

THE UNIVERSITY OF MANITOBA

A RAMAN LINEWIDTH INVESTIGATION  
OF MOLECULAR MOTION  
IN LIQUID BENZENE

by

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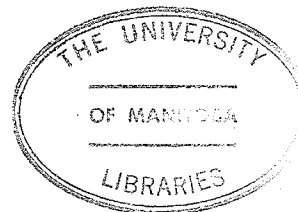
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## ABSTRACT

The reorientational and vibrational broadening of the  $992\text{ cm}^{-1}$   $A_{1g}$  Raman line of benzene has been investigated through linewidth analysis, in pure liquid benzene and in benzene-carbon tetrachloride liquid mixtures, over a range of temperatures. The results have been interpreted in terms of the molecular dynamics of the liquids studied.

It is concluded that tumbling motions of the benzene molecule are well described by a rotational diffusion model in the neat liquid, but appear to approach free rotor behaviour in the mixtures. Also, evidence has been found to suggest that an unusual, vibration-to-vibration energy transfer occurring during  $C_6H_6-C_6H_6$  collisions, dominates vibrational relaxation in pure liquid benzene.

Linewidth analysis techniques that were developed in the course of this work, are discussed.

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## CHAPTER 1

INTRODUCTION

Experiments involving absorption or scattering of radiation can contribute many insights to the study of molecular motion in fluids, particularly in regard to intermolecular forces and the dynamics of molecular collisions. The traditional sources of information about molecular forces, such as viscosity and virial coefficients, are largely insensitive to the angular dependence or "shape" of these forces. In contrast, certain spectroscopic effects occur because of, or are modified by, the presence of intermolecular torques. For this reason, spectroscopic methods are of value in investigating the nonspherical shape of intermolecular forces. Among these methods rank microwave, infrared, and magnetic resonance absorption; also, Rayleigh, Raman, and fluorescent light scattering.

Scattering experiments enjoy a peculiar advantage over absorption experiments probing comparable molecular energy levels. If incident radiation of a definite polarisation is used, the scattering process may preserve some of the directional information encoded in the incident electric field. If the scattered radiation is analyzed according to polarisation, the spectral profile will generally depend on the polarisation mode selected. Extra information about molecular interactions can be gleaned from this polarisation dependence. That this should be so, can be made intuitively plausible. One might consider a scattering molecule which, from the point of view of incident radiation, has spherical symmetry in the absence of perturbation by neighbouring molecules. (In the case of Raman scattering, for instance, the required symmetry consists in a spherical polarisability tensor.)

One might further suppose, that any environmental perturbation of the scattering molecule takes the form of intermolecular forces of spherical shape. If the experimental geometry has been arranged so that the polarisation vector of the incident radiation is normal to the scattering plane, then, by an elementary symmetry argument, the scattering process cannot be expected to change the direction of the polarisation vector. Any such change which is actually observed, must therefore be a manifestation of asphericity, either in the structure of the molecule or in the forces coupling it to its environment. Thus, when scattering molecules are selected, which are known to possess certain symmetry elements, a clear connection can sometimes be drawn between the depolarisation of the scattered radiation and the angular dependence of the intermolecular forces.

When applied to the analysis of Raman vibrational lines of certain symmetry species, the polarisation dependence of the scattering spectrum is a particularly convenient happenstance. If a few plausible assumptions are granted, it allows of a tidy separation of rotational line-broadening from that induced by other mechanisms (especially vibrational relaxation). This feature will be exploited in the course of our investigations.

In the present work, we shall examine the rotational broadening of the  $992\text{ cm}^{-1}$   $A_{1g}$  Raman vibrational line in liquid benzene, both as a neat liquid and in solution with  $\text{CCl}_4$ . An explicit description of the angular dependence of intermolecular forces is beyond the scope of this work, and, indeed, beyond the present state of the art. We shall, however, use lineshape parameters to derive rotational diffusion constants, which may be interpreted in terms of the degree to which,



and the manner in which, molecular reorientation is hindered by interactions with neighbouring molecules. Such hindrance would not exist if the coupling forces were spherical; the diffusion constants are thus related to the nonspherical shape of the forces. The temperature and concentration dependence of the diffusion constants may further illuminate the kinematic nature of molecular reorientation, and thence the dynamics governing it.

In addition to the study of molecular reorientation, we undertake to examine the temperature and concentration dependence of vibrational relaxation time for the Raman line in question, again by analyzing lineshapes. Insofar as vibrational relaxation occurs as a result of molecular collisions, these times are indicative of the "time between collisions", and are source of further information about the molecular dynamics of the fluid under study.

Only recently<sup>1</sup> have Raman and infrared lineshapes come to be regarded as a problem involving, or conversely as a clue to, the time dependence of molecular variables in a statistical ensemble. The formalism which relates lineshapes to molecular motion, is a time correlation function of the molecular variables. The use of correlation function expressions in analyzing lineshape data for liquids has now gained wide acceptance, as it has, indeed, in describing a wide range of disparate physical phenomena, particularly transport processes.<sup>2</sup>

#### References:

1. R. G. Gordon, J. Chem. Phys. 43, 1307 (1965).
2. R. Zwanzig, Ann. Rev. Phys. Chem. 16, 67 (1965).

## CHAPTER 2

## THEORY

In the following discussion, a quantum mechanical description of Raman light scattering will be formulated. Once the general connection between the spectral profile and the time dependence of molecular dynamic variables has been established, a framework will be constructed, within which lineshape parameters may be interpreted in terms of the motion of individual molecules.

