

FAR INFRA-RED MULTIPOLE INDUCED
ABSORPTION IN COMPRESSED GASEOUS C_2F_6 .

BY

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A C_2F_6 hexadecapole?

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ABSTRACT

The very weak far infra-red collision induced absorption band of hexafluoroethane (C_2F_6) has been detected using a polarising interferometer and a Rollin (He (λ) cooled) In/Sb crystal detector. The absorption, centred at $16cm^{-1}$ (296K) and markedly asymmetric with a high frequency shoulder, is treated in terms of a multipole induced dipole that gives rise to sets of rotational $\Delta J = 2$ (quadrupolar) and $\Delta J = 4$ (hexadecapolar) lines. These were dynamically broadened using the j - diffusion model of Gordon into bands the relative intensities of which were estimated by a self consistent field molecular orbital calculation of the non-zero elements of the quadrupole and hexadecapole moments.

This analysis reproduces the experimental data fairly well, but the calculated cross section is too small. The local charges on each atom of the C_2F_6 molecule estimated with m.o. theory were used to represent its electrostatic field as an alternative to the multipole expansion which tends to diverge at the very short intermolecular distance (R) needed for the R^{-10} hexadecapole field to become effective.

1. INTRODUCTION

Recent advances in theoretical and experimental techniques now make it possible to study the very far infra-red pressure induced rotational bands of relatively heavy and unsymmetrical molecules;¹⁻⁴ (Frost¹ has extended the theory to symmetric top molecules.) The frequency range over which measurements can be made has been extended to near 2cm^{-1} by the use of helium cooled Rollin detectors and a polarising interferometer. Non-dipolar molecules absorb in this region ($2 - 200\text{cm}^{-1}$) because intermolecular electrostatic fields distort the overall symmetry of a given molecule's electron cloud, producing upon "collision" a small dipole moment that changes in magnitude and direction rapidly with time. Thus compressed gaseous mixtures of rare gas atoms absorb, whereas the components when separated and moderately pressurised do not. A pair of colliding helium atoms, for example, will not possess a resultant electronic cloud of dipolar asymmetry, whereas a helium-neon pair will modulate the electromagnetic field over a broad band of far infra-red frequencies commensurate with the most probable frequencies at which interatomic collisions occur.

Atomic induced absorption is of a purely translational origin, a mechanism that persists in molecular fluids such as hydrogen and nitrogen as the absorption $\Delta J = 0$, where J is the rotational quantum number. A dipole moment set up between a pair of colliding molecules will in addition absorb by rotational means since even without relative translation of molecular centres, the effect on each other of their rotatory electrostatic fields will not cancel. A practical means of dealing with these intermolecular absorption mechanisms is to treat them separately. The rotational absorption is dealt with by expanding the field in terms of multipole tensors, which all vanish only in the case of spherical symmetry such as that of atoms.

Pseudo-spherical molecules such as SF₆ retain the higher multipoles (those above the hexadecapole for Oh symmetry), and thus display a weak, rotational induced absorption band at moderately high number densities.² The first non-vanishing multipole in a homogenous diatomic such as N₂ is the quadrupole, which produces a dipole on molecule A which is modulated by the rotational motion of the inducing molecule B. The symmetry of the quadrupole moment is such that it rotates twice as fast as the molecule itself and thus produces quantum absorptions with the selection rule $\Delta J = 2$, in contrast with the $\Delta J = 1$ rule for the rotation of a permanent dipole. Similarly, the first non-zero multipole moment for Td symmetry - the octopole, produces $\Delta J = 3$ absorptions, and the hexadecapole $\Delta J = 4$.

It is important to emphasize that point multipoles are mathematical limits of point charge distributions, and for highly asymmetric molecules may have tenuous links only with physical reality. Furthermore, the range of a hexadecapole field, falling off as R^{-10} (where R is the intermolecular vector) is so short that for it to be effective a pair of molecules would need to have their van der Waals shells nearly overlapping. This necessity tends to undermine the whole basis of the multipole series expansion, which diverges in this region. For this reason, the very concept of a point octopole or hexadecapole induced dipole has been questioned since the experimental evidence is sparse, especially for the latter, and up to now necessarily confined to simple molecules of high symmetry.

