrum.  It is not surprising therefore that they can fit what remains by a Lorentzian because what remains is effectively equivalent to a conventional low frequency dielectric loss curve (i.e. a Debye profile).

Dill et al. have also treated their data approximately by assuming that the second moment of the band is the classical single particle value, $6kT/I$.  Any difference from this second moment was attributed to the presence of pair correlations.  This is, of course, a shaky conclusion when the collision induced effects and the nature of the far wing are either not understood or not accounted for at all.

Despite the considerable effort gone into the scattering experiments (photons, phonons, and neutrons), the data is inconclusive as regards the nature of molecular dynamics and interactions.  The direct comparison of Raman and Rayleigh times will not therefore be incisive or even useful without the common reference of a

firm (and elaborate) theoretical basis such as that offered by computer simulatic
where well-defined assumptions are involved in the production of bandshapes and
their associated correlation functions.

(f) Mode-Mode Interaction and Depolarised Light Scattering

We follow the excellent review of development in this field by Searby et al.
(88). These workers have shown that many of the apparently different theories in
this area lead to the same or very similar, analytical forms for the intensity
profile $I(\omega)$. This means that, if experiments are not carried out over a wide
enough range of conditions, the data from depolarised light scattering cannot
discriminate between the theoretical models. It would, of course, be sensible
to use this technique as one experimental probe amongst many. Several theoretica
approaches have been made so far.

(1) Depolarised scattering light contains information about the so-called
"anisotropic fluctuations" in a molecular fluid which are dependent on reorientat
Leontovich (89) was the first to predict that the shape of the intensity profile,
$I(\omega)$, might be affected by overdamped transverse shear waves. Under certain
conditions (such as in the viscous liquid) this results in a dip at close to zero
frequency (or what appears, on a linear scale, to be close to zero frequency).

(2) Viscoelastic theories, such as those of Rytov (90) start from the assumpt
of a frequency-dependent shear modulus coupling stress and strain tensors. This
produces a lineshape which reflects the modulation of the strain tensor by shear
and longitudinal waves.

(3) There have been numerous theories based on the Mori form of the Liouville
equation (R6). Searby et al. (88) discuss their outward differences and fundamen
similarity. The approach is similar to that of Kivelson and Madden (52). Usuall
the method is to search for variables with which the fluctuating dielectric tenso
can be treated inside the column vector of the Mori equation. The primary variab
is a tensor describing the orientation characteristics on the molecular scale
(e.g. the polarisability tensor). The primary variable, or variables, is then
mixed with one or more secondary variables, usually a momentum density tensor
(or current density). Various authors have chosen different primary and secondar
variables. However, due to the structure of the Mori equation the theories
eventually come out with the same result. The analytical dependence of $I(\omega)$ on
$\omega$ differs only in that the constant terms have different physical meaning. This
is an unsatisfactory state of affairs brought about by the fact that the seemingl
simple geometrical shape of $I(\omega)$ at low frequencies can be reproduced analyticall
in a variety of ways. The opposite is true for far infrared spectra (when used i
combination with its low frequency adjunct, the dielectric loss), and it might
be advantageous to construct a variety of mode-mode theories for zero-THz
spectroscopy. It is noticeable that Ailawadi et al. (91) have produced a theory
which is different in that there are two primary variables, angular momentum and

stress, which produces a $I(\omega)$ (different from all the others) which does not fit the data of Searby et al. (88).

(4) De Gennes (92) has presented a theory which produces the same $I(\omega)$ as those above. This was developed for the isotropic phase of a liquid crystal. The primary variable is a traceless symmetric second rank tensor $\underset{=}{Q}_{\alpha\beta}$ describing local orientational order: the tensor order parameter. The secondary variable is a hydrodynamic velocity (or velocity field) from which he constructs a tensor describing the rate of shear ($\underset{=}{\varepsilon}_{\alpha\beta}$). The force conjugate (in Mori theory) to the shear rate tensor is the stress tensor and the force conjugate to the rate of change if the order parameter is obtained by expanding the free energy as a function of powers of $\underset{=}{Q}_{\alpha\beta}$ and then differentiating with respect to $\underset{=}{Q}_{\alpha\beta}$. This theory is valid for temperatures near the isotropic-nematic transition point of a liquid crystal, where some physical constants of the system diverge. There are further elements of $\underset{=}{Q}_{\alpha\beta}$ which do not interact with hydrodynamic modes and contribute an undisplaced central Lorentzian. The light scattered intensity for two variable theories takes the form:

$$I(\omega) \propto \sin^2(\theta/2)/(1 + \omega^2/\Gamma_1^2)\Gamma_1$$

$$+ \frac{B(1/\Gamma_2)\cos^2(\theta/2)\left[(k^4\eta^2/\rho^2\Gamma_2^2)(1-R) + \omega^2/\Gamma_2^2\right]}{(k^2\eta/\rho\Gamma_2 - \omega^2/\Gamma_2^2)^2 + (\omega/\Gamma_2)^2(1+(1-R)k^2\eta/\rho\Gamma_2)^2} \tag{11}$$

In general $B = 1$ and $\Gamma_1 = \Gamma_2 = \Gamma$. In this equation $\theta$ is the angle at which the light is scattered, k is the scattering wave vector, $\eta$ the normal shear viscosity and $\rho$ the density. $\Gamma$ is a correlation frequency $1/\tau$ where $\tau$ represents a different process in the various different theories,

(a) $\tau =$ correlation time for the anisotropic part of the polarisability density (Keyes/Kivelson (93), Gershon/Oppenheim (94)).

(b) $\tau =$ correlation time of the orientational order parameter (de Gennes (92)).

(c) $\tau =$ correlation time of the angular momentum density (Ailawadi and Berne (91)).

(d) $\tau =$ correlation time of a second rank tensor, identifiable with either an orientational density tensor or a stress tensor (Kivelson et al. (82)).

R is a dimensionless parameter expressing the coupling between the hydrodynamic modes and molecular anisotropy. Only the shear waves are able to couple to the primary variable in depolarised (VH) scattering geometry. In HH scattering at $\theta = \pi/2$ transverse velocity gradients cannot contribute but longitudinal gradients now can. For $\theta \neq \pi/2$ isotropic Brillouin scattering is present as well.

Searby and co-workers (88) point out that in VH geometry the scattering is a function only of R and $k^2\eta/\rho\Gamma$, which are both dimensionless. The second function is a ratio of two characteristic times; $1/\Gamma$ and the time $\rho/k^2\eta$. If R = 1 Rytov's

hydrodynamical theory appears. However, experimental evidence suggests that $R = 0.4$. Moreover, in the Rytov theory, $\tau$ is identified with the relaxation time of the shear strain tensor and is not a molecular parameter. The ratio of times can be divided into four regions:

(a) $\ll 1$; (b) $< 1$; (c) $> 1$; (d) $\gg 1$.

A Lorentzian of half-width $1/\tau$ is obtained if $R \to 0$ or $k^2 \eta/\rho\Gamma \to 0$.

(a) Here $\Gamma$ is large, the liquid is composed of small, simple molecules and is of low viscosity. The fine structure is very difficult to resolve by light scattering, but using the relation between $A(\omega)$ and $I(\omega)$ this difficulty is surmountable using zero-THz spectroscopy. The central dip seems often not to be observable at all.

(b) This may be used to classify the larger molecules and viscous liquids well above their freezing points. It seems that in a variety of liquids $R = 0.4$ produces a good fit to the data, even for molecules as different as $CS_2$ and ethyl benzoate. This is apparently not understood in terms of molecular light scattering theory.

(c) This corresponds to a point just above the freezing point. The whole bandshape is now as narrow as the splitting observed in case (a). The shear disturbances are propagative and are less than critically damped. As the viscosity is increased the eqn. (11) becomes increasingly invalid, and has to be modified by the introduction of higher order terms.

(d) This is a region where the viscosity approaches that of the super-cooled liquids approaching $T_g$, the glass transition point. The theory predicts a triplet spectrum for $R = 1$, and for $R < 1$ a central Lorentzian of width $1/\tau$ superimposed on a broader Lorentzian of width $\Gamma/(1-R)$. In this latter case the shear waves are no longer propagative but diffusive.

These predictions are contrary to what is found experimentally (88) where at sufficiently low temperatures a very weak doublet appears in the wings of the central line, indicating the presence of well-defined propagating shear waves. The spectra expressed in terms of $\omega^2 I(\omega)$ would be similar to those found in terms of $\alpha(\omega)$ (the power absorption coefficient) in the far infrared. The corresponding polarised spectra show no signs of structure. The doublet was first observed by Starunov et al. (95) in supercooled Salol. As the temperature is lowered the intensity of the doublet decreases as the transverse sound velocity increases.

The situation in the viscous liquid is therefore quite similar to that in zero-THz spectroscopy. There is an "$\alpha$ process" (42) very close to the existing line, a "$\beta$ process", a narrow, weak doublet peak at GHz frequencies, and a broad line out in the wings (at far infrared frequencies). The spectra apparently require three variable theories. A pertinent third variable would be the one describing the translational motion of the molecules.

The polarised light scattered from these systems have certain features in

common. There is an intense central Lorentzian (of half width $1/\tau$) and fine structure at the Brillouin frequencies ($\omega_B$). The calculated intensity of the fine structure tends to zero as $\omega_B/\Gamma \to 0$ and also as $\omega_B/\Gamma \to \infty$. There is often a dip at the Brillouin frequencies in the limit $\omega_B/\Gamma \ll 1$. In the case $\omega_B/\Gamma \gg 1$ the dip is replaced by a hump.

Having mentioned the hydrodynamic aspects of light scattering, we may approach the subject from the molecular point of view following Berne and Pecora (24). If we assume that vibrational, translational and rotational motions are decoupled then the spectrum depends on time correlation-functions of the form:

$$< D_{MK}^{(J)}(\Omega(o)) . D_{M'K'}^{(J')}(\Omega(t)) >$$

(i.e. that of Wigner rotation matrix elements). To illustrate the use of the kind of phenomenological theories now available, we choose Favro's theory (96) of rotational diffusion. We recognise the conditional probability density function $P_s(\Omega, t | \Omega_o)$ which specifies the probability distribution for the molecule to have Euler orientation $\Omega$ at t given $\Omega_o$ at t = 0. The Debye model for rotational diffusion, when applied to the general case of an anisotropic diffuser, is given by Favro:

$$\frac{\delta}{\delta T}\Big[ P_s(\Omega, t | \Omega_o) \Big] = - \sum_{i,j=x,y,z} \hat{I}_i \; \textcircled{H}_{ij} \hat{I}_j P_s(\Omega, t | \Omega_o)$$

where $\hat{I}_i$ and $\hat{I}_j$ are the angular momentum operators of the quantum mechanical anisotropic rigid rotor. $\hat{I}$ is the total angular momentum operator, $\hat{I}_z$, that about the space fixed axis, z' and $I_z$ that about the body fixed axis, z (e.g. that of highest symmetry). $\textcircled{H}_{ij}$ is the rotational diffusion tensor. The body fixed axis may be chosen for convenience as those for which $\textcircled{H}_{ij}$ is diagonal. These are not, in general, those for which the inertial tensor is diagonal, or those for which $\textcircled{H}_{ij}$ is diagonal, or for which the polarisability tensor is diagonal. If we write,

$$\textcircled{H} = \begin{bmatrix} \textcircled{H}_{xx} & 0 & 0 \\ 0 & \textcircled{H}_{yy} & 0 \\ 0 & 0 & \textcircled{H}_{zz} \end{bmatrix}$$

then for a spherical diffuser, $\textcircled{H}_{xx} = \textcircled{H}_{yy} = \textcircled{H}_{zz} = \textcircled{H}$. For a symmetric diffuser $\textcircled{H}_{xx} = \textcircled{H}_{yy} = \textcircled{H}_{\perp}$; $\textcircled{H}_{zz} = \textcircled{H}_{//}$. In general, $\textcircled{H}_{xx} \neq \textcircled{H}_{yy} \neq \textcircled{H}_{zz}$.