### I. Quantum Mechanical Description of Light Scattering:

Following Gordon<sup>1</sup>, we begin with the polarisability formula developed by Placzek<sup>2</sup> for non-resonant Raman scattering. These authors give the cross section (probability per unit solid angle  $\Omega$ , per unit angular frequency  $\omega$ , that an incident photon will be scattered into  $d\Omega d\omega$ ) as

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{\omega^{(1)}\omega^{(2)3}}{c^4} \sum_{i,f} |\langle i | \hat{\epsilon}^{(1)} \cdot \hat{\alpha} \cdot \hat{\epsilon}^{(2)} | f \rangle|^2 \rho_i \delta(\omega_{fi} - \omega) \quad \dots (2.1)$$

Here,  $\omega = \omega^{(1)} - \omega^{(2)}$ , where  $\omega^{(1)}$  and  $\omega^{(2)}$  are the angular frequencies of the incident and scattered photons, respectively;  $\hat{\epsilon}^{(1)}$  and  $\hat{\epsilon}^{(2)}$  are unit vectors along the directions of the electric vectors of the incident and scattered photons, respectively;  $|i\rangle$  and  $|f\rangle$  range over the (many-particle) eigenfunctions of the scattering system, and have energy eigenvalues  $E_i$  and  $E_f$ ;  $\omega_{fi}$  is the Bohr frequency  $(E_f - E_i)/\hbar$ ;  $\rho_i$  is the probability of finding the scattering system initially in state  $|i\rangle$ ;  $\hat{\alpha}$  is the polarisability tensor of the scattering system, evaluated in the lab frame.

(NOTE: Equation (2.1) differs by the factor  $\omega^{(1)}/\omega^{(2)}$  from the form given in References 1. and 2., because these authors measure radiation fluxes

in terms of energy, rather than number of photons.)

This formula represents the conventional Schrödinger picture of Raman spectroscopy, in that it focuses attention on the energy levels, rather than the time development, of the system. It has little interpretive value, for, since there is no classical analogue of a single quantum state, it does not allow any classical correspondence to be exploited. The Heisenberg picture, on the other hand, leads naturally to the expression of a spectrum as the Fourier transform of a time correlation function, and yields the classical result in the appropriate limit.

In order to proceed from (2.1) to the corresponding Heisenberg form, one introduces the Fourier representation of the Dirac  $\delta$  function:

$$\delta(\omega) = (2\pi)^{-1} \int_{-\infty}^{\infty} dt \exp(i\omega t), \quad \text{whence}$$

$$\begin{aligned} \frac{d^2\sigma}{d\Omega d\omega} &= \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \sum_{if} \rho_i \langle i | \hat{\mathcal{E}}^{(1)} \cdot \hat{\mathbf{a}} \cdot \hat{\mathcal{E}}^{(2)} | f \rangle \langle f | \hat{\mathcal{E}}^{(1)} \cdot \hat{\mathbf{a}} \cdot \hat{\mathcal{E}}^{(2)} | i \rangle \int_{-\infty}^{\infty} dt \exp i \left[ \frac{E_f - E_i}{\hbar} - \omega \right] t \\ &= \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \sum_{if} \rho_i \langle i | (\hat{\mathcal{E}}^{(1)} \cdot \hat{\mathbf{a}} \cdot \hat{\mathcal{E}}^{(2)}) \exp(iE_f t/\hbar) | f \rangle \\ &\quad \times \langle f | (\hat{\mathcal{E}}^{(1)} \cdot \hat{\mathbf{a}} \cdot \hat{\mathcal{E}}^{(2)}) \exp(-iE_i t/\hbar) | i \rangle, \end{aligned}$$

where, in the last step, the multipliers  $\exp(iE_f t/\hbar)$  and  $\exp(-iE_i t/\hbar)$  have been taken inside the scalar products, and the linearity of the operator  $\hat{\mathcal{E}}^{(1)} \cdot \hat{\mathbf{a}} \cdot \hat{\mathcal{E}}^{(2)}$  has been used. This result may be re-expressed by introducing the Hamiltonian  $H$  of the matter (excluding the interaction of the radiation and matter). Since  $|i\rangle$  and  $|f\rangle$  are eigenstates of  $H$  with eigenvalues  $E_i$  and  $E_f$ , one may write<sup>3</sup>

$$\begin{aligned} \exp(iE_f t/\hbar)|f\rangle &= \exp(iHt/\hbar)|f\rangle && \text{and} \\ \exp(-iE_i t/\hbar)|i\rangle &= \exp(-iHt/\hbar)|i\rangle, && \text{whence} \end{aligned}$$

$$\begin{aligned} \frac{d^2\sigma}{d\Omega d\omega} &= \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \sum_{if} \rho_i \langle i | (\hat{\epsilon}^{(1)} \cdot \vec{a} \cdot \hat{\epsilon}^{(2)}) \exp(iHt/\hbar) | f \rangle \\ &\quad \times \langle f | (\hat{\epsilon}^{(1)} \cdot \vec{a} \cdot \hat{\epsilon}^{(2)}) \exp(-iHt/\hbar) | i \rangle. \end{aligned}$$