In this paper we explore the far infra-red quadrupole and hexadecapole induced band of C₂F₆, a non-dipolar symmetric top molecule for which a small point quadrupole component⁸ Q_{ZZ} and a large hexadecapole component ϕ_{ZZZZ} can be defined mathematically. In the staggered conformation this molecule has D_{3d} symmetry and thus no non-zero elements of the octopole. It has one independent element of the quadrupole and two of the hexadecapole, of which ϕ_{ZZZZ} is the

largest. In the sparsely populated eclipsed conformation, it has some finite elements of all three of the above multipoles. Thus the $\Delta J = 4$ set of transitions should be, ab initio, a major contributor to the high frequency part of the observed band. The formal quantum mechanical equation for hexadecapole - induced dipole absorption in symmetric tops is developed here from the general Frost equation¹, and the set of lines broadened into a band using a version of the j - diffusion model of collisional broadening. Values of Q_{ZZ} and Φ_{ZZZZ} are calculated here by an ab initio self consistent field molecular orbital method and in this way the relative contributions of quadrupole and hexadecapole can be estimated. Due to the continued absence of satisfactory theoretical methods, phenomena such as translational induced absorption (of the rare gas type), and induced absorption due to overlap distortion of electron clouds, have not been treated here explicitly, our main aim being to detect some evidence of a hexadecapole - induced absorption. We furthermore confine our treatment to bimolecular impacts, using measurements at a maximum of less than 20 bar of gas.

EXPERIMENTAL

The power absorption spectra were recorded using a Michelson/N.P.L interferometer modified to operate in the polarizing mode as described by Martin and Puplett [11]. In principle the interferometer is that shown in Figure 3 of the above reference and is reproduced below. (Fig 1)

Polarizer P_1 is a circular grid wound with $10\mu\text{m}$ tungsten wire with $50\mu\text{m}$ spacing*. This grid can be spun about its centre point thus acting as a polarizing chopper blade. P_2 is of similar construction to P_1 but is held in a fixed configuration ie either with the windings perpendicular or horizontal. The beam divider D, is again of similar construction but in this case the windings are at 45° to those of P_2 [12]. The "roof-top" reflecting mirrors were manufactured to be $90^\circ \pm 1'$ arc \neq .

A collimated beam is plane polarized at P_1 in the plane normal to the page. It is then divided by the wire grid polarizer D into a beam A, polarized with its E vector at 45° to the paper and beam B polarized at 90° to A. The "roof-top" reflectors act as polarization rotators and beams A and B are recombined at D. The recombined beam finally passes through polarizer P_2 (the analyzer) which has its axis parallel to or at 90° to that direction. The beam reaching the detector is plane-polarized with an amplitude which varies periodically with path-difference in the same way as the normal Michelson interferometer.

For a monochromatic source that is [11]

$$I_p = I_0/2 [1 + \cos \delta]$$

$$\text{and } I_t = I_0/2 [1 - \cos \delta]$$

where $\delta = (2\pi/\lambda)\chi$, (where χ is the path difference) and I_0 is the intensity of the plane polarized beam incident on D. The case I_p is for parallel P_1 and P_2 and I_t is for crossed P_1 and P_2 .

Polarizing grids have reflection and transmission coefficients close to 100% for their respective planes of polarization [13], from frequencies close to zero up to $1/2d \text{ cm}^{-1}$ where $1/d$ is the spatial frequency of the wires. Grids have the advantage of eliminating "hooping" as found with Mylar or Melinex beamsplitters [14]. The response curve for the interferometer should be flat with frequency falling off at $1/(2d) \text{ cm}^{-1}$. This, however, does not take into allowance the frequency response of the mercury arc lamp which rises with increasing frequency; so although we do not see the full benefits of a flat frequency response at low frequency we do gain over other far infra-red modulation techniques (amplitude and phase modulation) with an increased response at wave numbers $\leq 10 \text{ cm}^{-1}$ plus an increased spectral range with a single beam divider due to the elimination of "hooping".

The interferometer was not evacuable as we were interested in the range $2\text{-}50\text{cm}^{-1}$ where water vapour absorption can be considered negligible, particularly so below 30cm^{-1} which was our main region of interest. The detector was a liquid helium cooled InSb Rollin detector [15]. The resolution was 2cm^{-1} in all cases.

The sample was contained within a specially constructed metre cell with TPX (poly 4 methyl pent-1-ene) windows, placed between P_2 and the detector. Matheson research grade C_2F_6 was used without further purification.

The cell was purged beforehand with a few atmospheres of rare gas until no change in absorption could be registered upon evacuation.