In the most general case, even in Debye/Favro theory (with no "inertial" or "memory" effects) the spectrum consists of five overlapping Lorentzians. The rotational correlation functions is a sum of five exponentials - of the symbolic form

$$I_{VH}^{\alpha}(q,t) = \frac{1}{15} < N > \sum_{i=1}^{5} A_i \exp(-(q^2 D + \hat{i}_i)t)$$

(with notation of Berne and Harp (R.10).

With the zero-THz absorption band we can see that Favro/Debye theory is qualitatively inapplicable at high frequencies essentially because it produces a plateau as $\omega \rightarrow \infty$ in the power absorption coefficient $\alpha(\omega)$. The theory may be classified as a zeroth order approximant of Mori's continued fraction expansion (25) of the dynamical equation of motion (Liouville or von Neumann). The next approximant (corresponding basically with McClung's extension (R7) of Gordon's M and J diffusion models) regains transparency $(\alpha \rightarrow \infty)$ (i.e. has a finite spectral moment), but cannot reproduce the characteristic shift in the peak value of $\alpha(\omega)$ observed experimentally (for example, along the orthobar in $CH_3F$ (58)). We do not, therefore, wish to use the extended diffusion models. We must aim at a Favro/Mori theory where the second memory tensor of the asymmetric top is exponentially decaying, this being the minimum requirement in zero-THz spectroscopy even of the simplest kind (i.e. not involving specialities such as viscous or glassy solvents), and for the correct definition of the mean square torque. If we are to neglect rotation/translation coupling we must solve numerically the resulting Mori/Favro approximant, which will be expressed in terms of the quantities $\Gamma_{xx}$, $\Gamma_{yy}$, $\Gamma_{zz}$, i.e. the characteristic frequencies of the assumed exponential decay of the second memory tensor.

## The Mori/Favro Approximant

Favro's theory allows us to determine the Brownian diffusion of a non-spherical body through the following equation:

$$\frac{\partial}{\partial t} [P(\underset{\sim}{\Omega}, t)] = -\hat{M} \cdot \underline{\underline{D}} \cdot \hat{M} \, P(\underset{\sim}{\Omega}, t)$$

where $\underline{\underline{D}}$ is a diffusion tensor and $\hat{M}$ the quantum mechanical angular momentum operator. However, the Markhovian nature of this equation means that memory effects are neglected.

A rigorous analytical solution of this equation is available only for symmetric tops when the eigenstates of the operator $\hat{\Gamma} = \hat{M}\underline{\underline{D}}\hat{M}$ are given by the Wigner rotation matrix elements, $D^L_{MK}(\underset{\sim}{\Omega})$. If, by using a quantum-mechanical formalism, we denote with $|\alpha>$ the eigenstates of the diffusion operator in the symmetric top cases, the general solution is given by:

$$|P(\underset{\sim}{\Omega}, t)> = \sum_{\alpha\alpha'} C_{\alpha'} |\alpha><\alpha|\pi><\tilde{\pi}|\alpha'> e^{-E_\pi t}$$

where $|\pi>$ and $E_\pi$ are eigenstates and eigenvalues of $\hat{\Gamma}$, respectively. The vector $\underset{\sim}{C} = (C_1, C_2, \ldots)$ denotes the initial condition of our physical system. As usual, the operator $\hat{\Gamma} = \hat{M} \cdot \underline{\underline{D}} \cdot \hat{M}$ must have an eigenvector whose eigenvalue vanishes. The other eigenvalues have to be provided by positive real numbers. If we focus our attention on the state: $|\underset{\sim}{A}> = (|\alpha_1>, |\alpha_2>, \ldots)$ we have the matrix form:

$$\dot{\underset{\sim}{A}} = \hat{\Gamma} \cdot \underset{\sim}{A} + \underset{\sim}{f}$$

where, according to Kivelson and Ogan (97), the rapidly fluctuating force may be replaced by its time average, which is vanishing. This equation may also be regarded as the Markhov limit of the following Mori/Zwanzig/Kubo type of equation:

$$\dot{\underset{\sim}{A}} = \int_{0}^{t} \underset{\sim}{\Phi}(t,\tau)\underset{\sim}{A}(\tau)d\tau + \underset{\sim}{f}(t) \tag{12}$$

The structure of the memory kernel $\underset{\sim}{\Phi}$ is defined by the continued fraction expansion of its Laplace transform. By using the continued fraction concept the eqn. (12) may be replaced by:

$$\frac{d}{dt}\underset{\sim}{V}(t) + \underset{\sim}{A}\underset{\sim}{V} + \underset{\sim}{S}\underset{\sim}{V}(t) = \underset{\sim}{F}(t)$$

where $\underset{\sim}{A} = \begin{bmatrix} \underset{\sim}{0} & \underset{\sim}{\omega}_{12} & \underset{\sim}{0} & \underset{\sim}{0} & \cdots\cdots \\ \underset{\sim}{\omega}_{21} & \underset{\sim}{0} & \underset{\sim}{\omega}_{23} & \underset{\sim}{0} & \cdots\cdots \\ \underset{\sim}{0} & \underset{\sim}{\omega}_{32} & \underset{\sim}{0} & \underset{\sim}{\omega}_{34} & \cdots\cdots \\ \vdots & \vdots & \vdots & \vdots & \end{bmatrix}$

$$\underset{\sim}{S} = \begin{bmatrix} \underset{\sim}{0} & \underset{\sim}{0} & \cdots & \underset{\sim}{0} \\ \vdots & & & \vdots \\ \underset{\sim}{0} & \cdots\cdots\cdots & \underset{\sim}{\gamma} \end{bmatrix} \quad \text{and} \quad \underset{\sim}{F}(t) = \begin{bmatrix} \underset{\sim}{0} \\ \vdots \\ \underset{\sim}{f}(t) \end{bmatrix}$$

The friction matrix is related to the fluctuating force through the fluctuation dissipation theorems.

$$< \underset{\sim}{F}(t)\underset{\sim}{F}^{T}(s) > = 2\underset{\sim}{\gamma}\delta(t-s)$$

By using the Kivelson/Ogan theory we can regard the second-order Mori truncation as a suitable way to take into account memory effects. When we make a second-order Mori truncation and the matrices $\underset{\sim}{\Delta}_1^2$ and $\underset{\sim}{\gamma}$ are assumed to be diagonal in the $\pi$ basis set, the Markhovian approximation results in:

$$\frac{d}{dt}\underset{\sim}{A} = -\underset{\sim}{\Delta}_1^2\underset{\sim}{\gamma}^{-1}\underset{\sim}{A}$$

where now $\underset{\sim}{A} = (|\pi_1>, |\pi_2>, \ldots |\pi_i>)$ and $|\pi_i>$ is a generic eigenvector of the diffusion operator $\Gamma$. So we need $E_{\pi} = <\pi|\Delta_1^2\gamma^{-1}|\pi>$. If we assume that $\Delta_1^2$ and $\gamma$ are diagonal matrices of the $\pi$ basis set we have:

$$(\Delta_1^2)_{\pi} = \gamma_{\pi}E_{\pi}$$

The Mori truncation at the second-order provides the following set of differential equations:

$$\frac{d}{dt} \begin{pmatrix} \pi_i \\ \pi_i{}' \end{pmatrix} = \begin{pmatrix} 0 & \Delta_i \\ -\Delta_i & -\gamma_i \end{pmatrix} \begin{pmatrix} \pi_i \\ \pi_i{}' \end{pmatrix} \quad i = 1, \ldots, \infty$$

This is equivalent to a damped-oscillator, or M-diffusion type of formalism. We need the truncation at third order. Since the Wigner rotation matrix elements are a complete basis set any function $f(\underset{\sim}{\Omega})$ may be expressed in the following form:

$$f(\underset{\sim}{\Omega}) = \sum_{ij} c_{ij} |\alpha_i(\underset{\sim}{\Omega})> <\alpha_j(\underset{\sim}{\Omega})|$$

If the functions $\pi_i$ are, in turn, linear combinations of the $\alpha_i$'s spanning the whole vector space we can also write:

$$f(\underset{\sim}{\Omega},t) = \sum_{ij} b_{ij} |\pi_i(\underset{\sim}{\Omega},t)> <\pi_j(\underset{\sim}{\Omega})|$$

$$f(\underset{\sim}{\Omega}) = \sum_{ij} b_{ij} |\pi_i(\underset{\sim}{\Omega})> <\pi_j(\underset{\sim}{\Omega})|$$

These formulae allow us to obtain the expansion of any correlation function involving Eulerian angles. In fact:

$$< f(\underset{\sim}{\Omega}) f(\underset{\sim}{\Omega},t) > = <\pi_1 | f(\underset{\sim}{\Omega}) f(\underset{\sim}{\Omega},t) | \pi_1 >$$

$$= \sum_{j\mu\mu'} (b_{ij})^2 c_j^{(\mu)*} c_j^{(\mu')} e^{-\epsilon_j(\mu')t}$$

It is evident that analogous formulae will be obtained when the damped oscillator (or M and J diffusion models) are replaced by the "itinerant oscillator" which is the second order Mori truncation, in this case applied direct to orientation.

Although the basic structure of the theory is well-defined, it will not be possible in general to produce rigorous expressions for the spectra of diffusing asymmetric tops because of the difficulty of over-parameterisation already mentioned. The above equations have to be modelled in some way. Again, therefore, we are led to the conclusion that a computer simulation of the molecular and hydrodynamic properties thought to be contributing to the Rayleigh/Brillouin lineshape is the better way of proceeding.

V.    SURVEY OF PUBLISHED DATA

(i)   Methylene Chloride ($CH_2Cl_2$). (Note: references in this section refer to those given on pages 48-57).

A literature search of the relevant material on $CH_2Cl_2$ (Freon 30) has revealed the following conclusions.

(i)    A great deal of infrared, acoustic and N.M.R. work has been carried out. The amount of Raman work published is smaller.

(ii)    Thermodynamics studies are fairly well covered, but there is a lack of virial coefficient data. In particular, there are no second dielectric virial coefficients in the literature.

(iii)  There is a fairly large amount of work on intermolecular potentials, but it is difficult to say whether this will be sufficient to build a reliable potential for the simulations until these specialists begin their investigations during the course of the project.

