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EDITOR'S ANNOUNCEMENT.

'Advances in Molecular Relaxation Processes' was first published in November 1967 and will shortly commence its tenth year of publication.

In 1973, as a consequence of suggestions from authors and advice from the Editorial Board, it was decided to widen the coverage of this journal to include papers based on static equilibrium studies. In practice it has been found that the wider scope of the journal has attracted, in the main, authoritative papers based on molecular interaction processes.

In these circumstances, it has been decided to recognize this trend by changing the name of the journal to "Advances in Molecular Relaxation and Interaction Processes". (This new name will appear on the journal starting with the first issue of Volume 10.)

General inflation and, in particular, the large increase in printing production costs, have necessitated a change in the format of the journal. Authors are asked to note that, in future, papers submitted for publication should be prepared in the form of camera ready copy typescript. Full details are given in the General Information section of this issue.

W.J.ORVILLE-THOMAS.

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AN EXPERIMENTAL STUDY AND CLASSICAL TREATMENT OF THE FAR INFRA-RED INDUCED DIPOLAR ABSORPTION IN GASEOUS ETHYLENE

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ABSTRACT

The far infra-red absorption spectrum of the compressed gas ethylene has been measured in the region 10-200 cm^{-1} at pressures from 14.7 to 55.7 bar at 296 K. The origin of the broad bands observed is a bimolecular collision induced absorption as indicated by the dependence of the total integrated intensity on the square of the molecular number density. The quantum theory [6] of resonant, multipole induction, giving rise to sets of rotational transitions is an inadequate description of the observed broad continua, the peaks of which shift from 125 cm^{-1} to 150 cm^{-1} over the pressure range investigated. However, they are matched satisfactorily by a spectral function $c(\omega)$, generated from an approximation to its related classical autocorrelation function $c(t)$, containing two equilibrium averages $K_o(o)$ and $K_1(1)$ (which are related to the coefficients in the Maclaurin expansion of $c(t)$); and a width parameter γ. All three phenomenological parameters vary with pressure, contrary to the quantum prediction of their constancy, and go through a smooth minimum at ca. 30 bar, where the correlation time τ is longest.

INTRODUCTION AND THEORETICAL CONSIDERATIONS

Non-dipolar molecular gases absorb in the far infra-red frequency region (1-400 cm^{-1}) because the fields of neighbouring molecules induce a temporary dipole in bimolecular or higher order collisions. However, an atomic gas will not absorb because of the centro-symmetry of a two sphere encounter. Mixtures of inert gases and molecules show a very broad far infra-red band [1] in which the integrated absorption intensity is proportional to powers of the number density (N); N^2, for example, indicating a predominance of bimolecularly induced moments.

Using a quantum approach, Van Kranedonk [2] and others [3] initiated theoretical studies on these absorptions in the fifties. A fundamental approximation [2] involved dividing the induced dipole moment into two parts: an isotropic part due to overlap moments at short distances, and an anisotropic part (resulting from the long-range effect of the electric multipole moments [4]) giving rise to rotational transitions. The non-resonant part, due to close collisions, tends to affect the higher frequency end of the spectrum [5], since the short time behaviour of the correlation function [6] is involved. The theory has been reviewed by Foley [7] and is available for linear [3], spherical top [8] and symmetric top molecules.

Basic assumptions in this quantum treatment restrict its general validity and applicability:

(i) A rotational Eigenstate of the interacting pair is taken as the product of those of each molecule, which is accurate only for an intermolecular potential U(R) depending only on the intermolecular separation R. Angle dependent contributions (e.g. the quadrupole-quadrupole [5]) cannot be considered. Therefore, the theory is strictly valid for spherically symmetric molecules only.

(ii) It produces a set of discrete lines ($J \rightarrow J + n$, $K = \pm \Delta J$, where n is integral and J and K are the rotational quantum numbers). Observed absorptions are broad bands for all molecules except H_2 and possibly the hydrogen halides [10].

For oxygen [1], cyanogen [5], and ethylene (this work) the representation of the band in terms of sets of $J \rightarrow J + 2$ lines (quadrupole induced dipole absorption) is particularly disappointing, the theory predicting a frequency of maximum absorption ($\bar{\nu}_{max}$) lower than actually observed. Thus the limitations of the quantum model are reached for relatively simple molecules.