One may invoke the completeness relation

$$\sum_f |f\rangle\langle f| = 1$$

to remove the sum over final states:

$$\begin{aligned} \frac{d^2\sigma}{d\Omega d\omega} &= \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \sum_i \rho_i \langle i | [\hat{\epsilon}^{(1)} \cdot \vec{a} \cdot \hat{\epsilon}^{(2)}] \\ &\quad \times [\exp(iHt/\hbar) (\hat{\epsilon}^{(1)} \cdot \vec{a} \cdot \hat{\epsilon}^{(2)}) \exp(-iHt/\hbar)] | i \rangle. \end{aligned}$$

The second square bracket within the scalar product may be recognized<sup>4</sup> as the time - dependent operator  $\hat{\epsilon}^{(1)} \cdot \vec{a} \cdot \hat{\epsilon}^{(2)}$ , evaluated at time  $t$ , and may be written as  $\hat{\epsilon}^{(1)} \cdot \vec{a}(t) \cdot \hat{\epsilon}^{(2)}$ , since  $\hat{\epsilon}^{(1)}$  and  $\hat{\epsilon}^{(2)}$  are constant in time. The first square bracket may likewise be recognized as the same operator at time 0, and written as  $\hat{\epsilon}^{(1)} \cdot \vec{a}(0) \cdot \hat{\epsilon}^{(2)}$ . Thus,

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \sum_i \rho_i \langle i | [\hat{\epsilon}^{(1)} \cdot \vec{a}(0) \cdot \hat{\epsilon}^{(2)}] [\hat{\epsilon}^{(1)} \cdot \vec{a}(t) \cdot \hat{\epsilon}^{(2)}] | i \rangle.$$

The weighted sum over expectation values corresponding to the various initial states, constitutes a quantum statistical average, which we denote by  $\langle \rangle_0$  :

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \langle [\hat{\epsilon}^{(1)} \cdot \vec{a}(0) \cdot \hat{\epsilon}^{(2)}] [\hat{\epsilon}^{(1)} \cdot \vec{a}(t) \cdot \hat{\epsilon}^{(2)}] \rangle_0 \dots (2.2)$$

If the average  $\langle \rangle_0$  is interpreted as a classical ensemble average, one recovers the classical description<sup>5</sup> of Raman scattering, as the Fourier transform of a time correlation function.

## II. Reduction of Polarisability to that of Single Molecule:

In (2.2), the polarisability tensor  $\tilde{\alpha}$  pertains to a whole group of interacting molecules exposed to the incident radiation, and consists, we assume, in the sum of the polarisabilities of the individual molecules. Thus, every product of  $\tilde{\alpha}(0)$  and  $\tilde{\alpha}(t)$  will contain cross terms between the polarisabilities of different molecules. If it is assumed that there are no angular correlations among the orientations of neighbouring molecules, then the ensemble averages of these cross terms will vanish, and the correlation function in (2.2) will equal  $N$  times the single-molecule correlation function, where  $N$  is the number of molecules contributing to the scattering. When we take cognizance of this cancellation of cross terms, (2.2) stands as written above, but  $\frac{d^2\sigma}{d\Omega d\omega}$  will now be interpreted as the cross section per scattering molecule, and the polarisability tensor  $\tilde{\alpha}$  as that of a single molecule. The reduction we have just effected, is central to our objective of describing the scattering spectrum in terms of the motion of a single molecule.

Felicitous though it may be to neglect angular correlations, the assumption involved should be applied only with strict reservations. The evident existence of hindered rotations in liquids must be due to intermolecular torques, whose presence implies that the potential energy of interacting molecules is a function of their relative orientations. As a result, some relative orientations will be more energetically favourable than others, and a degree of angular correlation

is inevitable. Quantitative calculations of such effects are difficult to find in the literature, so that no satisfactory treatment can be given here.

One may proceed further to evaluate the expression within the ensemble average of (2.2). It is assumed that the scattering system is isotropic - i.e., that the molecule - fixed axes are randomly oriented with respect to the polarisation vectors  $\hat{\epsilon}^{(1)}$  and  $\hat{\epsilon}^{(2)}$  - as will, indeed, be the case for a liquid or gas sample. The ensemble average of (2.2) may be performed by averaging independently over molecular orientations and over molecular eigenstates. The separation of the two averages is justified by the fact, that the eigenstates are indifferent to the orientation of the molecule in the lab frame. They could depend on orientation only through the interaction of the matter with the incident radiation, and we have postulated in I. that this interaction may be excluded from the Hamiltonian which determines the eigenstates.