(iv)   There is a sparse amount of modern spectral work such as light scattering but the zero-THz region spectra have been extensively analysed.

(v)    There is one available Kerr effect study. The polarisability of the molecule is known, but the anisotropy of polarisability less accurately so. However, there are some estimates of the effective charges on each atom, which could be used to calculate a quadrupole moment.

As pointed out by Brier and Perry (R8) it is clear that, despite the apparent proliferation of papers on this molecule, there has been no coordination of measurements with the available techniques - which ought to have given information on different aspects of the molecular dynamics of $CH_2Cl_2$ in the liquid phase and in solution. Zero-THz work has brought out some interesting aspects of $CH_2Cl_2$ behaviour in ultra-viscous or vitreous environments, hardly touched for $CH_2Cl_2$ by other techniques.

There have been no spectroscopic studies on $CH_2Cl_2$ liquid under kbar of applied pressure. There have, however, been thermodynamic properties reported between 4 kbar (mpt = $-46^{\circ}C$) and 30 kbar (mpt = $157^{\circ}C$), and these data have influenced the choice of conditions set out in section VI. Simulations of $CH_2Cl_2$ at kbar pressures are possible, although to simulate $CH_2Cl_2$ in an ultra-viscous or vitreous environment such as decalin or toluene/pyridine is probably outside present day capability, especially as the molecular dynamical evolution is spread over twelve decades of frequency via the $\alpha$, $\beta$ and $\gamma$ dielectric loss peaks. Nevertheless, this does not preclude spectroscopic study by near infrared, Raman, etc., and especially acoustic, N.M.R. and viscoelastic methods.

(a)  Infrared Spectroscopy

As we have already pointed out at length the key papers on this topic are those of van Woerkom et al. (39,47), which revealed the strong interaction of rotation and vibration. From these papers it is clear that it is not, in general, possible to factorise the rotovibrational correlation function into its rotational and vibrational components.

(b) Raman Spectroscopy

Boldeskul et al. (66) have measured the $A_1$ type Raman bands of the liquid (both $I_{VV}$ and $I_{VH}$ intensities) during excitation by a He/Ne laser. Contours of the anisotropic and isotropic Raman band components were obtained. The correlation functions of vibrational and orientational relaxation for the $A_1$ vibrational bands were calculated but there is no indication whether the vibration-rotation coupling was factorised or not.

Baranov et al. (67) have recorded infrared and Raman spectra over a wide temperature interval in the solid, liquid and gaseous states. The predominant role of dipole-dipole interaction in the condensed phase was confirmed by the magnitude of the frequency shifts in the gas to liquid phase transition. At temperatures much greater than the melting point, the line broadening due to Brownian motion showed an 'Arhenius' temperature behaviour. The infrared and Raman work pursued during the course of the project will be of interest to establish the role of vibration-rotation coupling over the complete liquid range.

The effect of the 'internal' field on Raman scattering cross-sections (i.e. the increasing amplitude of incident Raman scattered radiation brought about by the dielectric nature of the liquid) studied by Nestor et al. (65) using liquid and gas phase spectra. The cross-section for each Raman band is greater for molecules in the liquid state due to the internal field effect.

(c) Rayleigh and Brillouin Scattering and Ultra-Sound Relaxation Measurements

Van Konynenburg and Steele (78) have reported a study of $CH_2Cl_2$ by depolarised light scattering at one temperature. Collision induced contributions were shown to be important at short times. The long time behaviour of the correlation functions was compared with several models. Infrared vibration-rotation data were used to supplement the Rayleigh wing data, the former being corrected for refractive index variation, isotope splitting and hot bands. Stokes and anti-Stokes intensities were measured out to about $100 \text{ cm}^{-1}$ from the band centre.

Brillouin scattering measurements of vibrational relaxation have been made by Caloin and Candau (99) as a function of temperature and scattering angle ($90^{\circ}$ and back scattering). Experimental spectra were compared with the calculated ones by assuming a single or double relaxation of the vibrational specific heat. The observed vibrational relaxation was interpreted by assuming that energy transfer was produced in bimolecular collisions. Such an interpretation is not based on molecular theory but this is now possible by simulation of such correlation functions of the off-diagonal elements of the molecular stress tensor. The paper by Caloin and Candau covers a range of temperature, and it would be interesting to repeat the Brillouin scattering measurements at the same conditions as the hyper and ultrasonic experiments planned for the project as a whole. There are some fifty papers available (see bibliography) on acoustic studies in liquid $CH_2Cl_2$. A laser-stimulated Brillouin scattering experiment at 4416 Å and 4765 Å

was carried out by Gustafsson et al. (100). The Brillouin scattering at 90° was obtained with an Ar ion laser, a He-Cd laser and a pressure scanned Fabry-Perot spectrometer. The hypersonic velocities of the thermal wave between 4.8 GHz and 7.2 GHz were determined from the frequency shift between the Stokes and anti-Stokes lines. No hypersound dispersion was observed. The recent papers on sound dispersion in liquid $CH_2Cl_2$ can be briefly summarised as follows.

Ultra and hyperacoustic measurements on $CH_2Cl_2$ in the region 0.2 GHz to 3 GHz were carried out by Davidovich et al (98). Scattering of the absorption coefficient of sound is observed in $CH_2Cl_2$ in this region. Acoustic dispersion is produced by vibrational relaxation. Takagi et al. (101) have recently observed considerable velocity dispersion in the range 60 to 700 MHz at 293 K. The hypersonic velocity in $CH_2Cl_2$ was measured by Brillouin scattering. There was no dispersion between the frequency region 700 MHz and 1 GHz. The volume viscosity was found to be much greater than three times the shear viscosity.

(d) <u>N.M.R. relaxation</u>

There has been a great deal of work on N.M.R. relaxations of various kinds in liquid $CH_2Cl_2$ some of which covers a broad temperature range. But, as Brier and Perry (R8) point out, the results between different groups are not directly comparable in the majority of instances.

Recently Sandhu (128) has measured the spin-lattice relaxation time $(T_1)$ of protons and deuterons in $O_2$-free samples of $CH_2Cl_2/CD_2Cl_2$ and $CD_2Cl_2$ respectively over the temperature range from the melting point to the boiling point at 1 bar. The spin-rotation interaction makes no contribution and the rotational and translational contribution are 70% and 30% (respectively) of the total relaxation rate. It is clear that in N.M.R. spectroscopy the broadest range of temperature and pressure is relevant in the attempt to extract maximum molecular dynamical information. The simulation back-up in the project will no doubt help to clarify the modelling problems which the N.M.R. spectroscopists encounter. These are typified in Sandhu's work, because apparently he finds no easy route to interpretation of the overall data and the rotational correlation times disagree with the values predicted by the various models. N.M.R. studies up to kbar of pressure will, no doubt, help to define these problems even more closely.

(e) <u>Far Infrared/Microwave (or Zero-THz) Spectroscopy</u>

Towards the end of the 1970's some papers have been published (136-140) which contain attempts at extending low frequency dielectric work to far infrared frequencies, and to interpret the complete bandshape. Using this method provides any modelling technique with a difficult challenge, because the spectroscopic information is available as dielectric loss, $\varepsilon''(\omega)$ and power absorption coefficient $\alpha(\omega)$ (neper $cm^{-1}$). The analytical difficulties are fully exposed only when the spectroscopic work is extended to supercooled and vitreous solutions. For example, dielectric losses of a glassy solution of $CH_2Cl_2$ in decalin were determined (136)

at kHz and THz frequencies between 107 and 148 K. The low frequency part of the loss curve exhibits a peak which shifts upwards by about two decades with a 4 K increase in temperature, and at the glass to liquid transition temperature moves very quickly out of the audio-frequency range towards the microwave. The far infrared peak in the loss curve is displaced by 30 $cm^{-1}$ to 90 $cm^{-1}$ in the glass as compared with 60 $cm^{-1}$ in the liquid solution (at 293 K). It is argued that, in addition to the well-documented primary and secondary ($\alpha$ and $\beta$) losses in glasses and polymers, there exists in general a tertiary ($\gamma$) process at far infrared frequencies. This is part of the dynamical evolution in a wide range of disordered solids. This was subsequently followed up by a series of other papers intended to characterise the ($\alpha$, $\beta$, $\gamma$) loss triad over the twelve decades of frequency experimentally available. These show that the molecular dynamical evolution in $CH_2Cl_2$ under certain conditions is much more complicated than hitherto envisaged, because significant dynamical features are discernible on ps time scales (the far infrared) which evolve gradually into those occuring on immensely longer time-scales (seconds and longer). The whole process ought, in principle, to be described by the orientational correlation function of the resultant dipole in the sample. This would require a molecular dynamics simulation (on present-day computers) lasting approximately $10^9$ years! It is possible, however, to simulate the $\gamma$ part of the overall loss, which appears in the far infrared and is measured as a power absorption coefficient, $\alpha(\omega)$. This in itself would be a major achievement of the molecular dynamics simulators.

(f)  Incoherent, inelastic neutron scattering

As Brier and Perry (R8) point out in their review, there has been no attempt to derive or deduce detailed models for the translational or rotational dynamics of the totally asymmetric molecular dynamics associated with this molecule. The neutron scattering data reported in this paper were obtained on a time-flight instrument (IN5) at the high flux reactor of ILL, Grenoble. Restrictions on the maximum rotor speeds meant that the full design resolution capability of this spectrometer was not available. As a compromise between energy resolution and momentum transfer requirements, the experiments were performed with an incident neutron energy of $E_o$ = 1.236 meV and an energy resolution of 4 per cent. The scattering angles were $14^o$ to $90^o$. There is scope for adding to all these variables in a new series of experiments. The experimental results were presented as efficiency corrected neutron counts per second (scattered neutron flux) for the given sample dimensions and orientation, normalised to unit incident flux. It is emphasised that multiple scattering is a severe practical difficulty with neutron scattering from liquids.

To describe the conclusions of the work we can do no better than quote Brier and Perry. "The second half of the paper demonstrates the considerable difficulties of liquid dynamics investigation. Firstly, there is the problem of assembling

reliable dynamical data for a given molecular liquid. In this connection it is
vital to be aware of the limitations and assumptions involved in both the measure-
ment itself and the subsequent analysis to yield an a.c.f. or a correlation time.
Secondly, there is the problem as to whether the available data are sufficiently
varied and accurate to make a critical test of any model of the liquid dynamics.
Here, the importance of adjusting reported measurements to common conditions,
particularly temperature, and retaining realistic uncertainty limits, cannot
be stressed too strongly. Thirdly, there is the general problem of the lack
of theoretical models, particularly for the case of non-isotropic angular motion."...
..."We conclude that, for different reasons, neither the infrared nor the neutron
scattering measurements provide reliable first order (1 = 1) data for this molecule.
The available n.m.r. (1 = 2) data have required particularly careful consideration
and some adjustments and corrections of the published data have been proposed".
And again: "Our overall conclusion is that, despite the numerous studies on $CH_2Cl_2$,
no clear picture of the reorientational dynamics has yet emerged, even of a semi-
quantitative nature. By no means can this be totally ascribed to the low symmetry
of the $CH_2Cl_2$ molecule. Admittedly, with a true symmetric top molecule there is
the considerable advantage of knowing "a priori" that the reorientational motion
about two of the principal axes is equivalent. Nevertheless, investigations of
these systems are not without similar serious difficulties. The recent evaluation
by Steele (R1) of the data for $CH_3I$, a liquid which has been extensively studied
by many techniques, contains several cautionary statements concerning the presence
of some serious unresolved problems in the interpretation of the correlation time
data and that 'the correlation time data should be regarded as subject to revision
when better methods of estimating non-rotational spectral intensities have been
developed for non-spherical molecules'. Already since that review, it has been
shown that correlated motions most probably do contribute to the depolarised
Rayleigh scattering measurements, contrary to the earlier evidence".