In this work we consider a classical rotational mechanism of absorption (so that any translational mode absorption [1-3] is not treated explicitly) and generate a broad band using a suitable approximation to its classical autocorrelation function, c(t). This is naturally one of both molecular orientation and interaction. Our expression for the band contour contains three phenomenological parameters, two equilibrium averages $K_o(o)$ and $K_1(1)$ having the units of s^{-2}, together with a frequency parameter γ. The former two are related to terms in the Maclaurin series for c(t) and are dependent on a spatial average of U(R) (and thus on its derivative with respect to angular displacement - the torque on a given molecule). The latter is a width parameter, γ^{-1} being related to the duration of a collision.

Spectral contours (continua) generated by this model are l.m.s. fitted to experimental f.i.r. data on compressed ethylene up to 55.8 bar at 296 K. The parameters $K_o(o)$, $K_1(o)$ and γ vary with pressure, each going through a minimum at ca. 30 bar. The contour of the $J \rightarrow J + 2$ lines of the quantum theory is determined solely by Maxwell-Boltzmann statistics, and is independent of U(R) and also pressure. Experimentally this is not observed; had it been so there would be constancy in the parameters of the classical model. However, the quantum model does allow an order of magnitude estimate of the molecular quadrupole moment (Q) of ethylene, to be made.

The classical c(t) and its approximation

The general relation between a correlation function and its spectral function c(ω) is:

$$c(t) = \int_0^{\infty} \cos \omega t \; d\, c(\omega) \qquad (1)$$

This equation is applicable to rotational absorptions provided that the molecular orientational fluctuations are continuous, random, and independent of time.

The small, temporary, induced molecular dipole in a system of non-dipolar molecules can be written as:

$$\underset{\sim}{\mu}(t, \sum_i \sum_{n=2}^{\infty} \tilde{\tilde{A}}_{i}, \underset{\sim}{R}_i^{-n}) \qquad (2)$$

where there are (i+1) molecules present, and where the effect of the molecular fields is summarised by the multipoles $\tilde{\tilde{A}}$ i, n. A correlation function for the ensemble can now be defined as:

$$c(t) = \sum_{ij} < \underset{\sim}{\mu}_i(o) . \underset{\sim}{\mu}_j(t) > \tag{3}$$

the brackets denoting averaging over all (p,q) space. The correlation is between the magnitude and direction of the resultant $\underset{\sim}{\mu}_i$ at t = o and $\underset{\sim}{\mu}_j$ at a time t later. The classical correlation function is an equilibrium, even function of time [1], and its Maclaurin expansion is in even powers of t. We include correlations between the induced dipoles on different molecules (i.e. the cross-correlations) in eqn. 3.

The correlation function c(t) can be represented in terms of an integro-differential equation by Kubo's [12] general theory.

$$\dot{c}(t) = - \int_o^t K(t-\tau)c(\tau)d\tau \tag{4}$$

where K (the memory function) is defined by:

$$\sum_{ij} < \underset{\sim}{\mu}_i(o) . \mu_j(o) > K(t) = \sum_{ij} < F_i(o) . F_j(t) >$$

F being the fluctuating torque on a molecule originating from the motions of other molecules. By making K(t) a suitable empirical function, it is possible to calculate c(t), and thus c(ω), analytically. A particularly useful representation is that of Mori [13], who showed that the set of memory functions $K_o(t)$, ..., Kn(t) obey a set of coupled Volterra equations:

$$\frac{\partial}{\partial t} K_{n-1}(t) = - \int_o^t K_n(t-\tau) K_{n-1}(\tau) d\tau \tag{5}$$

with n = 1, ..., N.

Upon taking Lapace transforms this yields:

$$C(p) = \frac{C(o)}{p+K_o(p)} = \frac{C(o)}{p+\frac{K_o(o)}{p+K_1(p)}} \tag{6}$$