RESULTS AND INTERPRETATION

The absorption of compressed gaseous C_2F_6 is shown in fig (2) at three number densities. It is an asymmetric broad band peaking at about 16cm^{-1} with a marked high frequency shoulder, so that there is a continuing significant contribution at near 40cm^{-1} , the limit of our interferometer. The data are for 4.93, 9.59, and 17.8 bar (10^{-20} N = 1.29, 2.69, and 5.63 molecules cm^{-3} respectively), and the reproducibility between successive runs at the same pressure is satisfactory. The integrated intensities of all three bands are much greater than the $0.002 \pm 0.0008\text{cm}^{-2}$ of a much narrower forbidden a_{1u} torsional vibration mode recently observed¹⁶ in one atmosphere of C_2F_6 at 67.5cm^{-1} : a band from which a barrier to internal rotation of $1333\text{-}1367\text{cm}^{-1}$ (ca. 16 kJ mole^{-1}) was estimated. It is unlikely, therefore, that more than a small fraction of the high frequency wing can be assigned to this intramolecular a_{1u} mode, and furthermore, with such an internal barrier, the C_2F_6 molecules would populate overwhelmingly the staggered conformation at any one instant at ambient temperature of 296K .

Thus it is reasonable to treat the experimental data in the $2-40\text{cm}^{-1}$ range in terms of a mechanism of quadrupole and hexadecapole induced dipole absorption, generated by bimolecular collisions of C_2F_6 molecules in D_{3d} symmetry. The equation linking the observed absorption cross section with the theoretical is thus:

$$A_1 = \int_{\nu_{\text{min}}}^{\nu_{\text{max}}} \alpha(\nu) d\nu = (A^Q + A^\Phi) N^2 \quad \dots\dots 1$$

where A^Q and A^Φ are sums over all J of coefficients defined by Frost¹. A^Q is written out explicitly elsewhere³, and A^Φ is a summation over J of equ. (1A) in the appendix, derived from the general Frost equations. Since A^Q and A^Φ are sums of quantum line absorptions, and the data, in common with nearly all induced absorptions¹⁷ at these pressures and frequencies, are broad bands, a means of collisional line broadening is needed if a meaningful comparison is to be made between theory and experiment. It is important to distinguish this broadening from translationally induced absorption (rare gas type): the former produces no extra absorption of its own but merely gives each $\Delta J = 2$ or $\Delta J = 4$ line a finite half width. Birnbaum et.al. found² the latter to be confined in extent to below 10cm^{-1} in a molecule as light as CO_2 . In the case of C_2F_6 , its contribution would be found at even lower frequencies, out of our range.

The broadening is treated rather simply here in terms of Gordon's naive but very useful j - diffusion model,¹⁸ so that the C_2F_6 molecules are assumed to undergo periods of free rotation, interrupted at a mean interval of time τ by elastic impacts that randomise into a Boltzmann distribution each molecular angular momentum vector, and randomise completely the molecular orientation. The quantum equations such as (1A) of the appendix may be made to follow the Gordon hypothesis as shown elsewhere,⁹ the relevant transform being given for the hexadecapole component in equ. (3A). The final expression for $\alpha(\omega)$, the theoretical absorption coefficient as a function of angular velocity may be expressed as a continuum:

$$\alpha(\omega) = (\epsilon^\infty - \epsilon_0)\omega^2 \bar{C}(\omega)$$

..... 2

where $\bar{C}(\omega) = \bar{C}_Q(\omega) + \bar{C}_\phi(\omega)$, a sum of two broad bands. In equ. (2), $(\epsilon^\infty - \epsilon_0)$ is the total dispersion, $n(\omega)$ the frequency dependent refractive index (effectively unity), and c the velocity of light.

$\bar{C}_\phi(\omega)$ is related to $C(t)$ of equ. (3A) by:

$$\bar{C}_\phi(\omega) = \frac{\Gamma(1 - \tau^{-1} \Gamma) - \tau^{-1} \Lambda^2}{(1 - \tau^{-1} \Gamma)^2 + \tau^{-2} \Lambda^2} \quad \text{..... 3}$$

$$\text{with: } \Gamma(\omega, \Omega) = \frac{1}{C(0)} \int_0^\infty f(\Omega) \left[\frac{\tau^{-1} (\Omega^2 + \omega^2 + \tau^{-2})}{(\Omega^2 - \omega^2 + \tau^{-2})^2 + 4\omega^2\tau^{-2}} \right] d\Omega$$

$$\Lambda(\omega, \Omega) = \frac{1}{C(0)} \int_0^\infty f(\Omega) \left[\frac{\omega (\Omega^2 - \omega^2 - \tau^{-2})}{(\Omega^2 - \omega^2 + \tau^{-2})^2 + 4\omega^2\tau^{-2}} \right] d\Omega$$

$$\text{with } C(t) = \int_0^\infty f(\Omega) \cos \Omega t dt.$$

The component $\bar{C}_Q(\omega)$ is similarly defined elsewhere⁹. Thus we have $\bar{C}_Q(\omega)$ as a continuum representation of the set of $\Delta J = 2$ lines, and $\bar{C}_\phi(\omega)$ as that of the $\Delta J = 4$ set.