It seems likely that the availability of new molecular dynamics algorithms
will ease the problem of interpretation encountered previously in neutron
scattering.

(g) Vibrational Population Lifetimes

There is one paper by Laubereau et al. (72) on C-H stretching modes excited
by picosecond IR pulses. The generated excess population is then monitored by
anti-Stokes scattering of subsequent ultrashort probe pulses. The observed time
constants vary between 1 and 2 ps depending on the individual molecule and
surroundings. Theoretical calculations show that rotational coupling, Fermi
resonance, Coriolis coupling and resonance energy transfer can all strongly affect
vibrational population lifetimes. Experimental data were reported on five
molecules. The results for $CH_2Cl_2$ show that initially the anti-Stokes scattering
signal decays rapidly, but that, at longer times, the decay rate is slower with a

decay time of 40 ± 10 ps. The data suggest the same result for different experimental conditions. With infrared radiation of 2985 $cm^{-1}$ and 3050 $cm^{-1}$ both the $\nu_1$ and $\nu_4$ CH stretching modes were excited using pulses of bandwidth $\Delta\bar{\nu} = 30$ $cm^{-1}$. The initial rapid decay of the measured signal is explained by fast transfer between the neighbouring C-H stretching modes, and the longer relaxation times by transition to overtone and combination levels of the molecule.

(h)  Pulsed High Field Dielectrics and Electro Optics.

These techniques are still in the development stage but are potentially very revealing. We include among them the first attempts (by Prof. Leibler and her collaborators in Warsaw) to define the extent of the Faraday and Kerr effects in the far infrared using carcinotron radiation and impulse methods. The results would be interpreted with a theory of non-linear response for the rise and decay transients. It is expected that, in analogy with such work on liquid crystals (or mesophases), the application of electric and magnetic fields to liquids monitored by far infrared spectroscopy will result in information on collective effects rather than on individual molecular motion.

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This is a compilation of papers on the topics of interest to the scheme.  It
is not exhaustive but fairly comprehensive up to the end of 1979.

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(ii)  Methyl Fluoride

(a)  Infrared and Raman Spectroscopy

Blanchard et al. (3) have recently described the infrared and Raman spectra of solid methyl fluoride. The crystal structure is centrosymmetric, with four molecules in the unit cell. Infrared polar tensors and effective charges have been evaluated by Newton and Person (2). The rotation-vibration constants of $CH_3F$ have been evaluated by Norris et al. (5) from the $\nu_3$ band. Rotational constants are also given by Graner (7).

(b)  Far-Infrared and Dielectric Spectroscopy

The work of Gerschel et al. (8,10,11) on the liquid in this frequency region forms the basis of the project conditions for $CH_3F$ and is described briefly in this section. The relative permittivity and far infrared absorption were used to evaluate angular correlations in $CH_3F$, avoiding the approximations inherent in dielectric theory. Static permittivities were evaluated in terms of the Kirkwood factor $g^{(1)}$. The data were compared with a derivation using Onsager's formula and Wertheim's mean spherical model solution. These results are supplemented to some extent by Tremaine and Robinson (14), who measured the static permittivity $\epsilon_o$ in the liquid from the melting point to the boiling point. The deviation of the dielectric constants of the polar fluoromethanes from the values predicted from the Onsager equation cannot be entirely due to non-spherical shapes. Gerschel et al. (8,10,11) have also measured microwave relaxation times and far infrared spectra of $CH_3F$ were determined over the complete liquid range beneath the critical point. On gradual approach of the dense gas-like situation from the expanded liquid, the far infrared and microwave characteristic times converge. The occurrence of specific alignment effects caused local enhancement of dipole moments, as indicated by the refractive index of $CH_3F$ along the bands, giving increased integrated intensities.

Bossis and Quentrec (9) have used a hierarchy of memory functions to test these data. Agreement is good along the co-existence line to the triple point. At low temperatures there is evidence of coupling of local orientational order to hydrodynamic modes. Evans et al. (13) used the Langevin equation for the symmetric top to describe the far infrared/dielectric data of Gerschel et al. An inertia corrected Langevin equation used with no further refinement fails qualitatively to explain the short time details of the reorientational process.

(c)  N.M.R. Relaxation Spectroscopy

Trappeniers et al. (21) have recently described the critical anomaly in the proton chemical shift of methyl fluoride. The density and temperature dependence of the proton chemical shift in $CH_3F$ was measured between $40^{\circ}C$ and $60^{\circ}C$ up to 1000 bar. The shielding constant exhibits a cusp-like finite anomaly in the gas/liquid critical region.

Again there has been a great deal of study of the gaseous state by N.M.R. spectroscopy. Amstrong and Courtney (17) have measured the spin-lattice relaxation times at room temperature from 0.03 to 10 amagat. Values of the effective spin-rotation constant and cross-section for molecular reorientation were derived. Pausak and Waugh (18) have determined the density dependence of the proton spin-rotation relaxation time while Miyajima and Nishimoto (19) have measured the $^{13}C$ N.M.R. spectrum. Some N.M.R. work has also been carried out in liquid crystal solvents which partially order the molecule. Burnell et al. (22) find that $CH_3F$ is rapidly exchanging between at least two sites which have slightly different geometries and orientational parameters of different sign.

It is clear that not much data is available on N.M.R. relaxation in liquid $CH_3F$. Experiments under the conditions used by Gerschel et al. (Section VI) would be interesting and revealing.

## (d)  Brillouin and Ultra-Sound Relaxation

There is little information available about these in $CH_3F$ and work completed during the course of the project would be original.

## (e)  Thermal Neutron Scattering

The work carried out by Malm et al. (23) has been summarised in a more recent publication (24). In this paper a small amount of data is presented for the methyl halides, including $CH_3F$ and $CH_3I$. Time of flight spectra were measured at $22^{o}C$ ($CH_3F$) and $50^{o}C$ ($CH_3I$), and compared with the Gaussian formalism of Agarwal and Yip (25). This means, of course, that only the gas phase spectrum is given for $CH_3F$ and for $CH_3I$. High purity samples were used and contained in a thin walled (0.075 cm) cylindrical aluminium holder six inches in diameter. The scattering experiments were carried out using a cold neutron time of flight spectrometer in which the full cold spectrum transmitted by a refrigerated beryllium filter was incident on the sample and the analysis of the scattered beam was accomplished using a pulse modulator. All of the data were taken at a scattering angle of $27^{o}$ using a chopper speed of 5000 r.p.m. Under these conditions the time resolution of the instrument varies from 1% at 4 Å to 2.5% at 1 Å. This corresponds to an energy resolution of 2% at 5 meV to 5% at 85 meV. However these values must be modified due to the energy spread in the incident beam. In practice this was taken into account by folding all calculated cross sections with the measured incident spectrum before comparing with experiment. The spectra were corrected for background, detector efficiency, air and aluminium absorption in the scattered beam, and modulator transmission. The authors state that the inclusion of multiple scattering corrections, which tend to increase inelastic scattering while decreasing elastic contributions would further improve the agreement. Practically the only conclusion from this work is that the Agarwal/Yip formalism describes reasonably well the observed differential scattering cross-section from $CH_3F$ gas (or $CH_3I$ vapour at $50^{o}C$). A non-Gaussian correction gives only slight improvement.

(f)  Kerr Effect and Polarisability Anisotropy

Bogard et al. (27) have recently measured the Rayleigh scattering depolarisation ratios and molecular polarisability anisotropy for the gas at 488, 514.5 and 632.8 nm. The hyper-polarisability term in $CH_3F$ is significantly large. An atom-dipole interaction study of the molecular second hyper-polarisability has been carried out by Sundberg (31). The theoretical and experimental second hyper-polarisabilities agree to within 15%. van Ditzhuysen et al. (3) have considered gradients in the stream velocity of a gas consisting of optically anisotropic molecules which give rise to an alignment of rotational angular momenta, observable as a birefringence. Comparison was made with data from light scattering and the Senftlebeen-Beenakker effect. It is clear that measurements on the dynamical Kerr effect will be revealing at all frequencies, especially when carried out with carcinotron sources in the far infrared. If $CH_3F$ were to be dissolved in a viscous or glassy environment it is probably that the relaxational features observable in electric permittivity experiments on the $\alpha$ and $\beta$ processes could also be observable by birefringence. The far infrared Faraday effect at the present conditions would also prove revealing as regards collective behaviour, especially if the order of magnitude of the increment in the power absorption coefficient is larger than expected on the basis of classical theory. There have been no measurements to date of non-linear (high-field) dielectric increments or transients.

(g)  Thermodynamics

The choice of $CH_3F$ as a molecule for study is supported by the considerable amount of  information available about the intermolecular potential function. The dielectric and pressure second virial coefficients were reported by Copeland and Cole (34) from 273 K to 417 K. These data were reproduced to 5% or better with a model pair potential that incorporated:

(i)  a Lennard-Jones (6,12) central-force potential from viscosity data of Casparian and Cole (42).

(ii) electrodynamic interactions described in terms of the permanent dipole moment ($\mu$), quadrupole moment (Q) and average polarisability ($\alpha$) and effects due to the anisotropy of repulsive forces in terms of the Buckingham/Pople shape factor (D). Optimum values for $CH_3F$ are $\epsilon/k = 199$ K; $\sigma = 3.80$ Å; $\mu = 1.85$ D; $\alpha = 2.97 \times 10^{-24}$ $cm^3$; $Q = 2.3 \times 10^{-26}$ e.s.u.; $D = 0.25$. These parameters are useful for any future attempt to produce a satisfactory potential for simulation purposes. Singh and Singh (43) have studied second and third virial coefficients using a preaveraged pair potential model which includes a dipole repulsion term. The dipole dispersion and repulsion 3 body non-additive interactions were taken into account in evaluating the third virial coefficient. A large number of sets of force parameters were found and

and all reproduce the second virial data with equal consistency and accuracy. Using these parameters the third virial coefficient was calculated. The values are different for different sets of parameters. A comparison of the experimental and calculated values of the third virial therefore leads to a unique set of force parameters for an assumed potential model. For $CH_3F$ a set of force parameters was found which gives good agreement between theory and experiment. Transport properties such as viscosity and thermal conductivity are also well known for $CH_3F$. For example, Casparian and Cole (42) have described a method in which capillary flow is measured by the decay of the capacitance difference of gases in two reservoirs connected to the ends of the capillary. The viscosity is determined from the time constant in the temperature range $20^{\circ}C$ to $150^{\circ}C$. The parameters for the Lennard-Jones (6,12) intermolecular potential were derived by using the theory of Monchik and Mason (44). These parameters give a much better description of the central force than those from pressure virial coefficients.