C(ω) is the Fourier-Laplace transform of C(p) and can be generated from a simple approximation to $K_N(p)$. The first order truncation:

$$K_1(p) = K_1(o) \exp(- \gamma t) \tag{7}$$

ensures evenness in $C(t)$ up to t^5, while also keeping down the number of phenomenological zero time terms $K_N(o)$ to two: $K_o(o)$ and $K_1(o)$. The correlation function is now:

$$C(t) = \frac{\cos(\beta t)}{1 + \Gamma} + \frac{1}{\beta}\,\frac{\alpha_1 + \Gamma\alpha_2}{1 + \Gamma}\,\sin\beta t\,\exp(-\alpha_1 t) + \frac{\Gamma}{1 + \Gamma}\exp(-\alpha_2 t) \tag{8}$$

where $\Gamma = \dfrac{2\alpha_1(2\beta^2 - \alpha_1^{\,2})}{\alpha_2(3\alpha_1^{\,2} - \beta^2 - \alpha_2^{\,2})}$, with:

$$\alpha_1 = -S_1 - S_2 + \gamma/3; \quad \alpha_2 = \tfrac{1}{2}(S_1 + S_2) + \gamma/3;$$

$$\beta = \frac{\sqrt{3}}{2}(S_1 - S_2).$$

The parameters S_1 and S_2 are defined by:

$$S_1 = \left[-\frac{B}{2} + \left(\frac{A^3}{27} + \frac{B^2}{4}\right)^{1/2}\right]^{1/3}$$

$$S_2 = \left[-\frac{B}{2} - \left(\frac{A^3}{27} + \frac{B^2}{4}\right)^{1/2}\right]^{1/3}$$

where $A = K_o(o) + K_1(o) - \gamma^2/3$

$$B = \frac{\gamma}{3}\left(\frac{2\gamma^2}{9} + 2K_o(o) - K_1(o)\right).$$

The correlation time, τ_c, is now given as:

$$\tau_c = \sum_{ij}\int_o^\infty \langle \underset{\sim}{\mu}_i(o).\,\underset{\sim}{\mu}_j(t)\rangle\,dt = \frac{1}{1+\Gamma}\left(\frac{2\alpha_1 + \Gamma\,\alpha_2}{\alpha_1^{\,2} + \beta^2} + \frac{\Gamma}{\alpha_2}\right) \tag{9}$$

The complex spectral function, $C(\omega)$, is obtained by Fourier-Laplace inversion:

$$C(\omega) = \frac{K_1(o) - \omega^2 - i\omega\gamma}{i\omega^3 - \omega^2\gamma - i\omega(K_1(o) + K_o(o)) + \gamma K_o(o)}$$

The far infra-red absorption is conveniently described in terms of the optical absorption coefficient per unit path length of absorber, $\alpha(\omega)$, which has the units of neper cm^{-1}, by the Beer-Lambert law, and is linked to the real part of $C(\omega)$ as follows:

$$\alpha(\omega) = \frac{(\varepsilon_o - \varepsilon_\infty)\Lambda}{n(\omega)\, C} \omega^2 \text{Real}\left[C(\omega)\right]$$

$$\text{with Real}\left[C(\omega)\right] = \frac{K_o(o)K_1(o)\gamma}{\gamma(K_o(o) - \omega^2)^2 + \omega^2\left(\omega^2 - (K_o(o) + K_1(o))\right)^2}$$

Therefore $\alpha(\omega)$ is asymptotic as ω^{-4} at high frequencies; Λ is an internal field correction [14], which is approximately unity for gases, but of more significance in the case of liquids. $(\varepsilon_o - \varepsilon_\infty)$ is the total dispersion, equivalent, through the Kramers-Krönig relations, to the total absorption, and $n(\omega)$ is the frequency dependent refractive index, again close to one for gases.

Relation with the classical limit of the quantum theory

From the general theory [9] of pressure induced absorption, it can be shown [15] that for bimolecular, quadrupole-induced absorption in linear molecules, $C(t)$ is given in the classical limit (i.e. for the contour of $J \to J + 2$ set of lines) by:

$$C(t) = \chi_o \int_o^\infty f(\bar{\nu}) \int_o^\infty 4\pi R^{-6} \exp(-U(R)/kT)\, dR \cos(2\pi\bar{\nu}ct)\, d\bar{\nu} \qquad (11)$$

where

$$f(\bar{\nu}) = \left(\frac{\bar{\nu}}{2B} - \frac{2B}{\bar{\nu}}\right) \exp\left(-\frac{hcB}{4kT}\left(\frac{\bar{\nu}}{2B} - 3\right)\left(\frac{\bar{\nu}}{2B} - 1\right)\right)$$

with χ_o a constant and B the rotational constant (in cm^{-1}). $U(R)$ is radially averaged in the above equation. If we define:

$$C(t) = \sum_{n=o} (-1)^n M_{2n} \frac{t^{2n}}{(2n)!} \qquad (12)$$

$$= \sum_{ij} \langle \underset{\sim}{\mu}_i(o) . \underset{\sim}{\mu}_j(t) \rangle$$

we have, by stationary properties in time:

$$M_{2n} = \left\langle \left(\frac{d^n \underset{\sim}{\mu}}{dt^n} \right)^2 \right\rangle \tag{13}$$

$$\propto \int_0^\infty \alpha(\omega)\, \omega^{2n-2}\, d\omega \tag{14}$$

with $\omega = 2\pi\bar{\nu}c$ the angular velocity in rad s^{-1},
thus

$$m_2 \propto \chi_a . \int_0^\infty f(\bar{\nu}) \int_0^\infty 4\pi R^{-6} \exp(-U(R)/kT)\, dR\, d\bar{\nu} \,. \tag{15}$$

From equations (12) and (4), it follows that K(t) must also have an even powered Maclaurin series and, in particular, it follows that:

$$K_o(o) = M_2,\ K_1(o) = M_2 + \frac{M_4}{M_2} \,. \tag{16}$$

From equations (15) and (16), it is clear that both $K_o(o)$ and $K_1(o)$ are dependent on the radial average of U(R) in this particular case of bi-molecular impacts of linear molecules. It is also apparent that $K_o(o)$, $K_1(o)$ and γ should not vary with pressure in the classical limit of the quantum theory since the J→J + 2 contour does not change with number density - the intensity of each line varies simply as N^2. However, we find experimentally that the observed contour does change with number density - invoking a resultant variation in the classical $K_o(o)$, $K_1(o)$ and γ. Thus the real U(R) is pressure dependent.

Physical interpretation of the first order truncation

It is well known [16] that the simplest model $K(p) = \gamma$, or $K(t) = \gamma\delta(t)$, where $\delta(t)$ is a delta function, neglects all dynamical coherence, i.e. does not take account of molecular inertia. It is a model involving a randomisation of molecular orientation, the correlation function (being exponential) having a term in t. The 'zeroth order" truncation $K_o(p) = K_o(o) \exp(-\gamma t)$ leads to a correlation function even up to t^2, and corresponds [16] to the randomisation of the molecular angular velocity vector in direction at each elastic collision - the M diffusion model.

The torque goes to infinity at each impact, and therefore is not defined at all t. Analogously, the first order termination used here is physically equivalent to a randomisation of the direction of the molecular angular acceleration vector at each collision, the torque derivative now having singularities, the correlation function being even up to t^5.

EXPERIMENTAL

Far infra-red absorption spectra were obtained using a Grubb Parsons, N.P.L., amplitude modulated cube interferometer at an instrumental resolution of 4 cm^{-1}. The original air-cooled lamp housing was replaced by a more efficient water-cooled unit.

Samples of pure ethylene were contained in a high pressure variable path length cell [9] with Z cut crystalline quartz windows 7 mm thick. T.P.X. (poly 4-methylpent-1-ene) windows were used for work in the 100-200 cm^{-1} region, where strong quartz bands occur. Individual spectra were obtained by ratioing the mean of three transformed interferograms at a cell path length of 14.3 mm (the limit of the cell) to the mean of three transformed interferograms at zero path length. This system, though adequate above 28.4 bar, needed modifications at lower pressures. Absorptions below 28.4 bar were measured with a fixed path length cell (137.6 mm) comprised of a gold-plated copper light pipe with T.P.X. windows embedded in a stainless steel sheath. The cell was evacuated to *ca*. 10^{-2} torr to provide background interferograms.

The cells were prepared by purging repeatedly with dry nitrogen, followed by evacuation to a few millibars, together with heating to greater than 373K to remove adsorbed moisture (which absorbs strongly in this frequency range). Matheson CP grade (99.5 p.c.) ethylene was used after purification by several freeze-pump-thaw cycles to remove volatile impurities.

Uncertainty in the molecular number density (N) arises in part from the uncertainty in the Budenberg gauge reading and from uncertainty in the experimental [17] compressibility factors (Z). An estimated uncertainty in N being ± 3%. The scatter in $\alpha(\bar{\nu})$ is mainly electronic noise arising from the amplification required to overcome the absorption of radiation by the windows. An estimated uncertainty in the integrated intensity, defined by:

$$A_1 = \int_{\text{band}} \alpha(\bar{\nu})\,d\bar{\nu}$$

is then evaluated at ± 10%, where $\alpha(\bar{\nu})$ is the absorption coefficient in units neper cm^{-1}.