Assuming isotropy of the scattering system, we shall first average explicitly over molecular orientations. Letting  $I_{\parallel}$  and  $I_{\perp}$  \* denote the cross sections when  $\hat{\epsilon}^{(1)}$  and  $\hat{\epsilon}^{(2)}$  are, respectively, parallel and perpendicular to each other, one obtains<sup>6</sup> from (2.2):

$$I_{\parallel}(\omega) = \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \left\langle \frac{1}{15} \sum_{jk} [2a_{jk}(0)a_{jk}(t) + a_{jj}(0)a_{kk}(t)] \right\rangle$$

$$\text{and } I_{\perp}(\omega) = \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \left\langle \frac{1}{30} \sum_{jk} [3a_{jk}(0)a_{jk}(t) - a_{jj}(0)a_{kk}(t)] \right\rangle,$$

where  $\langle \rangle$  now denotes the usual thermal (Boltzmann) average.

Next, one may separate  $\hat{\alpha}$  into its anisotropic (traceless) and spherical parts:

---

\*  $I_{\parallel}$  and  $I_{\perp}$  will subsequently be referred to as the "polarised" and "depolarised" spectra, respectively.

$$a_{ij} = \bar{\alpha} \delta_{ij} + \beta_{ij} \quad , \quad \text{where} \quad \bar{\alpha} = \frac{1}{3} \text{Tr}(\hat{\alpha}) .$$

Writing the summations over j and k in trace (Tr) notation, one readily gets <sup>6</sup>

$$I_{\parallel}(\omega) = \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \langle \bar{\alpha}(0)\bar{\alpha}(t) + \frac{2}{15} \text{Tr}[\hat{\beta}(0) \cdot \hat{\beta}(t)] \rangle \quad \dots (2.3a)$$

$$\text{and} \quad I_{\perp}(\omega) = \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \langle \frac{1}{10} \text{Tr}[\hat{\beta}(0) \cdot \hat{\beta}(t)] \rangle \quad \dots (2.3b)$$

It is convenient to define the isotropic or "trace" scattering by

$$I_{iso}(\omega) = \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \langle \bar{\alpha}(0)\bar{\alpha}(t) \rangle , \quad \dots (2.4a)$$

and the anisotropic scattering by

$$I_{anis}(\omega) = \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \langle \frac{1}{10} \text{Tr}[\hat{\beta}(0) \cdot \hat{\beta}(t)] \rangle \quad \dots (2.4b)$$

It is evidently possible, experimentally to separate the anisotropic from the trace scattering: from (2.3), we see that

$$I_{anis}(\omega) = I_{\perp}(\omega) \quad \dots (2.5a)$$

$$\text{and} \quad I_{iso}(\omega) = I_{\parallel}(\omega) - \frac{4}{3} I_{\perp}(\omega) . \quad \dots (2.5b)$$

### III. Separation of Reorientational and Vibrational Broadening Mechanisms:

We shall now investigate the form taken by (2.4), when a vibrational Raman spectrum is considered, and when certain assumptions are adopted in regard to correlations among motions in the various degrees of

freedom of the scattering molecule.

In Gordon's original treatment<sup>1</sup>, it was postulated that the polarisability tensor  $\vec{\alpha}$  is constant in time, if referred to a coordinate system which rotates with the molecule. The time dependence of  $\vec{\alpha}$ , as evaluated in the lab frame, was thus taken to arise solely through molecular reorientation, with the result that other line-broadening mechanisms were neglected. More recent authors<sup>6,7</sup> have taken explicit account of vibrational broadening.

Following Bartoli and Litovitz<sup>7</sup>, we shall consider the polarisability tensor  $\vec{\alpha}$  to be modulated by each of the Raman-active normal vibrations of the molecule. These vibrations are assumed harmonic. A Taylor series expansion of  $\alpha_{jk}$ , in powers of the normal co-ordinates  $q^p(t)$ , yields, to first order,

$$\alpha_{jk}(t) = \alpha_{jk}^0(t) + \sum_p \alpha_{jk}^p(t) q^p(t),$$

where  $\alpha_{jk}^0(t)$  is the equilibrium ( $q^p=0$ ) polarisability, and where

$$\alpha_{jk}^p(t) \equiv \partial \alpha_{jk}(t) / \partial q^p(t) \Big|_{q^p=0}.$$

Here,  $\alpha_{jk}^0$  and  $\alpha_{jk}^p$  are taken to be constant when referred to the molecular axes, so that their time dependence in the lab frame arises solely through molecular reorientation. In principle, other processes, such as collisions, may contribute to the time dependence, so that the following treatment represents only a limited generalization of Gordon's approach.

Upon decomposing  $\vec{\alpha}$  into its spherical and traceless parts, we further break down  $\bar{\alpha}(t)$  and  $\beta_{jk}(t)$  in the manner of  $\alpha_{jk}(t)$  above.



The thermal averages occurring in (2.4) may then be re-expressed:

$$\begin{aligned}
 & \langle \text{Tr} [\vec{\beta}(0) \cdot \vec{\beta}(t)] \rangle \\
 &= \sum_{ij} \langle \beta_{ij}(0) \beta_{ij}(t) \rangle \\
 &= \sum_{ij} \left[ \langle \beta_{ij}^{\circ}(0) \beta_{ij}^{\circ}(t) \rangle + \sum_{\mu} \langle \beta_{ij}^{\circ}(0) \beta_{ij}^{\mu}(t) q^{\mu}(t) \rangle \right. \\
 & \quad \left. + \sum_{\mu} \langle \beta_{ij}^{\mu}(0) \beta_{ij}^{\circ}(t) q^{\mu}(0) \rangle + \sum_{\mu\nu} \langle \beta_{ij}^{\mu}(0) \beta_{ij}^{\nu}(t) q^{\mu}(0) q^{\nu}(t) \rangle \right] \dots \quad (2.6)
 \end{aligned}$$