There is therefore plenty of evidence for constructing reliable intermolecular potential in simulations of $CH_3F$. Work is already in progress in this field by Finney and co-workers (unpublished) using the unique multi-body algorithm developed initially for water. Non-additive effects are clearly important in the results already obtained by this group, and dynamical work is planned jointly with the Aberystwyth group. There is scope also for attempting to simulate subtle effects of external fields on transport properties. In conclusion:

(i) There is little dynamical work available for $CH_3F$ (liquid) as opposed to $CH_3F$ (gas). The only work of any note in the dielectrics/far infrared field, for example, is that of Gerschel and co-workers (8) on which the project conditions are based.

(ii) There are no literature data of any kind on kbar pressure work on $CH_3F$. It would therefore be interesting for one or two laboratories to measure the solidification temperatures of $CH_3F$ (liquid) at a set of kbar pressures, which for convenience should be those for $CH_2Cl_2$. 5, 10, 15, 20, 25, 30 kbar (see section VI). The $CH_3F$ liquid can, of course, be simulated under kbar conditions with the solidification points predicted in advance. It would be interesting to see (at a future date) how well these agree with the measured solidification points.

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(iii)  Methyl Iodide

Reviewers have indicated (R1-R4), and a literature survey confirms that methyl
iodide is one of the most studied liquids (a list of key papers is given here).
Nevertheless, there are many remaining inconsistencies and gaps in our knowledge
of it's dynamic properties.

(a)  Infrared and Raman Spectroscopy

There have been about 50 papers devoted to the determination of reorientational
and vibrational correlation times.  Griffiths (R2), Clarke (R3) and Yarwood and
Arndt (R4) have given the most up-to-date collection of data.  Both temperature
and pressure variations have been made (the latter only for Raman measurements on
the liquids).  Very little work has been done on rotation in dilute solutions
although the vibrational parts of the three $A_1$ bands have been subjected to a
thorough series of dilution experiments (R4), Campbell et al. (54) have clearly
shown the importance of studies at constant density (as well as constant pressure)
especially in attempts to elucidate the nature of the effective intermolecular
potentials.  For the $\nu_3$ ($A_1$) vibration they show that the vibrational relaxation
rate increases as the density is increased and decreases when the temperature is
increased at constant pressure.  These authors have used a model based on energy
relaxation in a binary collision to interpret these results but it has been pointed
out (R4) that such a model is inconsistent with measurements in $CCl_4$ and $CS_2$.  This
demonstrates that dilution studies are also essential.  The rotational diffusion
constant $D_\perp$ (for 'tumbling' motion of the $C_3$ axis) decreases as the pressure
increases (as expected ) but the $D_{//}$ values (obtained using combined Raman and
$CD_3I$ n.m.r. data) show the opposite dependence.  The inconsistency is explained
by invoking the idea of an electric field gradient (at the D atom) which does not
lie along the C-D bond.  This clearly needs reexamination, especially in terms of
new analytical models for 'spinning' motion of a symmetric top molecule (which is
certainly not diffusional).  Yet more doubt has been cast upon the consistency of
data from different laboratories by the recent publication (79) of $\tau_c$ data for
$\nu_3$ which show a radically different temperature dependence from those given by
Döge et al. (64).  At least part of this discrepancy almost certainly arises from
problems with 2nd moment determinations (R2).  As far as rotational motion is
concerned, a wide range of correlation times has been measured (R1-R3).  For
example, at about room temperature (290-300K) and 1 atm pressure , values given
(for $A_1$ bands) lie between 0.75 and 1.6 psec for $\tau_{2R}$ (Raman) and between 2.3-
3.2 psec for $\tau_{1R}$ (Infrared).  The $\tau$ values for $CD_3I$ are about 10% longer.  These
figures serve to emphasise the problems associated with the presence of hot bands,
refractive index variations, possible rotation/vibration interaction (making
$\tau_{2R}$ mode dependent), and the often erroneous procedure of assuming that $\tau_{vib}^{i.so} =
\tau_{vib}^{IR}$.  For E bands the situation is far worse since the bands are generally much
broader (giving greater spectral overlap) and are perturbed by 1st order Coriolis

coupling. Even more important is the probability that, in the liquid phase, contributions to the 'distinct' part of the correlation function are important for some, but maybe not all, vibrations. Although the $\tau_{2R}/\tau_{1R}$ ratio may be deduced to be $\sim 3$ corresponding to small step rotational diffusion (R6) it is obvious that this model is untenable when attempting to interpret the far infrared data (below). Some interesting data on Raman overtone bands have been published (69) but this promising approach had not been followed up.

(b)  Far Infrared/Microwave Spectroscopy

Very little work has been published (18,58,75,76,80) and even that has not been interpreted in any detail. The spectrum shows the usual intense 'Poley-Hill' absorption at a frequency ($\equiv$ 40-60 $cm^{-1}$) much higher than those expected for rotation of gas phase molecules. This immediately invalidates (R6) any interpretation based on the (Debye) rotational diffusion model or on the collision interupted free rotation models of Gordon and McClung (R7) (the so called J and M diffusion models). The data have been used to calculate effective dipole moments (76) in solution and to derive reorientational correlation times ($\tau_{FIR}$) between 3.1 and 3.65 ps, while a value of 4.65 ps is reported to have been obtained from dielectric measurements. It has also been shown (80) that how accurate rotational 2nd moments can be obtained in dilute solution in $CS_2$. In all cases the collision induced part of the spectrum (expected to be quite high for this molecule in view of a highly polarisable C-I bond) has been ignored with subsequent errors in the reported dynamic parameters.

(c)  Depolarised Rayleigh Scattering

There have been a number of studies, mainly aimed at studying the effects of multiparticle correlations on the molecular dynamics. Dill et al. (39) have reported reduced relaxation times, $< \tau_2 >$ between 1 bar and 2.5 kbar. This parameter doubles over the investigated pressure range, showing that the density fluctuations get slower at higher densities. Cheung et al. (33) have combined Raman and depolarised Rayleigh data (obtained at constant viscosity in isopentane/$CCl_4$ mixtures) to measure $\tau_{RAY}/\tau_{sp}$ ratios and extract the static correlation factor $g^{(2)}$ (R5). The values lie between 1 and 1.7 and show clearly the effects of cooperative motions affecting the Rayleigh spectra. Further evidence of such effects is provided by Patterson and Griffiths who studied the Rayleigh spectra over the whole liquid range between -23 and +41$^{\circ}$C.

Finally, Evans has analysed the data of Dill et al. (39) in terms of the memory function approach of Mori and concluded that the intermolecular torque dependent parameter $K_1(o)$ increases with increasing density (i.e. with increasing pressure at 296 K) and the correlation time $1/\gamma$ gets shorter. The fitted parameters reproduce the observed correlation function reasonably well but not perfectly, indicating the need for improved experimental data and/or more a sophisticated model.

(d) <u>Nuclear Magnetic Resonance Spectroscopy</u>

There have been a number of papers published on the determination of $(T_1)$ spin lattice relaxation times for $^1H$, $^2H$ and $^{13}C$ nuclei. If the various processes controlling to these nuclear spin relaxation times can be separated then rotational diffusion coefficients (or rotational relaxation times) can be extracted from the intramolecular, dipole-dipole contribution. This procedure has been fully described for $CH_3I$ by Steele (R1) and by Heatley (98). Both authors emphasise that the relaxation is controlled mainly by spin rotation interaction for both $^1H$ and $^{13}C$ nuclei (this being thought (91) due to $-CH_3$ group rotation). Separation of inter- and intra-molecular contributions is usually made by dilution in a non-magnetic solvent (e.g. $CH_3I$ in $CD_3I$) while spin rotation and dipole-dipole effects may be separated by using variable pressure (92). Nevertheless the extraction of $(T_1^{dd})_{intra}$ is usually difficult and subject to considerable errors. The problems are fewer with $^2H$ relaxation where the $T_1$ values are almost entirely controlled by the quadrupole interaction mechanism. Gillen et al. (91) have used $^2H$ measurements to derive values for the two rotational diffusion coefficients (having assumed a rotational diffusion model to calculate $D_\perp$ from $\tau_{FIR}$ since there is only one quadrupolar nucleus). The ratio $D_\perp/D_{//}$ is about 10 as expected for a highly anisotropic rotor. Heatley (98) gets a value of 12 using $^1H$ and $^{13}C$ relaxation measurements combined with the $^2H$ data. The effective rotational correlation times $\tau_{eff}$ ($= a \tau_{20} + b \tau_{21} + c \tau_{22}$) (from the data of Gillen et al.) is $1.8 \pm 0.5$ ps (as quoted by Steele (R1)). As indicated above, the values of $\tau_{22}$ and $\tau_{21}$ are approximately 10 times smaller than $\tau_{20}$. Raman values of $\tau_{20}$ lie in the 1.5 psec region (R1-R3). Since the values of $\tau_{10}$ (from far infrared data) are about 3.5 psec (50) it is unlikely that the rotational diffusion model ($\tau_{10}/\tau_{20} = 3$) is valid even for 'tumbling' motion. It is clearly shown by Gillen et al. (91) that 'inertial' effects are even more important for the rapid and almost 'free' rotation of the $-CH_3$ group. Sandhu (97) has measured the coefficient of self diffusion in $O_2$-free samples of liquid $CH_3I$ using a pulsed n.m.r. technique. The results show that $D_t$ is logarithmic in $1/T$ and the data agree well with a Stokes/Einstein relation, modified to include a microviscosity factor for translational motion.

(e) <u>Neutron and X-ray Scattering</u>

Very few neutron scattering measurements have been reported. We know only of those reported by Janik et al. (101), Fisher (102) and Malm (103).

Fisher measured the neutron scattering cross section (in barn/proton) for $CH_3I$. This increases with increasing neutron wavelength in the range 4 to 17 Å. The cross section for $CH_3I$ at 17 Å is 254 barn/proton and the slope (in barn/Å) of $\sigma$ vs neutron wavelength is 13.9. The latter is related to rotational barriers and decreases smoothly with increase of the n.m.r. rotational relaxation times. The neutron method was said to have some advantages for the separation of internal molecular rotations from reorientations of the whole molecule.

Neutron inelastic scattering method was used by Janik et al. (101) to study the lattice molecular dynamics of solid and liquid $CH_3I$. The spectrum obtained for solid $CH_3I$ was caused by lattice vibrations (wave no. region below $\sim 500$ cm$^{-1}$). Peaks obtained in the intermediate region were assigned to higher harmonics of the torsional vibrations. The spectrum obtained for liquid $CH_3I$ was regarded as proof of the freedom of translation motions in the liquid phase. Two different approaches to the fitting of a physical model to the liquid $CH_3I$ neutron spectra were considered by Malm (103). These involved (a) a series of expansion in terms of classical correlation functions and (b) a gaussian approximation for the intermediate scattering function. In both models translational-rotational coupling was ignored.