RESULTS AND DISCUSSION

The far infra-red spectra of ethylene at pressures from 14 to 56 bar are illustrated in Fig. 1. The line spectrum is that of the rotational $J \rightarrow (J + 2)$ absorptions predicted using Frost's quantum equation [6] for quadrupole-induced dipole absorption in symmetric top molecules, ethylene being approximately one of these ($A_o = 4.828$ cm^{-1} $B_o = 1.0012$ cm^{-1} $C_o = 0.8282$ cm^{-1}). The experimental data were fitted using equation (10) in a least mean squares algorithm, and the optimum values of $K_o(o)$, $K_1(o)$ and γ at each pressure are plotted in Fig. 2.

The integrated absorption intensity, A_1, was obtained from the area under these least mean square curves, and is plotted vs. N^2 in Fig. 3. The frequency of maximum absorption ($\bar{\nu}_{max}$) moves from about 125 cm^{-1} to 150 cm^{-1} from 14 bar to 56 bar, a shift which cannot be followed by the set of $J \rightarrow J + 2$ transitions, or by the classical M diffusion model. Neither of these models deals adequately with the changing nature of the intermolecular mean torque. The former employs the same radial U(R) at all pressures (i.e. the torque is constant) and the latter cannot move the position of $\bar{\nu}_{max}$ since the reorientation of the molecular angular momentum is assumed to take place during an infinitely short time, making no allowance for the concept of a finite and continuous torque.

Equation (10) is a more realistic model of the intermolecular forces and dynamics, which Fig. 3 shows to be predominantly bimolecular. The parameters $K_o(o)$ and $K_1(o)$ are related to the intermolecular potential averaged over orientations and angular velocities, and vary significantly (Fig. 2) even over our restricted range of number density. All three (including γ) go through a distinct minimum at <u>ca</u>. 32 bar, the correlation times going through a maximum at this same pressure (Table 1). This seems to imply that the collisions are longer lived at this number density and are at their most inelastic. We can say, since we deal only with the rotational dynamics, that a maximum amount of translational

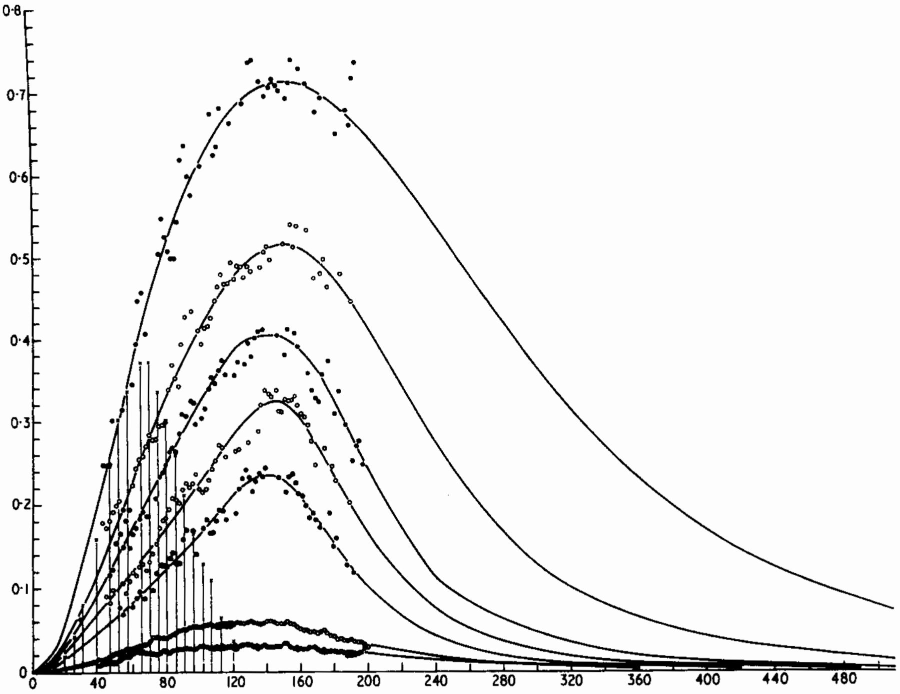

Fig. 1. Far infra-red absorption of compressed gaseous ethylene at 296K.
O Experimental: from top to bottom, 55.8 bar, 48.9 bar, 42.1 bar, 35.2 bar, 28.4 bar, 21.5 bar and 14.7 bar.
— Equation (1) least mean squares best fit, with the parameters of Fig. 2. The vertical bars represent the relative intensities of some of the J→J + 2 lines predicted by the quantum mechanical model of quadrupole induced absorption in a bimolecular collision of symmetric top molecules.
<u>Ordinate</u>: α/neper cm^{-1}; abscissa: $\bar{\nu}/cm^{-1}$.