The mean time between collisions (τ) may be estimated roughly from kinetic theory as 5.5, 11.5, and 24.0ps for our three number densities.

In order to evaluate equ (2) an estimate of Q_{ZZ} and ϕ_{ZZZZ} was made with a self consistent field molecular orbital calculation of the charge on each atom of the C_2F_6 molecule using a standard Harwell algorithm,¹⁹ the results of which are tabulated below.

Atom	(D _{3d} symmetry) Coordinates*		z Å	10 ¹⁰ Charge (e) / e.s.u
	x	y		
C	0	0	± 0.78	2.642
F	0	± 1.25	± 1.22	- 0.879
F	1.09	± 0.63	± 1.22	- 0.879
F	- 1.09	± 0.63	± 1.22	- 0.879

* (0,0,0) = mid point of C-C bond.

From the table we have the dipole and octopole components all zero, and⁸:

$$Q_{zz} = -0.53 \times 10^{-26} \text{ e.s.u.}$$

$$\Phi_{zzzz} = -2\Phi_{xxzz} = 8\Phi_{xxyy}$$

$$= \frac{1}{8} \sum_i e_i \left[35z_i^4 - 5(x_i^2 + y_i^2 + z_i^2)(6z_i^2) + 3(x_i^2 + y_i^2 + z_i^2)^2 \right]$$

$$= -18.53 \times 10^{-42} \text{ e.s.u}$$

The radial averages of the intermolecular potential $U_{AA}(R)$ were calculated by the method of Buckingham and Pople²⁰.

DISCUSSION

In equ. (1) Φ is the tensor magnitude related approximately to the scalar Φ_{ZZZZ} by²¹ $\Phi = (7/12)^{\frac{1}{2}} \Phi_{ZZZZ}$, so that the calculation outlined above yields:

$$\alpha_{\max}^{(Q)} : \alpha_{\max}^{(\Phi)} = 1 : 0.3.$$

Thus the type of absorption band predicted is similar to that observed, ie a low frequency peak with a substantial shoulder. This is true despite the fact that the s.c.f.m.o. calculation shows the molecule to have a large

hexadecapole moment and a very small quadrupole (commensurate with that of nitrogen or hydrogen⁸).

The set of $\Delta J = 2$ lines^{1-3, 5-7} peaks at 19.4cm^{-1} (see figure 2), but it is interesting to observe that broadening with j - diffusion shifts $\alpha_{\text{max}}^{(Q)}$ (or $\alpha_{\text{max}}^{(\Phi)}$) to lower frequencies, a result first observed by Frenkel and Wegdam²² for the $\Delta J = 1$ transitions in linear molecules. Furthermore, the peak frequency approaches that of the observed (16cm^{-1}) as τ , the mean time between elastic collisions, approaches zero, the rotational diffusion limit. However in this limit, the return to transparency is far too slow, a characteristic²³ of mechanisms which imply singularities in the intermolecular torque at every impact.

The experimental band is fitted best (fig 2) with a τ of 0.3 ps, an order of magnitude lower than the approximation from kinetic theory. The overall calculated bandshape is close enough to the observed to conclude that the origin of the band is predominantly quadrupole induction, with a high frequency contribution corresponding to $\Delta J = 4$ transitions, attributed here to a point hexadecapole source. However, there is a basic interpretative difficulty in that the data consists of an asymmetric but simple broadband which may arise from more than the two sources treated here. Our conclusions above may be modified, but probably not greatly so, by a more detailed study involving the following factors.

i Overlap absorption arising from the interpretation of van der Waals shells (repulsive regime⁶⁻⁷). Ho et.al². found this to contribute a 1% part of the total integrated intensity in compressed gaseous CO_2 , which has zero dipole and octopole, as in C_2F_6 (D_{3d}). The theory of this effect is at a primitive stage²⁴, and parameterised for H_2 only.

- ii Translational absorption ($\Delta J = 0$, non resonant), which is a low frequency effect of very low absorption cross section, especially for the massive, slow-moving C_2F_6 .
- iii Cross relaxation between sets of overlapping $J \rightarrow J + n$ lines ($n = 2, 4, \dots$). Very little is known about this³, especially when rotational constants are very small (as in C_2F_6) where the effect is more significant and difficult to measure.
- iv Angular dependence of the intermolecular potential, (ie non-Lennard-Jones), when the radial averaging used here would be an approximation.
- v Contributions from the octopole components of the C_2F_6 molecules not in D_{3d} (staggered) conformation. These are probably small since the internal rotation barrier is substantial¹⁶ at ambient temperature.