Some simplification occurs, if it is assumed that the  $q^{\mu}$  are not coupled to the orientation of the molecule, and that the normal modes may be treated as independent oscillators. Now, if  $q^{\mu}$  is uncorrelated with orientation, and hence with  $\beta_{ij}^{\circ}$  and  $\beta_{ij}^{\mu}$  (which depend only on orientation), then

$$\langle \beta_{ij}^{\circ}(0) \beta_{ij}^{\mu}(t) q^{\mu}(t) \rangle = \langle \beta_{ij}^{\circ}(0) \beta_{ij}^{\mu}(t) \rangle \langle q^{\mu}(t) \rangle.$$

For a harmonic oscillator,  $\langle q^{\mu}(t) \rangle = 0$ .

$$\therefore \langle \beta_{ij}^{\circ}(0) \beta_{ij}^{\mu}(t) q^{\mu}(t) \rangle = 0, \quad \dots (2.7a)$$

$$\text{and similarly } \langle \beta_{ij}^{\mu}(0) \beta_{ij}^{\circ}(t) q^{\mu}(0) \rangle = 0. \quad \dots (2.7b)$$

Moreover, if  $q^{\mu}$  is uncorrelated with orientation, then

$$\langle \beta_{ij}^{\mu}(0) \beta_{ij}^{\nu}(t) q^{\mu}(0) q^{\nu}(t) \rangle = \langle \beta_{ij}^{\mu}(0) \beta_{ij}^{\nu}(t) \rangle \langle q^{\mu}(0) q^{\nu}(t) \rangle.$$

If different normal modes are independent, then

$$\langle q^{\mu}(0) q^{\nu}(t) \rangle = \langle q^{\mu}(0) \rangle \langle q^{\nu}(t) \rangle = 0 \quad \text{for } \mu \neq \nu.$$

$$\therefore \sum_{\mu, \nu} \langle \beta_{ij}^{\mu}(0) \beta_{ij}^{\nu}(t) q^{\mu}(0) q^{\nu}(t) \rangle = \sum_{\mu} \langle \beta_{ij}^{\mu}(0) \beta_{ij}^{\mu}(t) \rangle \langle q^{\mu}(0) q^{\mu}(t) \rangle. \quad \dots (2.8)$$

With the results (2.7) and (2.8), (2.6) becomes

$$\begin{aligned} \langle \text{Tr}[\vec{\beta}(0) \cdot \vec{\beta}(t)] \rangle &= \sum_{ij} [\langle \beta_{ij}^{\circ}(0) \beta_{ij}^{\circ}(t) \rangle + \sum_{\mu} \langle \beta_{ij}^{\mu}(0) \beta_{ij}^{\mu}(t) \rangle \langle q^{\mu}(0) q^{\mu}(t) \rangle] \\ &= \langle \text{Tr}[\vec{\beta}^{\circ}(0) \cdot \vec{\beta}^{\circ}(t)] \rangle + \sum_{\mu} \langle \text{Tr}[\vec{\beta}^{\mu}(0) \cdot \vec{\beta}^{\mu}(t)] \rangle \langle q^{\mu}(0) q^{\mu}(t) \rangle. \quad \dots (2.6') \end{aligned}$$

Treating  $\vec{\alpha}$  as we have treated individual components of  $\vec{\beta}$ , we find

$$\langle \vec{\alpha}(0) \vec{\alpha}(t) \rangle = \langle \vec{\alpha}^{\circ}(0) \vec{\alpha}^{\circ}(t) \rangle + \sum_{\mu} \langle \vec{\alpha}^{\mu}(0) \vec{\alpha}^{\mu}(t) \rangle \langle q^{\mu}(0) q^{\mu}(t) \rangle.$$

Now, the time dependence of  $\vec{\alpha}^{\circ}$  and  $\vec{\alpha}^{\mu}$  was supposed to arise, if at all, through molecular reorientation. But  $\vec{\alpha}^{\circ}$  and  $\vec{\alpha}^{\mu}$  are, by definition, rotational invariants (since the trace of a matrix is invariant under rotation). Thus  $\vec{\alpha}^{\circ}$  and  $\vec{\alpha}^{\mu}$  are constant in time, and we may write

$$\langle \vec{\alpha}(0) \vec{\alpha}(t) \rangle = \langle (\vec{\alpha}^{\circ})^2 \rangle + \sum_{\mu} \langle (\vec{\alpha}^{\mu})^2 \rangle \langle q^{\mu}(0) q^{\mu}(t) \rangle. \quad \dots (2.9)$$