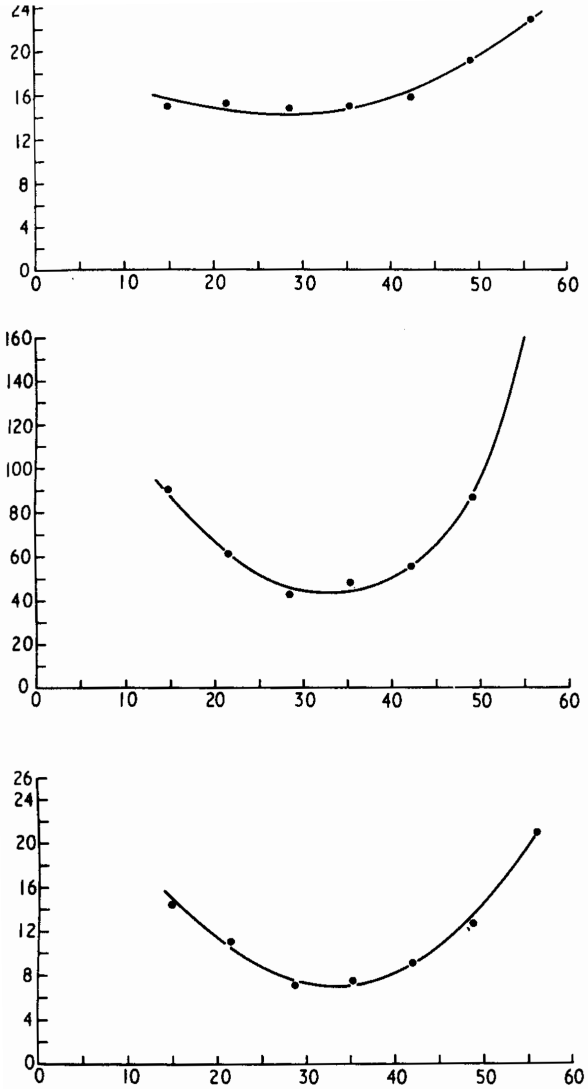

Fig. 2.

(a) Variation of $K_o(o)$ with pressure.
Ordinate: $K_o(o) / \frac{2kT}{I_B}$; abscissa: pressure/bar.

(b) Variation of $K_1(o)$ with pressure.
Ordinate: $K_1(o) / \frac{2kT}{I_B}$; abscissa: pressure/bar.

(c) Variation of γ with pressure.
Ordinate: $\gamma / \left(\frac{2kT}{I_B}\right)^{\frac{1}{2}}$; abscissa: pressure/bar.