(f) Summary

Although methyl iodide has been extensively studied by a wide range of techniques, a large number of discrepancies and ambiguities are manifest in the literature. As pointed out above, there is wide disagreement (R1-R3) between values obtained for the same correlation times in different laboratories even at atmospheric pressure and room temperature. If one then goes on to consider what information can be obtained about the mechanism of molecular relaxation and the nature of the effective intermolecular forces then the situation is even worse. Small step angular diffusion is the simplest, and still the most commonly used, model to describe molecular rotation, despite the fact that the ratio of $\ell=1$ amd $\ell=2$ correlation times varies drastically from the value of 3 required for this model (a ratio of 2 seems more likely on the basis of presently available data). Furthermore, the vibrational relaxation data may often be interpreted equally well using several different types of molecular interaction. With the expection of $\nu_2$, where it is known (64) that vibrational dephasing is controlled almost exclusively by resonant energy transfer due to transition dipole-transition dipole interactions, it is certain that more than one interaction process is effective in causing relaxation. For most vibrations therefore the situation is still unclear. This highly unsatisfactory state of affairs will not be resolved without coordinated experiments and some form of simulation back-up. In particular, a systematic estimation of the effects of induced absorption is required. The best way to do this is to carry out a series of measurements in the zero-THz region along the gas-liquid coexistence curve and into the super-critical region. These data could then be compared with those on gaseous $CH_3I$ pressurised to liquid-like densities (in the same way as that attempted by Baise for $N_2O$ (G98)). Attempts should be made to simulate the induced absorption by molecular dynamics. Thermodynamic data (2nd virial coefficients, for example) and work on intermolecular potentials is by no means as extensive as for the other two molecules and some work in these areas will definitely be needed.

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## VI. LIST OF PROPERTIES AND PRESET CONDITIONS

At the very basis of the aim of coordination is the selection of thermodynamic conditions which should be adhered to closely for easy inter-comparison of a wide range of data.

The range of conditions will of course be dependent on the choice of molecules. These were selected for the following reasons.

Methyl Chloride $(CH_2Cl_2)$ (Freon 30)

(i) This is a dipolar asymmetric top $(C_{2v})$ which is a liquid at room temperature. It has been widely used in industry as a solvent and degreasing agent and consequently many of its basic physical properties have been measured.

(ii) It has a wide liquid range of almost $140^{o}$ from the melting point to the boiling point at 1 bar. The critical temperature and pressure have been measured (table  ).

(iii) The variation of solidification temperature with applied pressures in the kbar range has been reported up to 30 kbar. The dependence of static permittivity on kbar pressure over a different (more restricted) range is also known. This facilitates measurements at constant volume over a temperature range. The relevant physical data are listed in tables 2 and 3.

(iv) By reference to the comprehesive (but not exhaustive) bibliography of section V it becomes clear that $CH_2Cl_2$ has been investigated with a variety of spectroscopic techniques, especially by infra-red and n.m.r. methods. The results of all this effort have already been discussed in section IV.

(v) There are infrared active vibrations with transition moment vectors parallel to any one of the axes of inertia so that the rotational motion of each axis may; be studied by choosing an appropriate vibrational band. In $CH_2Cl_2$, isotopic broadening factors are negligible compared with other sources of uncertainty. The infrared band intensities are presumably high enough to ensure that the collision induced absorption is small in comparison. There is no way of corroborating this statement quantitatively at present.

(vi) The liquid absorbs strongly in the zero-THz frequency region (static to far infrared) so that the multimolecule orientational correlation function can be measured with minimal interference from collision induced absorption. The same is true for scattering techniques such as depolarised Rayleigh and Raman. The zero-THz spectra of methylene chloride in a range of environments have been investigated (Section V ). The behaviour in viscous and vitreous solvents such as decalin is especially significant.

(vii) It has a predominantly incoherent neutron scattering cross-section, due to the presence of the equivalent hydrogen atoms. There are no low frequency vibrational inelastic features in a low energy neutron scattering experiment. This implies that the far infrared Poley absorption is also free from distortion at the high frequency side.

(viii) The $C_{2v}$ symmetry of the molecule is the same as that of water, so that the available water algorithms of the molecular dynamics simulators can be adapted straightforwardly for $CH_2Cl_2$ (which is believed to be weakly H-bonded in the neat liquid state).

(ix) Inertial or molecular shape considerations would predict symmetric-top behaviour. However, the complex nature of the intermolecular interaction with the dipole moment along the b-axis might invalidate such simple arguments. There is a need to make a comprehensive attack on the problem of asymmetric top reorientation in an attempt to resolve some of these problems.

(x) For N.M.R. spectroscopy the presence of C, H, D and Cl nuclei is an advantage in determining the reorientational anisotropy.

(xi) The large amount of work on acoustic relaxation means that it will be relatively straightforward to coordinate this technique with Brillouin and neutron scattering to investigate centre of mass motions and their relation to reorientation.

(xii) A number of different simulation algorithms have been developed to the stage where the coordinated treatment of a molecule such as $CH_2Cl_2$ is now possible from different computational viewpoints. The project will provide the necessary range of data needed to test out these algorithms at a fundamental level.

The choice of $CH_2Cl_2$ is therefore well supported by a variety of (albeit uncoordinated) results already in the literature. To pull all these threads together the following section deals with the preset conditions for $CH_2Cl_2$.

## Methyl Fluoride ($CH_3F$) and methyl iodide ($CH_3I$)

(i) These molecules are symmetric top rotors and so that overall rotational motion is less complicated than for $CH_2Cl_2$. The theoretical formalism for liquid phase rotation of a symmetric top molecule is relatively well developed.

(ii) Both molecules have been extensively studied by infrared and Raman spectroscopic techniques but relatively little has been reported on their far-infrared and microwave properties.

(iii) Neither molecule has naturally occurring isotopic modifications (of practically significant concentrations) so that band shape analysis is relatively straightforward.

(iv) Neither molecule has been extensively studied over a wide range of density and temperature.

## Suggested Conditions for Spectroscopic Technique and Simulation

It is emphasised that for the success of the scheme these conditions should be adhered to as closely as possible. Among them are listed studies up to kbar pressures which are highly desirable but technically difficult.

## A. Methylene chloride

(1) Liquid from the melting point to the boiling point at 1 atmosphere, i.e. $-96^{\circ}C$ to $40^{\circ}C$ at $10^{\circ}$ increments. i.e. $-96^{\circ}C$ (as close to the melting point as

possible), -85°C, ......, 35°C and one point as close to the boiling point as possible.

(2) Liquid under hydraulic pressure. For the data in tables 2 and 3.
1 atm = 1.01325 bar = 1.03323 kg cm$^{-2}$.

  (a) We suggest that the conditions of Bridgman be followed accurately. The necessary variations of melting point with pressure is given in table 2.

TABLE 2

| $10^{-2}$ Pressure/(kN m$^{-2}$) | Melting Temp. (°C) |
|---|---|
| 1.013 (atmospheric) | -96.7 |
| 4903 | -46.0 |
| 9803 | 0.0 |
| 14710 | 42.0 |
| 19613 | 82.0 |
| 24516 | 120.0 |
| 29746 | 157.0 |

All measurements should be carried out just above the melting temperature at each pressure, therefore -90°C; -40°C; 5°C; 50°C; 85°C; 125°C; 160°C.

It would be incisive to carry out measurements at constant volume by increasing the temperature of the pressure cell, if this is technically feasible. The complete set of pressure measurements would be as given in table 3.

TABLE 3

| Starting Pressure x $10^{-2}$/(kN m$^{-2}$) | Temperatures (°C) | | | |
|---|---|---|---|---|
| 4903 | -40 | -20 | 0 | 20 |
| 9803 | 5 | 25 | 45 | 65 |
| 14710 | 50 | 70 | 90 | 110 |
| 19613 | 85 | 105 | 125 | 145 |
| 24516 | 125 | 145 | 165 | 185 |
| 29746 | 160 | 180 | 200 | 220 |

  Notice that,

(i)  As the temperature is raised the initial pressure will, of course, increase at constant volume.

(ii)  At the extremes of pressure and temperature the liquid might decompose.

(iii)  Laboratories might find that it is not technically feasible to push the pressure too far.

(iv)  It is necessary to comtinue up to the boiling point at each pressure if possible.

  (b)  At room temperature (30°C) vary the external pressure in increments of

500 kN m$^{-2}$ until the liquid solidifies.  Take a measurement of the liquid just before solidification and of the solid at 30$^{\circ}$C.  Repeat at 50$^{\circ}$C.

(3)  Measurements in the liquid along the gas/liquid coexistence line from the boiling point (40$^{\circ}$C) to the critical point (245$^{\circ}$C, 60.9 atm) at increments of 25$^{\circ}$C.  Specifically the liquid under its own vapour pressure at b.p. (40$^{\circ}$C); 50$^{\circ}$C; 75$^{\circ}$C; 100$^{\circ}$C; 125$^{\circ}$C; ......; 225$^{\circ}$C; and at the critical point.  Measurements at further 25$^{\circ}$C increments into the supercritical region are desirable if technically possible.

(4)  In solution in carbon tetrachloride, and in decalin, at room temperature (25$^{\circ}$C) and pressure.  Concentrations (in mole % $CH_2Cl_2$): 100; 90; 80; 70; .....; 10; 0.

(5)  In ultra-viscous and vitreous environments.

(i)  In 10% decalin at 106 K, 110 K, 113 K, 115 K, 118 K, 138 K, 140 K, ($\alpha, \beta, \gamma$ loss peaks known at these temperatures).

(ii)  10% v/v $CH_2Cl_2$ in mixed glass forming solvents.

   (a)  1:7 Cholesteryl oleyl carbonate (OCC)/decalin: 106 K, 110 K, 112 K, 116 K, 144 K, 146 K, 150 K.

   (b)  1:9 toluene/decalin at 115 K, 118 K, 120 K, 123 K, 137 K, 141 K, 144 K.

   (c)  3:7 toluene/decalin 125.5 K, 128 K, 130 K, 133 K, 136 K.

   (d)  10% v/v $CH_2Cl_2$ in 10% pyridine/toluene at 110 K.

These last conditions may seem without obvious reasons, but they repeat those of Reid's work dealing with measurements across the ($\alpha, \beta, \gamma$) features of the zero-THz loss spectrum for $CH_2Cl_2$ solute over about twelve decades of frequency.  In each case of (5) the $CH_2Cl_2$ dynamics are drastically different from those at room temperature and its ($\alpha, \beta$) behaviour is unique with high activation energies in both cases.

(6)  The glassy state is one instance where the translation of the $CH_2Cl_2$ solute molecules takes place on a scale which is much slower than their torsional oscillation (which appears as the far infrared $\gamma$ process in vitreous decalin solvent for example).  The problem of rotation-translation coupling should therefore be eliminated when considering the $\gamma$ process from the point of view of molecular dynamics simulation and inelastic neutrons scattering.  Another way of eliminating translation is to use the rotator phase of $CCl_4$ as a solvent for $CH_2Cl_2$ and to compare the rotator phase and liquid spectra.