Although our (Q, Φ) point multipole expansion results are in fair agreement with the observed broad-band absorption the theoretical absolute integrated intensity is much too small as in many other studies of this kind^{1-3,17}. When the mean distance travelled between collisions becomes small, of the order of the molecular van der Waals field, it may be more realistic to use a local charge basis²⁵ for the field in the neighbourhood of a molecule, and this may go a long way towards explaining this difference in absorption cross section.

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The equation for hexadecapole induced absorption in symmetric top molecules may be written as:

$$I_{J \rightarrow J+4} = \frac{4\pi^3 \Phi^2 N^2}{3hcZ} \int_0^{\infty} 4\pi R^{-10} \exp(-U_{AA}(R)/kT) dRS(I,K)$$

$$\times \sum_{K=-J}^J \left[(1 - \exp(-hc\bar{\nu}_4(J)/kT)) \exp(-E_{JK}hc/kT)\bar{\nu}_4(J) \right.$$

$$\times \left[c(J,4,J';K,0,K')^2 \left[40(2J+1)\alpha_0^2 \right. \right.$$

$$\left. \left. + (280/9)(2J+1)^2 \delta^2 c(J,2,J';K,0,K')^2 \right] \right.$$

$$\left. + c(J,4,J';K,3,K')^2 \left[20(2J+1)\alpha_0^2 \right. \right.$$

$$\left. \left. + (40/3)(2J+1)^2 \delta^2 c(J,2,J';K,0,K')^2 \right] \right] ; \quad (1A)$$

where:

$$c(J,4,J';K,0,K')^2$$

$$= \left[\frac{35(J+K+4)(J+K+3)(J+K+2)(J-K+4)(J-K+3)(J-K+2)(J-K+1)(J+K+1)}{8(2J+1)(J+1)(2J+3)(J+2)(2J+5)(J+3)(2J+7)(J+4)} \right] ;$$

$$c(J,2,J';K,0,K')^2$$

$$= \left[\frac{3(J-K+2)(J-K+1)(J+K+2)(J+K+1)}{(2J+1)(2J+2)(2J+3)(J+2)} \right] ;$$

$$c(J,4,J';K,3,K')^2$$

$$= \left[\frac{8(J+K+7)(J+K+6)(J+K+6)(J+K+4)(J+K+3)(J+K+2)(J+K+1)(J-K+1)}{(2J+8)(2J+7)(2J+6)(2J+5)(2J+4)(2J+3)(2J+2)(2J+1)} \right]$$

In equ. (1A), N is the molecular number density (molecules cm^{-3}), Φ the relevant scalar¹⁰ of the hexadecapole moment, Z the rotational partition function³, $U_{AA}(R)$ the Lennard-Jones type intermolecular potential and J and K the usual rotational quantum numbers. The energy E_{JK} is defined by:

$$+C(J,4,J';K,3,K')^2 \left[20 \left(\frac{\bar{v}}{4B} - 4 \right) \alpha_0^2 + \frac{40}{3} \left(\frac{\bar{v}}{4B} - 4 \right) \delta^2 C(J,2,J';K,0,K')^2 \right]$$

$$x \cos(2\pi vct) d\bar{v};$$

where:

$$C(J,2,J';K,0,K')^2 = \left[\frac{3(\bar{v} - 4B(1 - 2K))(\bar{v} - 4B(3 - 2K))(\bar{v} - 4B(1 + 2K))}{8(\bar{v} - 4B)(\bar{v} - 16B)(\bar{v} - 12B)(\bar{v} - 8B)} \right];$$

$$C(J,4,J';K,0,K')^2 = \left[\frac{35(\bar{v} + 4B(2K + 3))(\bar{v} + 4B(2K + 1))(\bar{v} + 4B(2K - 1))(\bar{v} + 4B(2K - 3))}{64(\bar{v} - 16B)(\bar{v} - 12B)(\bar{v} - 8B)(\bar{v})(\bar{v} + 4B)(\bar{v} + 8B)(\bar{v} + 12B)(\bar{v} - 4B)} \right];$$

$$C(J,4,J';K,3,K')^2 = \left[\frac{(\bar{v} + 4B(2K + 9))(\bar{v} + 4B(2K + 7))(\bar{v} + 4B(2K + 5))(\bar{v} + 4B(2K + 3))}{64(\bar{v} + 12B)(\bar{v} + 8B)(\bar{v} + 4B)(\bar{v})(\bar{v} - 4B)(\bar{v} - 8B)(\bar{v} - 12B)(\bar{v} - 16B)} \right]$$

For each time instant t, the integration in equ. (3A) may be carried out using Simpson's rule on a fast machine such as the CDC 7600.