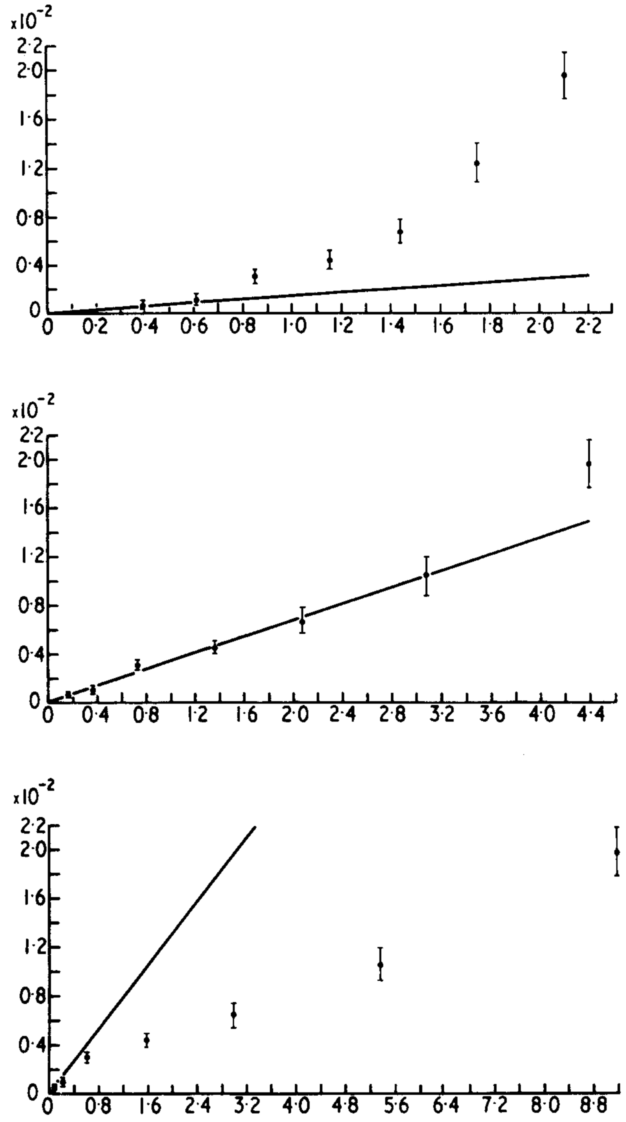

Fig. 3. Plot of integrated intensity A_1 against powers of N, the number dens
(a) A_1 vs. N; (b) A_1 vs. N^2; (c) A_1 vs. N^3.

<u>Ordinates</u>: A_1/neper cm^{-2}. <u>abscissae</u>: (a) 10^{20} N/molecules cm^{-3};
(b) 10^{40} N^2/(molecules cm^{-3})^2;
(c) 10^{60} N^3/(molecules cm^{-3})^3.

TABLE 1

Correlation times and inverse half-widths as a function of number density

PRESSURE (bar)	CORRELATION TIME τ_c/ps	γ^{-1}/ps
14.69	0.718×10^{-13}	0.688×10^{-13}
21.54	0.834×10^{-13}	0.899×10^{-13}
28.39	1.296×10^{-13}	1.40×10^{-13}
35.23	1.269×10^{-13}	1.32×10^{-13}
42.08	1.052×10^{-13}	1.10×10^{-13}
48.93	0.793×10^{-13}	0.79×10^{-13}
55.73	0.53×10^{-13}	0.48×10^{-13}

freedom is lost at this pressure, and dissipated into other modes. The correlation function is damped to zero in less than a ps at each pressure and is never exponential. The correlation time, τ_c, is roughly equal to the duration of collision, since the spectral band is proportional to the Fourier transform of the correlation function of the induced dipole. An estimate of the induced dipole(s) can be obtained by multiplying τ_c (the collision duration) by the average rate of change of the intermolecular distance (R_{AV}), which is defined by:

$$\tfrac{1}{2} m \dot{R}^2_{AV} = kT.$$

Thus p is proportional to τ_c at constant T, suggesting that the range of the induced dipole is a maximum at ca. 30 bar.

A typical correlation function and its associated normalised memory function, K(t), obtained in our present studies, are plotted on the same scale in Fig. 4. the latter is defined by:

$$K(t) = K_o(o) \exp(-\gamma t) \left[\cos at + \frac{\gamma a^{-1}}{2} \sin at\right]$$

$$\text{for } K_1(o) > \gamma^2/4$$

$$= K_o(o)\ \exp(-\gamma t)\left(1 + \gamma t/2\right)$$

for $K_1(o) = \gamma^2/4$

$$= K_o(o)\ \exp(-\gamma t)\left(\cosh bt + \frac{\gamma b^{-1}}{2}\ \sin h\ bt\right)$$

for $K_1(o) < \gamma^2/4$

where $a^2 = -b^2 = (K_1(o) - \gamma^2/4)$.