Use of the thermal averages (2.6') and (2.9) in (2.4) yields

$$I_{\text{iso}}(\omega) = \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \left\{ \langle (\vec{\alpha}^{\circ})^2 \rangle + \sum_{\mu} \langle (\vec{\alpha}^{\mu})^2 \rangle \langle q^{\mu}(0) q^{\mu}(t) \rangle \right\} \quad \dots (2.4'a)$$

$$\begin{aligned} \text{and } I_{\text{anis}}(\omega) &= \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \left\{ \frac{1}{10} \text{Tr}[\vec{\beta}^{\circ}(0) \cdot \vec{\beta}^{\circ}(t)] \right. \\ &\quad \left. + \sum_{\mu} \langle \frac{1}{10} \text{Tr}[\vec{\beta}^{\mu}(0) \cdot \vec{\beta}^{\mu}(t)] \rangle \langle q^{\mu}(0) q^{\mu}(t) \rangle \right\} \dots (2.4'b) \end{aligned}$$

The terms involving equilibrium polarisabilities ( $\bar{\alpha}^{\circ}, \bar{\beta}^{\circ}$ ) correspond to Rayleigh scattering. In the present approximations, the isotropic Rayleigh scattering is elastic, since the Fourier transform of the time - constant  $\langle (\bar{\alpha}^{\circ})^2 \rangle$  is proportional to  $\delta(\omega)$ . The anisotropic Rayleigh scattering, however, is reorientationally broadened, because of the time dependence of  $\bar{\beta}^{\circ}$  which arises through reorientation. The scattering terms involving polarisability derivatives ( $\bar{\alpha}^{\prime}, \bar{\beta}^{\prime}$ ) correspond to vibrational Raman lines, the anisotropic components of which are broadened in a similar manner by reorientation. It might thus seem a matter of indifference, whether one attempts to study reorientation through Raman or through Rayleigh lineshapes. It will be recalled, however, that the above results presume the absence of angular correlations among neighbouring molecules, which, we have conceded, is a slender reed to lean on. Had we allowed for such correlations, cross terms between the polarisabilities of different molecules would have survived the process of ensemble averaging; the correlation functions which appear in (2.4') would represent only the "self" terms of a sum over all pairs of molecules. The appropriate generalization of (2.4') would include also the "distinct" terms, for each of which, the product occurring in every angular bracket of (2.4') is taken between quantities evaluated on two distinct molecules. At this point, a crucial difference can be discerned between the Raman and Rayleigh terms. It may still be argued that the distinct Raman terms vanish. Each such term contains a factor  $\langle q_i^{\prime}(0) q_j^{\prime}(t) \rangle$ , where  $i$  and  $j$  are distinct particle subscripts; this factor vanishes if, as might be expected, the vibrational phases of different molecules

are independent. Any correlation which persists despite the randomising effect of vibrational phases, is bound to be less important than that which infests the Rayleigh terms, on which no redeeming grace descends. Thus, the Raman spectrum will be a more faithful manifestation of the motion of an individual molecule than will the Rayleigh.

Granted that (2.4') holds, at least in regard to the Raman terms on each side of the equations, we focus attention on a single Raman vibrational line corresponding to the  $\mu$ 'th normal mode. So long as this line does not overlap significantly with any other line, we may, without serious inaccuracy, write

$$I_{iso}^{\mu}(\omega) = \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \langle (\alpha^{\mu})^2 \rangle \int_{-\infty}^{\infty} dt \exp(-i\omega t) \langle q^{\mu}(0)q^{\mu}(t) \rangle$$

$$\text{and } I_{anis}^{\mu}(\omega) = \frac{\omega^{(1)}(\omega^{(2)})^3}{2\pi c^4} \cdot \frac{1}{10} \int_{-\infty}^{\infty} dt \exp(-i\omega t) \langle \text{Tr}[\hat{\beta}^{\mu}(0) \cdot \hat{\beta}^{\mu}(t)] \rangle \langle q^{\mu}(0)q^{\mu}(t) \rangle ,$$

where  $I^{\mu}$  denotes the truncated spectrum obtained by taking the actual scattering spectrum in some interval around the modal vibration frequency in question - large enough to include any measurable structure of this line, but small enough to exclude that of any other line - and by letting the spectrum vanish outside this interval. If we ignore the slow variation of  $\omega^{(2)}$  within the interval, and regard the factors in front of the integrals as constants, then the spectra are evidently, within a multiplicative constant, Fourier transforms of the correlation functions occurring in the integrands, and conversely, the latter are, within a constant, inverse transforms of the spectra:

$$\hat{I}_{iso}^p(t) \sim \langle q^p(0) q^p(t) \rangle \quad \dots (2.10a)$$

and 
$$\hat{I}_{anis}^p(t) \sim \langle \text{Tr}[\vec{\beta}^p(0) \cdot \vec{\beta}^p(t)] \rangle \langle q^p(0) q^p(t) \rangle, \quad \dots (2.10b)$$

where 
$$\hat{I}(t) \equiv \int_{-\infty}^{\infty} d\omega \exp(i\omega t) I(\omega).$$

Defining the "reorientational spectrum"  $I_{or}(\omega)$  by the relation

$$\hat{I}_{or}^p(t) \sim \langle \text{Tr}[\vec{\beta}^p(0) \cdot \vec{\beta}^p(t)] \rangle \quad \dots (2.11)$$

(the nomenclature is motivated by the orientation dependence of  $\vec{\beta}$ ), we have from (2.10),

$$\hat{I}_{or}^p(t) \sim \hat{I}_{anis}^p(t) / \hat{I}_{iso}^p(t). \quad \dots (2.12a)$$

The corresponding relation in the frequency domain, by the Fourier deconvolution theorem, is

$$I_{anis}^p(\omega) \sim I_{iso}^p(\omega) * I_{or}^p(\omega), \quad \dots (2.12b)$$

where \* denotes the folding operation.