COMPARISON WITH POINT CHARGE FIELD (APPENDIX 2)

For a molecule of D_{3d} symmetry we show in this section that the multipole expansion of the potential (and thus the flux density) due to an array of point charges (the molecule) at a point P relative to a reference O in the molecule is a poor one, and further quantum theories should take account of this fact.

Buckingham⁽²⁶⁾ has reviewed the relevant theory. Consider a distribution of point charges e_i at points (x_i, y_i, z_i) represented by the vectors r_i from an origin O in the molecule. We wish to find the potential ϕ at $P(X, Y, Z)$, or R , from O, where $R > r_i$ for all i . We have, charge by charge:

$$\begin{aligned} \phi &= \sum_i \phi_i = \sum_i e_i R_i^{-1} \quad \dots\dots\dots (A) \\ &= \sum_i e_i [(X-x_i)^2 + (Y-y_i)^2 + (Z-z_i)^2]^{-\frac{1}{2}} \end{aligned}$$

with R_i as the distance between e_i and P. In the Maclaurin expansion of ϕ Buckingham has evaluated the terms up to the octopole, but here we need to include the hexadecapole term:

$$\frac{1}{4!} \left(\frac{\partial^4 (1/R_i)}{\partial r_{i\alpha} \partial r_{i\beta} \partial r_{i\gamma} \partial r_{i\delta}} \right)_0 r_{i\alpha} r_{i\beta} r_{i\gamma} r_{i\delta}$$

where the $\alpha, \beta, \gamma, \delta$ subscripts are shorthand tensor notations explained by Buckingham. For example:

$$R_i^2 = (R_\alpha - r_{i\alpha}) (R_\alpha - r_{i\alpha}) \quad \dots\dots\dots (B)$$

Here we use equation (B) to complete the multipole expansion inclusive of the hexadecapolar case for the general charge distribution of any symmetry:

$$\begin{aligned}
 \phi &= \frac{q}{R} + \mu_{\alpha} \frac{R}{R^3} + \frac{H_{\alpha\beta}}{3R^5} (3R_{\alpha} R_{\beta} - R^2 \delta_{\alpha\beta}) \\
 &+ \frac{\Omega_{\alpha\beta\gamma}}{5R^7} [5R_{\alpha} R_{\beta} R_{\gamma} - R^2 (R_{\alpha} \delta_{\beta\gamma} + R_{\gamma} \delta_{\alpha\beta})] \\
 &+ \frac{\Phi_{\alpha\beta\gamma\delta}}{35R^9} [35R_{\alpha} R_{\beta} R_{\gamma} R_{\delta} - 5R^2 (R_{\alpha} R_{\beta} \delta_{\gamma\delta} \\
 &+ R_{\alpha} R_{\gamma} \delta_{\beta\gamma} + R_{\alpha} R_{\delta} \delta_{\beta\gamma} + R_{\beta} R_{\gamma} \delta_{\delta\gamma} + R_{\beta} R_{\delta} \delta_{\alpha\gamma} \\
 &+ R_{\gamma} R_{\delta} \delta_{\alpha\beta}) + R^4 (\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma})] \\
 &+ \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (C)
 \end{aligned}$$

Here q , μ_{α} , $H_{\alpha\beta}$, $\Omega_{\alpha\beta\gamma}$, and $\Phi_{\alpha\beta\gamma\delta}$ are the symmetrised multipoles and the δ 's are Kronecker symbols. For D_{3d} symmetry Kielich⁽⁸⁾ has listed the non-vanishing elements of $H_{\alpha\beta}$ and $\Phi_{\alpha\beta\gamma\delta}$. If we now compare $\left(\frac{-\partial\phi}{\partial R}\right)$ from eqns (A) and (C) for a point 20 \AA away from the molecule it is found that the first value obtained for the radial component of the flux density is two orders of magnitude less than that from eqn (C) using point charge and elements of $H_{\alpha\beta}$ and $\Phi_{\alpha\beta\gamma\delta}$ from our s.c.f. molecular orbital calculation. This is a discrepancy far more serious than hitherto found by Davies et al⁽²⁵⁾. For what it is worth, eqn (C) reduces, for exactly symmetric distributions to:

$$\begin{aligned}
\phi &= \frac{q}{R} + \mu \frac{\cos \theta}{R^2} + \frac{H}{2R^3} (3\cos^2 \theta - 1) \\
&+ \frac{\Omega}{2R^4} (5 \cos^3 \theta - 3 \cos \theta) + \frac{\Phi}{8R^5} (35 \cos^4 \theta - 30 \cos^2 \theta \\
&+ 3) + \dots \dots \dots \dots \dots \dots \dots \dots \dots (D)
\end{aligned}$$

where the multipoles are now defined by the fact that no components thereof are mutually independent.