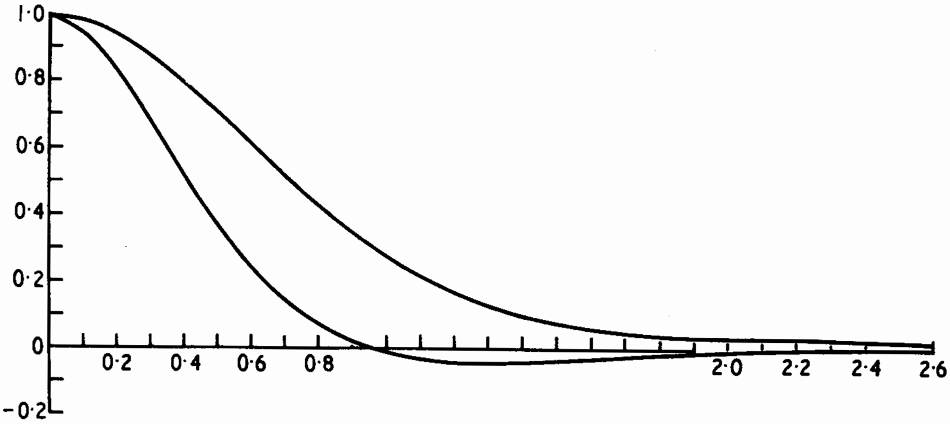

Fig. 4. Plot of C(t)/C(o) and K(t)/K(o) at 21.5 bar.
<u>Ordinate</u>: f(t); <u>abscissa</u>: 10 x time (t)/ps.

Thus K(t), the correlation function of the external random torque is not a pure exponential, and by Doob's theorem, the system is not statistically Markovian, i.e. its future behaviour is dependent on past events. The memory function is damped out to zero in approximately the same time as the correlation function. This suggests that induced dipolar absorption occurs only during the lifetime of the interaction giving rise to it, and therefore the induced dipole, and its corresponding correlation function, disappears.

Despite the obvious (Fig. 1) shortcomings of the quantum mechanical del of J→(J + 2), quadrupole-induced absorption lines, we can estimate order of magnitude for the molecular quadrupole moment of ethylene ing the following Frost equation [6] for symmetric top molecules:

$$A^{Q}_{J\rightarrow J+2} = \frac{4\ \pi^{3}Q^{2}N^{2}}{3hcZ} \int_{o}^{\infty} 4\pi R^{-6}\ \exp(-\ U(R)/kT)dR$$

$$X \sum_{K=-J}^{J} (1 - \exp(-\bar{\nu}hc\ (J)/kT))S(I,K)$$

$$X\ \exp(-\ E_{JK}hc/kT)\bar{\nu}(J)(18\ \alpha_{o}^{2}\ f_{2}(J,K) + \frac{48}{5}\ \delta^{2}f_{2}^{2}(J,K))$$

ere

$$\bar{\nu}(J) = 2B(2J + 3),$$

$$f_{2}(J,K) = \frac{(J-K+2)(J-K+1)(J+K+2)(J+K+1)}{(J+1)(J+2)(2J+3)}$$

th

$$\int_{band} \alpha(\bar{\nu})d\nu = \sum_{J} A^{Q}_{J\rightarrow J+2}\ .$$

re, Z is the rotational partition function given by:

$$\sum_{J}\sum_{K=-J}^{J} g(J,K)\exp(-E_{JK/kT});\quad \text{where}$$

$g(J,K) = (2J + 1)S(I,K)$. The nuclear spin weighting factor is ven by:

$$S(I,K) = {}^{1}/3(2I + 1)(4I^{2} + 4I + 3) \quad \text{for } K = 0;$$

$$= {}^{1}/3(2I + 1)(4I^{2} + 4I + 3) \quad \text{for } K \neq 0;\ = \text{mult. of } 3;$$

$$= {}^{1}/3(2I + 1)(4I^{4} + 4I) \quad \text{for } K \neq 0;\ \neq \text{mult. of } 3.$$

ith I as the nuclear spin quantum number of the off axis nuclei in the mmetric top (taken as those of H for ethylene). The transition energes E_{JK} are given by $BJ(J + 1) + (A - B)K^{2}$ where A (cm^{-1}) is a rotatnal constant orthogonal to B. α_{o} and δ are the mean molecular polarability and the anisotropy of polarisability, respectively. Since the set of J→J + 2 lines generated by the above equation is so far away from the true absorption (Fig. 1), the equation of the respective integrated intensities of both sides is a recondite exercise, but leads to a value of

$$|Q| = 9.9 \times 10^{-25} \text{ e.s.u.}$$

This compares with Kielich's value of 1.3 x 10^{-25} e.s.u. taken from results of techniques unrelated with the far infra-red induced absorption. Until the detailed nature of $K_0(o)$, $K_1(o)$ and γ of equation (10) is better understood, the quantum treatment still retains the advantage of having only a single unknown Q, compared with the three unknowns in the classical model.

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