Either of equations (2.12), together with (2.5), provides a way to extract  $I_{or}^p$ , and the attendant information about molecular reorientation, from the data ( $I_{||}$  and  $I_{\perp}$ ) which are available experimentally.

Having accomplished the separation of rotational from vibrational line broadening, we consider the effect of any other broadening influences, such as intermolecular collisions, which may be operative. An approach occasionally adopted<sup>8,9</sup> is to assume that non-reorientational broadening processes are statistically independent of the vibration

and reorientation, and that they contribute equally to the isotropic and anisotropic scattering. The effect of such processes is represented by modifying the polarisability derivatives ( $\bar{\alpha}^p, \bar{\beta}^p$ ) by a multiplicative factor  $f(t)$ . With  $f(t)$  taken to be uncorrelated with  $q^p(t)$  and with orientation, (2.10) would be replaced by

$$\hat{I}_{iso}^p(t) \sim \langle q^p(0)q^p(t) \rangle \langle f(0)f(t) \rangle$$

and 
$$\hat{I}_{anis}^p(t) \sim \langle \text{Tr}[\bar{\beta}^p(0) \cdot \bar{\beta}^p(t)] \rangle \langle q^p(0)q^p(t) \rangle \langle f(0)f(t) \rangle,$$

and (2.12) would follow as before. This method is not rigorous; one must therefore hope that non-reorientational broadening mechanisms are of secondary importance. The approach has, however, at least an instructive value, in that it emphasises the unique status of reorientation as the only broadening process under which  $\bar{\alpha}^p$  may be expected to remain invariant. It is this feature which, in principle, enables a relatively simple separation of the reorientational spectrum.

#### IV. Rotational Diffusion -

##### Derivation of Diffusion Constants from Lineshapes:

Through equations (2.12) and (2.5), we have demonstrated the possibility of determining the reorientational spectrum from experiment. Our next objective is to use the information in the spectrum, quantitatively to characterise the reorientational motion itself. This will be accomplished through the derivation of rotational diffusion constants in terms of the linewidths of reorientational spectra.

From equation (2.11), and by our assumption that  $\bar{\beta}^p$  depends only on molecular orientation, it is evident that  $\hat{I}_{or}(\omega)$  is determined in principle, once we have statistical knowledge of the time development of the angular distribution for an ensemble of molecules. The problem

of describing this time development is amenable to analysis if one considers that each molecule undergoes a large number of random rotations in any macroscopic time interval. Descriptions of molecular reorientation that conform to this pattern of motion are referred to as rotational Brownian motion models, in correspondence with the familiar case of microscopic translational motion in fluids, which likewise proceeds in random steps. Reorientation models in this category, which further stipulate that the individual angular steps are of small size, are more specifically designated as rotational diffusion models. This is because an ensemble of molecules, all prepared in the same initial orientation, and undergoing small-step rotational Brownian motion, will tend in the course of time to spread out in Euler angle space, in much the same way as particles undergoing translational Brownian motion tend to diffuse in ordinary space. In the case of translational Brownian motion, the size of individual step is immaterial to the nature of the motion - a change in the size of step affects only the length scale on which the phenomenon is viewed, without changing the equations that govern the motion. In the rotational case, however, a large step size results in a qualitatively different description of the motion, as compared with a small step size. That this difference might be expected, is suggested by the fact that angles are dimensionless quantities, so that a "large" angle cannot be made equivalent to a "small" angle by a change of scale.

Treatments of rotational Brownian motion which allow for large step sizes, have been offered<sup>10,11</sup> in the literature. These theories reproduce the results of rotational diffusion models in the small-step limit, and give at least formal solutions of the time development of the angular distribution, for arbitrary step size. They do not,

however, provide a simple interpretation of the motion on the basis of lineshape parameters, when they are applied to cases intermediate between the diffusion limit and the "free" (unhindered) rotation limit. The theory of Reference 11., moreover, is readily applicable only to linear and spherical top molecules. Accordingly, the following discussion will be confined to small-step diffusion.

A definitive treatment of rotational diffusion is given by Favro<sup>12</sup>, who derives a quantum-statistical diffusion equation for anisotropic rotational motion, that is analogous to the classical Fokker-Planck equation for translational Brownian motion. Favro obtains,

$$\frac{\partial}{\partial t} P(\vec{\Omega}, t) = - \sum_{jk} \hat{M}_j D_{jk} \hat{M}_k P(\vec{\Omega}, t). \quad \dots (2.13)$$