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FIGURE CAPTIONS

Fig 1 Schematic diagram of polarizing interferometer

Fig 2 Absorption of compressed gaseous C_2F_6 at 296K.

+ 17.8 bar; \odot 9.59 bar; Δ 4.93 bar.

(1) $\Delta J = 2$ curve broadened by j - diffusion.

(2) $\Delta J = 4$ " " " " " " .

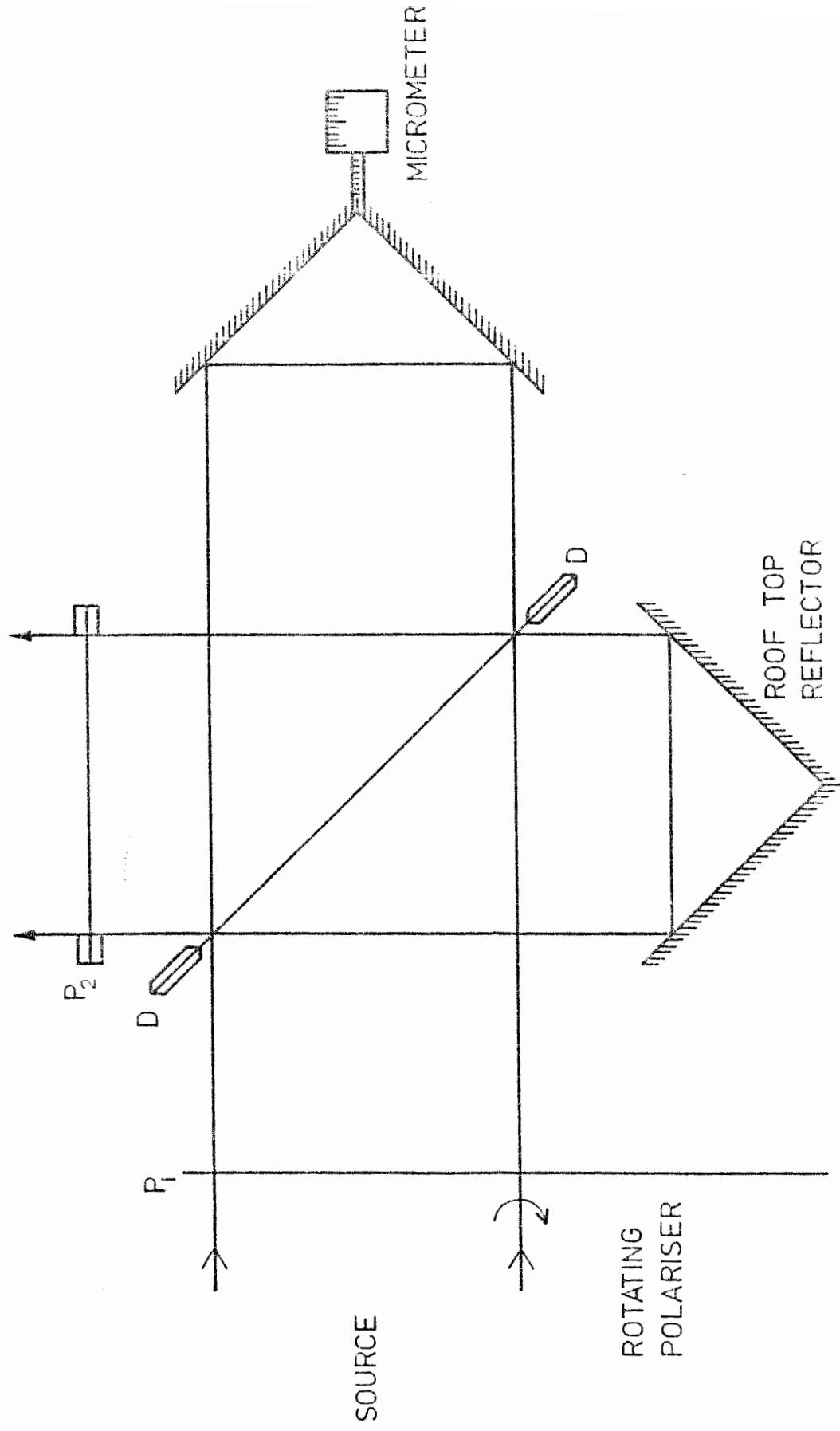
(3) Curve (1) + curve (2), normalised to the data at 17.8 bar

The stick spectrum is of some of the $\Delta J = 2$ absorptions ($K = 0$).