B.  Methyl Fluoride

As we have already pointed out in section ( V ), the details of the $CH_3F$ potential function are exceptionally well known, partly because of the availability of second and third pressure virial coefficient data.  This molecule is one which has also been earmarked by West German scientists for a coordinated study.  It is a gas at room temperature and for this reason much less is available in the literature on the liquid phase.  The work of Gerschel et al. along the gas/liquid

coexistence line is taken as the basis for further spectroscopic study. The measurements provide an ideal basis for extension to other techniques and for simulation with molecular dynamics.

In this study it was found that there is apparently a weak density dependence of the mean square torques, since molecular multipole interactions are long-ranged and not sensitive to the mean intermolecular separation. The local anisotropy of the structure appears to be a consequence of specific molecular properties other than shape factors, therefore multipolar interaction should be used in the molecular dynamics simulation. These are reproduced from the paper in table 4. Here $T_t$ denotes the triple point temperature and $T_c$ the critical temperature.

TABLE 4

Mean square torques from Gerschel, Brot, Dimicoli, Joffre and Riou: Methyl Fluoride along the Orthobar (G58)

| $T_r = \dfrac{(T - T_c)}{(T_c - T_t)}$ | 0.01 | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|---|---|---|---|---|---|---|---|---|---|---|
| $< N_\perp^2 >$ $(10^4\,cm^{-2})$ | 97 | 94 | 91 | 88 | 86 | 84.5 | 83 | 82 | 81 | 80 |
| $< N_\perp^2 >^{\frac{1}{2}}/kT$ | 10.75 | 9.2 | 8.1 | 7.2 | 6.5 | 5.9 | 5.4 | 4.9 | 4.6 | 4.3 |

In this paper the $CH_3F$ was studied at 15 K intervals from $T_t$ to $T_c$. The liquid was maintained in equilibrium with its own vapour along the orthobaric or coexistence curve. This is a set of conditions which is easily reproducible by other experimentalists, by simply heating the liquid (in equilibrium with the vapour) in a closed cell.

TABLE 5

Zero-THz data for $CH_3F$ along the orthobar

| $T_R$ | $\bar{\nu}_{max}/(cm^{-1})$ | $\varepsilon_o$ | $n_{IR}^2$ | $\varepsilon_{\infty D}$ | $\tau_D$/ps | $\tau_\mu$/ps |
|---|---|---|---|---|---|---|
| 0.01 | 92 | 49 | 1.79 | 3.7 | 6.6 | 4.57 |
| 0.10 | 84 | 40 | 1.775 | 3.5 | 4.4 | 3.06 |
| 0.20 | 79 | 32.8 | 1.76 | 3.25 | 3.1 | 2.17 |
| 0.30 | 75 | 26.9 | 1.73 | 2.95 | 2.2 | 1.55 |
| 0.40 | 71 | 22.5 | 1.695 | 2.7 | 1.55 | 1.10 |
| 0.50 | 66.5 | 18.6 | 1.65 | 2.4 | 1.1 | 0.78 |
| 0.60 | 62.5 | 15.6 | 1.60 | 2.1 | 0.8 | 0.57 |
| 0.70 | 58.5 | 12.9 | 1.55 | 1.9 | 0.6 | 0.43 |
| 0.80 | 54.0 | 10.4 | 1.475 | 1.7 | 0.5 | 0.36 |
| 0.90 | 50.0 | 8.2 | 1.405 | 1.5 | 0.45 | 0.33 |
| 0.93 | | 7.2 | 1.35 | 1.45 | 0.42 | 0.31 |

($\varepsilon_o$ = static permittivity; $\bar{\nu}_{max}$ = far infrared peak absorption frequency;

$n_{IR}$ = refractive index at the end of the far infrared dispersion; $\varepsilon_{\infty D}$ = intersection point on the $\varepsilon'$ axis of the Debye semicircle; $\tau_D$ and $\tau_\mu$ are values of the Debye relaxation time with and without internal field corrections.)

In addition a set of measurements of $CH_3F$ in $CCl_4$ is essential to remove dipole-dipole interaction. The concentrations should be ideally the same as those for $CH_2Cl_2$, i.e. 100; 90; 80; 70; ......; 10; 0. Carbon tetrachloride is chosen as being suitable for light scattering and for NMR and neutron scattering (no interference with the solute properties because there are no hydrogen atoms).

It is emphasised that, as far as possible, these conditions should be matched **exactly** by all experimentalists and also by the simulators, if dilution studies by simulation are not too costly.

For convenience the vapour pressure data for $CH_3F$ are reproduced in table 6. Note $T_c$ = 317.6 K, $T_t$ = 131.0 K; $(T_c - T_t)$ = 186.6 K.

TABLE 6

| Temp./K | Vapour Pressure/kN m$^{-2}$ | $T_R$ |
|---------|-----------------------------|-------|
| 132.9 | 0.675 (at 135 K) | 0.01 |
| 149.6 | 3.638 (at 150 K) | 0.1 |
| 168.2 | 20.508 (at 170 K) | 0.2 |
| 186.8 | 57.02 (at 185 K) | 0.3 |
| 205.4 | 172.17 (at 205 K) | 0.4 |
| 224.0 | 419.62 (at 225 K) | 0.5 |
| 242.0 | 737.82 (at 240 K) | 0.6 |
| 261.2 | 1410.7 (at 260 K) | 0.7 |
| 279.8 | 2460.4 (at 280 K) | 0.8 |
| 298.4 | 3999.4 (at 300 K) | 0.9 |

As mentioned in section V there are no kbar pressure data available for $CH_3F$ liquid, but the same pressure (or their nearest equivalents) should be used for $CH_3F$ as for $CH_2Cl_2$. Specifically, this means:

(i) Just above the melting temperature at each kbar pressure.

(ii) At room temperature, vary the external pressure in increments of 500 kg cm$^{-2}$ until the liquid solidifies. Take a measurement of the liquid just before solidification and of the solid.

These essentially constant volume measurements should, of course, be supplemented by those on the liquid from the normal freezing point (at 1.0 bar) of 131.2 K to the boiling point at 1 bar, 194.65 K. Note that $CH_3F$ has a much smaller liquid range than $CH_2Cl_2$. Specifically these measurements on the liquid should be carried out (at 1.0 bar):

(i)   As close to the freezing point as possible;

(ii)  140 K, and in 10 K increments to 190 K;

(iii) As close to the boiling point as possible.

Finally it has already been mentioned that dilution studies for $CH_3F$ in $CCl_4$ would be essential for the problem of electrodynamics typified in dipole-dipole interaction. This might well persist in dilute solution (as Deutch et al. have recently suggested using hydrodynamics via Oseen tensors), but presumably would not be so powerful a force in setting up the collective oscillations mentioned by Gerschel and co-workers.

In $CCl_4$ rotator phase solvent the translational movement of the $CH_3F$ solute molecules would be slowed substantially compared with that in liquid $CCl_4$ solvent. $CH_3F$ itself does not form a rotator phase. It would be advantageous therefore to measure and simulate $CH_3F$ in dilute solution in rotator phase $CCl_4$ if technically feasible. It might be difficult to dissolve enough $CH_3F$ in $CCl_4$ for this purpose. In this case benzene might prove a substitute. Benzene forms a reorientational solid phase as opposed to a true rotator phase. Conditions for this experiment may be specified as "very dilute solution of $CH_3F$ in $CCl_4$ just below normal freezing point of the solution".

C. Methyl Iodide

Again for this species there seems to be no available literature data on the liquid subjected to kbar of pressure. In consequence the set of conditions drawn up below are based upon linear extrapolation from those suggested for closely related molecules.

(1) **Liquid** from melting point (207 K) to the boiling point (315 K) at one atmosphere pressure ($\cong 1.013$ bar $\equiv 101.3$ kN m$^{-2}$) at 10 K increments, i.e. (a) as close to the m.p. as possible, at 210 K, etc. up to 310 K, and as close to the boiling point as possible.

(2) Liquid under Hydraulic Pressure

(a) **Studies** on the liquid at constant volume just above the melting point for pressures up to 30 kbar, and hence at **increments** of $\sim$ 20 K for each pressure. The necessary data is given in tables 7 and 8.

TABLE 7

Melting point of $CH_3I$ as a function of pressure

| Pressure/atm | Melting point* |
|---|---|
| 1 | -66°C, 207 K |
| 1,000 | -52°C, 221 K |
| 5,000 | 3°C, 276 K |
| 10,000 | 72°C, 345 K |
| 15,000 | 142°C, 415 K |
| 20,000 | 211°C, 484 K |

* Obtained from values at 1 atm and 1000 kg cm$^{-2}$ using a linear relationship.

TABLE 8

Data for temperature/pressure studies at constant volume

| Initial Pressure/atm | Temperature/$^{\circ}$C | | | | |
|---|---|---|---|---|---|
| 1 | - 65 | -15 | 35 | 85 | 135 |
| 5,000 | 5 | 25 | 45 | 65 | |
| 10,000 | 75 | 95 | 115 | 135 | |
| 15,000 | 145 | 165 | 185 | 205 | |
| 20,000 | 215 | 235 | 255 | 275 | |

(3) Measurements of the liquid along the gas/liquid coexistence line from the boiling point (315 K) to the critical point (528 K, 66.3 atm). This involves study of the liquid under its own vapour pressure (table 9) at $25^{\circ}$C increments and at further $25^{\circ}$C increments into the super-critical region, if feasible (decomposition may be a problem for $CH_3I$).

TABLE 9

Vapour pressure of $CH_3I$ as a function of temperature

| Temperature | | Vapour pressure/kN m$^{-2}$ |
|---|---|---|
| 315 K | 42$^{\circ}$C | 99.379 |
| 340 K | 67$^{\circ}$C | 216.73 |
| 365 K | 92$^{\circ}$C | 419.52 |
| 390 K | 117$^{\circ}$C | 740.10 |
| 415 K | 142$^{\circ}$C | 1213.90 |
| 440 K | 167$^{\circ}$C | 1879.4 |
| 465 K | 192$^{\circ}$C | 2779.5 |
| 490 K | 217$^{\circ}$C | 3701.3 |
| 515 K | 242$^{\circ}$C | 5489.4 |

(4) In solution in $CCl_4$ and in decalin at room temperature ($250^{\circ}$C and pressure; concentrations (in mole % $CH_2I$) 100, ......, 90, 80, 70, ......, 10, 5, 2, 1% (low concentrations in an attempt to extrapolate to "single particle" dynamics).

(5) In ultra-viscous and vitreous environments.

In 10% decalin, from liquid nitrogen temperature to room temperature. As in $CH_2Cl_2$ careful measurements should be made around the glass transition temperature.

Physical Properties

I. Methylene Chloride (Reference to list given in section V)

The following is a selection of useful physical properties for methylene chloride, structural, thermodynamic and electrostatic.

(1) Structure and Moments of Inertia have been determined by Myers and Gwinn (158b) using microwave spectroscopy.