Here,  $P(\vec{\Omega}, t) d^3\Omega$  is the probability at time  $t$ , of finding a randomly chosen member of an ensemble of similar rigid bodies undergoing rotational diffusion, to be in the volume element  $d^3\Omega$  of Euler angle space. Also,  $\hat{M}_i$  is the  $i$ 'th component of the "rotation" operator, which is related to the quantum-mechanical angular momentum operator  $\hat{L}_i$  for a representative rotor, by

$$\hat{M}_i = \hbar^{-1} \hat{L}_i \quad \dots (2.14)$$

The  $D_{jk}$  form the components of the "diffusion tensor", defined by

$$D_{jk} \equiv \frac{1}{2\tau} \langle \epsilon_j \epsilon_k \rangle, \quad \dots (2.15)$$

where  $\epsilon_i$  is the angular excursion about the  $i$ 'th axis executed in the time  $\tau$ , and where  $\langle \rangle$  denotes an ensemble average. (It is assumed that  $\langle \epsilon_j \epsilon_k \rangle$  is proportional to  $\tau$  for sufficiently long  $\tau$ , so that the  $D_{jk}$  are well defined. Also, it is assumed that a "sufficiently long"  $\tau$  is



still short enough, that the  $\epsilon_i$  remain essentially infinitesimal: the tensor transformation properties of the  $D_{jk}$  then follow from the vector character of small rotations  $\vec{\epsilon}$ .) The designation of the  $D_{jk}$  as "diffusion constants" is motivated by the relation, similar to (2.15), which holds for translational diffusion constants.<sup>13</sup>

To solve the angular distribution  $P(\vec{\Omega}, t)$ , one seeks a Green's function or "evolution" function for (2.13), which will generate  $P(\vec{\Omega}, t)$  from a known initial distribution  $P(\vec{\Omega}, 0)$ . In terms of the Green's function  $G$ , one writes

$$P(\vec{\Omega}, t) = \int d^3\Omega' P(\vec{\Omega}', 0) G(\vec{\Omega}'|\vec{\Omega}, t). \quad \dots(2.16)$$

Physically, one may expect a suitable  $G$  to exist, if the following superposition principle obtains: that the probability, that a rotor with given orientation  $\vec{\Omega}'$  at time 0, will have reoriented into  $d^3\Omega$  at time  $t$ , is independent of the initial angular distribution  $P(\vec{\Omega}', 0)$ . For, then one may compute independently the contribution to  $d^3\Omega$  at time  $t$ , from the population of each element  $d^3\Omega'$  at time 0, as implied by (2.16).

Now, if (2.16) is to hold for arbitrary  $P(\vec{\Omega}', 0)$ , then it is readily seen that, for any fixed  $\vec{\Omega}''$ ,  $G(\vec{\Omega}''|\vec{\Omega}, t)$  must be a solution of the diffusion equation (2.13). This is shown by setting  $P(\vec{\Omega}', 0)$  equal to  $\delta(\vec{\Omega}' - \vec{\Omega}'')$  in (2.16): then,

$$P(\vec{\Omega}, t) = \int d^3\Omega' \delta(\vec{\Omega}' - \vec{\Omega}'') G(\vec{\Omega}'|\vec{\Omega}, t) = G(\vec{\Omega}''|\vec{\Omega}, t).$$

Since  $P(\vec{\Omega}, t)$  is a solution of (2.13) so is  $G(\vec{\Omega}''|\vec{\Omega}, t)$  for arbitrary  $\vec{\Omega}''$ .

Let us suppose that the operator

$$\hat{A} = \sum_{j,k} \hat{M}_j D_{jk} \hat{M}_k$$

possesses a complete orthonormal set of eigenfunctions  $\psi_n(\vec{\Omega})$ , with corresponding eigenvalues  $\lambda_n$ . Then, for fixed  $\vec{\Omega}'$  and  $t$ ,  $G(\vec{\Omega}'|\vec{\Omega}, t)$  may be expanded in the  $\psi_n(\vec{\Omega})$ :

$$G(\vec{\Omega}'|\vec{\Omega}, t) = \sum_n c_n(\vec{\Omega}', t) \psi_n(\vec{\Omega}). \quad \dots (2.17)$$

Since  $G(\vec{\Omega}'|\vec{\Omega}, t)$  must satisfy (2.13), one may write

$$\begin{aligned} \sum_n \left[ \frac{\partial}{\partial t} c_n(\vec{\Omega}', t) \right] \psi_n(\vec{\Omega}) &= - \sum_n c_n(\vec{\Omega}', t) \hat{A} \psi_n(\vec{\Omega}) \\ &= - \sum_n [\lambda_n c_n(\vec{\Omega}', t)] \psi_n(\vec{\Omega}). \end{aligned}$$

By the orthogonality of the  $\psi_n$ , it is possible to equate their coefficients term-by-term:

$$\frac{\partial}{\partial t} c_n(\vec{\Omega}', t) = -\lambda_n c_n(\vec{\Omega}', t).$$

Hence, 
$$c_n(\vec{\Omega}', t) = c_n^0(\vec{\Omega}') e^{-\lambda_n t}.$$

Substitution into (2.17) yields

$$G(\vec{\Omega}'|\vec{\Omega}, t) = \sum_n c_n^0(\vec{\Omega}') e^{-\lambda_n t} \psi_n(\vec{\Omega}). \quad \dots (2.17')$$

The  $c_n^0(\vec{\Omega}')$  are to be determined from the initial condition, that  $P(\vec{\Omega}, t) \rightarrow P(\vec{\Omega}, 0)$  as  $t \rightarrow 0$ , for arbitrary  $P(\vec{\Omega}, 0)$ . By (2.16), this condition will require