Average of all Isotopes

C-Cl   = 1.7724 ± 0.0005 Å

C-H    = 1.068 ± 0.005 Å

$\hat{ClCCl}$ = 111° 47' ± 1'

| Isotope | $10^{40} I_A/gm \ cm^2$ | $10^{40} I_B/gm \ cm^2$ | $10^{40} I_C/gm \ cm^2$ | $\mu/D$ |
|---|---|---|---|---|
| $CH_2Cl_2^{35}$ | 26.2142 | 252.64 | 273.69 | 1.61(8) |
| $CH_2Cl^{35}Cl^{37}$ | 26.3157 | 259.60 | 280.73 | 1.62(3) |
| $CH_2Cl_2^{37}$ | 26.419 | 266.88 | 288.11 | |
| $CDHCl_2^{35}$ | 30.844 | 253.80 | 277.16 | 1.61(6) |
| $CDHCl^{35}Cl^{37}$ | 30.966 | 260.74 | 284.23 | 1.62(5) |
| $CD_2Cl_2^{35}$ | 35.432 | 255.43 | 280.23 | 1.64(4) |
| $CD_2Cl^{35}Cl^{37}$ | 35.575 | 262.37 | 287.31 | 1.64(0) |

(2)   Static Dielectric Permittivity and Density as a Function of Pressure

These have been measured recently in two papers by Schormak et al. and Hartmann et al.

| At 30°C | | | At 50°C | | |
|---|---|---|---|---|---|
| P/atm | $\varepsilon_o$ | Density $(g/cm^3)$ | P/atm | $\varepsilon_o$ | Density $(g/cm^3)$ |
| 1 | 8.649 | 1.3078 | 40 | 7.757 | 1.2587 |
| 178 | 8.860 | 1.3325 | 205 | 7.939 | 1.2716 |
| 697 | 9.298 | 1.3886 | 502 | 8.239 | 1.3087 |
| 959 | 9.524 | 1.4103 | 747 | 8.451 | 1.3279 |
| 1342 | 9.770 | 1.4387 | 1057 | 8.673 | 1.3506 |
| 2048 | 10.171 | 1.4893 | 1446 | 8.923 | 1.3852 |
| 3074 | 10.708 | 1.5505 | 1963 | 9.198 | 1.4219 |
| 4063 | 11.159 | 1.5963 | 2685 | 9.550 | 1.4658 |
| 4883 | 11.545 | 1.6276 | 3491 | 9.878 | 1.5064 |
| | | | 4280 | 10.167 | 1.5401 |
| | | | 5121 | 10.439 | 1.5725 |

It is emphasised that the permittivity and density should be remeasured at the recommended set of conditions.

Thermodynamic Conditions

Critical temperature = 245°C; critical pressure = 60.9 atm.  A paper by E.W. McGovern (Ind. and Eng. Chem., 35(1943)1230-39) gives the vapour pressure vs. temp. curve from -15°C to 220°C, the density of the liquid vs. temperature, the density of the saturated vapour vs. temp. and a table of physical properties. Some selected values for $CH_2Cl_2$:

Mol. weight = 84.94

Freezing point = -96.7°C

Boiling point = $39.8^{\circ}C$

Latent heat of vapourisation (at b.p.) = 78.7 cal $gm^{-1}$

Specific heat of the liquid at $20^{\circ}C$ = 0.28 cal/gm/$^{\circ}C$

Specific heat of the vapour (at $40^{\circ}C$ at 1 atm) = 0.155 cal/gm/$^{\circ}C$

Thermal conductivity of the liquid at $20^{\circ}C$ = 0.092 C.H.U./hr./(sq. ft.)/($^{\circ}C$/ft.)

Thermal conductivity of the vapour (b.p.) = 0.00438 C.H.U./hr./(sq. ft.)/($^{\circ}C$/ft.)

Density of the liquid ($d_4^{20}$) = 1.326 gm/$cm^3$

Viscosity (centipoise) of the liquid at $20^{\circ}C$ = 0.425

Refractive index, $n_D$, of the liquid = 1.4244 at $20^{\circ}C$

Dielectric static permittivity of the liquid = 9.1 ($20^{\circ}C$)

Dielectric static permittivity of the vapour = 1.0109 ($40^{\circ}C$)

Heat of formation of the liquid = 28.6 kcal/mole

Heat of formation of the vapour = 2.17 kcal/mole

   Also in this paper are charts of solubility in water, latent heat, specific heat (liquid and vapour), viscosity (liquid and vapour), thermal conductivity (liquid and vapour) and diffusivity in air at 1 atm all against temperature.

Dielectric Properties and Polarisability

   The polarisability and the anisotropy of the polarisability are known from a paper by Iszak and le Fevre (145) on the molar Kerr constant in solution. This is $P_2$ ($CCl_4$) = 69.24 $cm^3$; $P_2$ (benzene) = 69.05 $cm^3$. This paper lists a range of experimentally determined liquid state dipole moments, the majority in benzene solution (1.44 to 1.62 D). In $CCl_4$ they are 1.49 D to 1.59 D. The paper provides a detailed description of attempts to reproduce the measured Kerr constant theoretically with bond polarisabilities, induction etc.

   In gaseous $CH_2Cl_2$ at $83.5^{\circ}C$/760 mm, $b_1$ = 5.96 $\overset{\circ}{A}^3$; $b_2$ = 8.47 $\overset{\circ}{A}^3$; $b_3$ = 5.02 $\overset{\circ}{A}$ are given by Stuart, which compare with Iszak and le Fevre: $b_1$ = 6.25 $\overset{\circ}{A}^3$; $b_2$ = 7.82 $\overset{\circ}{A}^3$; $b_3$ = 5.21 $\overset{\circ}{A}^3$ (at infinite dilution).

Collected Values of the Dipole Moment

   In the dilute gas, according to isotope, from 1.61(6) D to 1.64(4) D. In benzene, from 1.44 D to 1.62 D. In $CCl_4$, from 1.49 D to 1.59 D. There is one value of 1.91 D.

   The quadrupole and higher moments of $CH_2Cl_2$ are apparently unknown experimentally.

Hyperpolarisabilities

   Miller et al. (150) provide the second and third order non-linear optical polarisabilities.

Charge Distributions

   A study by Del Re (180), using a simple molecular orbital LCAO method provides a calculated dipole moment of 1.7 D.

| Atoms | | | (1) | (2) | (3) |
|---|---|---|---|---|---|
| $H_2$ | C | $Cl_2$ | + 0.105e | + 0.024e | -0.117e |
| (1) | (2) | (3) | | | |

where e is the charge on the electron.  These can be used to calculate rough
values of the higher multipoles about a given reference origin.

## Second Virial Coefficients

One of the most valuable methods of studying intermolecular forces consists
of the direct measurement of the deviations of real gases from the equation of
state of the perfect gas.  The state of a real gas is described by means of the
following equation:

$$PV_m = A + \frac{B}{V_m} + \frac{C}{V_m^2} + \ldots\ldots$$

due to Kammerlingh-Onnes.  A, B and C are the first, second and third virial
coefficients, and are temperature dependent.

For $CH_2Cl_2$:

| $T(^{\circ}C)$ | $-B_p \ cu^3/mole$ |
|---|---|
| 50 | 676.5 |
| 75 | 544.8 |
| 100 | 467.2 |
| 125 | 389.2 |
| 150 | 348.9 |

The virial coefficient method is applicable to arbitrary quantities Q describing
the property of a real gas:

$$Q = A_Q + \frac{B_Q}{V_m} + \frac{C_Q}{V_m^2} + \ldots\ldots$$

where $A_Q$, $B_Q$, $C_Q$ are the first, second, ... virial coefficients of the measurable
quantity Q.  For example, Q can be molecular electric polarisation.  Buckingham
(R14) proposes its use for molecular refraction and Kerr constants, and Kielich (R16)
for the Cotton-Mouton effect, light-scattering and field-gradient-induced optical
birefringence.  So far no experimental values are available for methylene
chloride.

## II.  Methyl Fluoride

Molecular weight = 34.034
Boiling point at 1 bar = 194.65 K
Freezing point at 1 bar = 131.2 K
Triple point = 131 K
Critical temperature = 317.6 K

Gas density at 273 K, 1 bar = 1.5451 gm/litre

Density of liquid at 213 K = 0.8328 gm/cm$^3$

Critical pressure = 58 bar (852.6 p.s.i.a.)

Critical density = 0.275 gm cm$^{-3}$

Latent heat of vapourisation at b.p. = 118.46 cal/gm

Specific heat at 298 K, 1 bar = 0.3221 cal/g/$^o$C

Entropy, gas, at 298 K, 1 bar = 53.25 cal/mole/$^o$C

Heat of formation at 298 K = -59 ± 2 kcal/mole

Dipole moment = 1.8555 ± 0.0015 D

C-F bond dist. = 1.3852 Å; C-H = 1.106 Å

$<$ HCH = 109$^o$ 50' ± 3'

Polarisability = 2.97 x 10$^{-24}$ cm$^3$ mole$^{-1}$

Moment of inertia, $I_x = I_y = 33$ x 10$^{-40}$ gm cm$^2$

$\qquad\qquad I_z = 5.5$ x 10$^{-40}$ gm cm$^2$

Liquid densities (gm cm$^{-3}$), 133 K, $\rho$ = 0.955; 153 K, $\rho$ = 0.93; 173 K, $\rho$ = 0.91;

$\quad$ 193 K, $\rho$ = 0.88; 233 K, $\rho$ = 0.79; 270 K, $\rho$ = 0.675; 293 K, $\rho$ = 0.59.

Estimated values of the quadrupole moment, polarisability etc. are given in section VIc.

III.  Methyl Iodide

Molecular weight = 142

Melting point = 66.45$^o$C

Boiling point = 42.5$^o$C/760 mm

Static permittivity, $\epsilon_o$ = 7.1 ± 0.1 at 20$^o$C

Density, $\rho$ = 2.3346 gm cm$^{-3}$; $\rho_4^{20}$ = 2.2819 gm cm$^{-3}$; $\rho_4^{30}$ = 2.25102.

In the solid at -195$^o$C; $\rho$ = 2.994 gm cm$^{-3}$, at -79$^o$C; $\rho$ = 2.840 gm cm$^{-3}$

Refractive index, $n_D^{20}$ = 1.53173; $n_{He}^{15}$ (yellow) = 1.534

Structural factors

r(C-H) = 1.0958 Å; $\quad$ H$\hat{C}$H = 111$^o$ 50'; $\quad$ H$\hat{C}$I = 106$^o$ 58'.

Second Virial Coefficients

| $-B_p$/cm$^3$ mol$^{-1}$ | T/K |
|---|---|
| 600 | 323 |
| 490 | 353 |
| 420 | 383 |

Viscosity

$\eta$ = 0.594 cP; $\eta_{15}$ = 0.518 cP; $\eta_{30}$ = 0.460 cP

Critical Constants

$T_c$ = 255$^o$C; $P_c$ = 66.3 atm; $\rho_c$ = 0.83 gm cm$^{-3}$

Acknowledgements

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