Ordinate $10^2 \alpha (\bar{\nu}) / \text{neper cm}^{-1}$

Abcissa $\bar{\nu} / \text{cm}^{-1}$.

DETECTOR

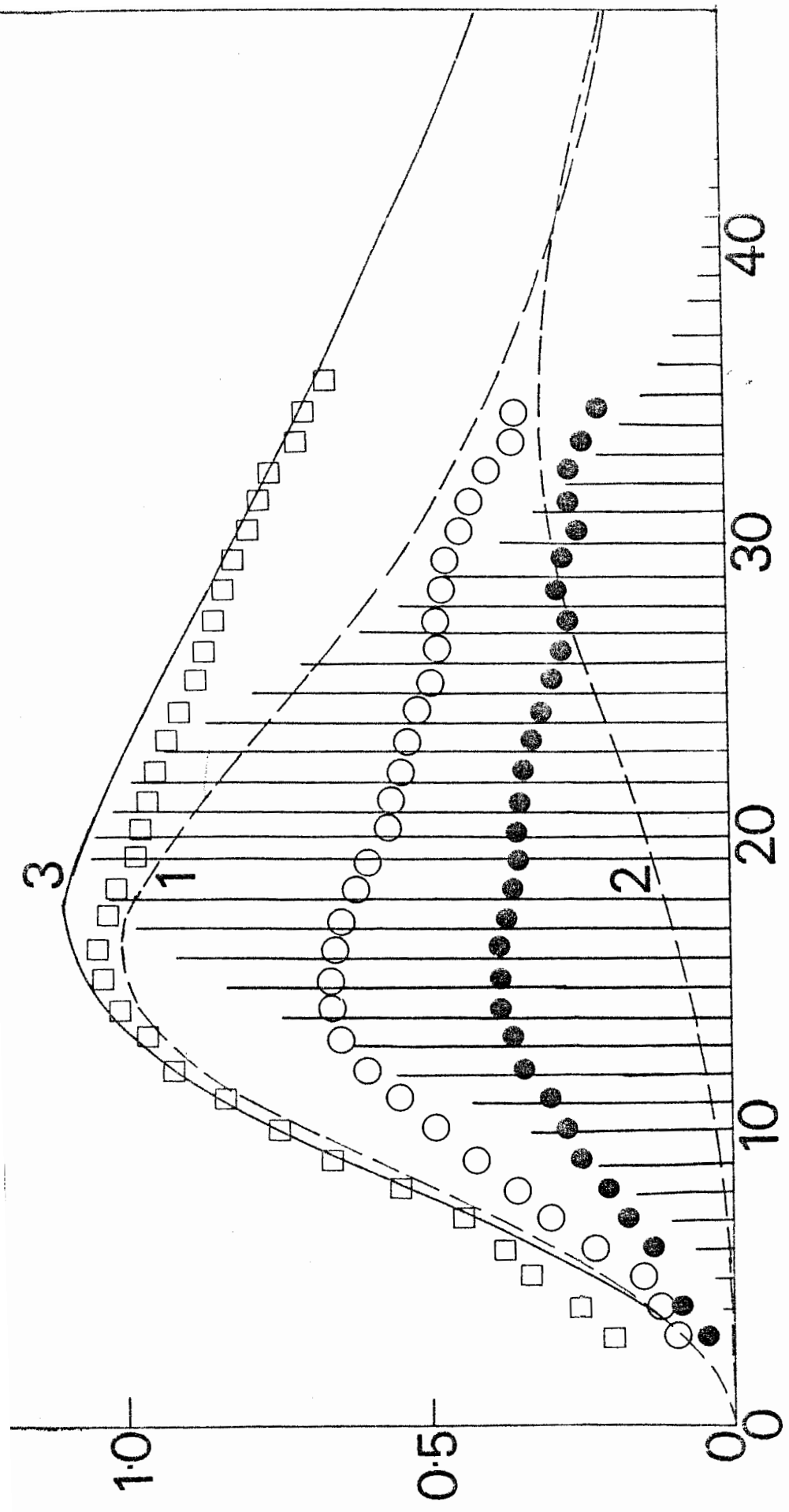


SOURCE

ROTATING
POLARISER

ROOF TOP
REFLECTOR

MICROMETER



Plot of E_{max} vs. E_{min}

A Fokker/Planck type diffusion equation is developed for Brownian motion of the general dynamical variable in Hilbert space. The limits of applicability of this equation are discussed carefully and analytical probability distribution functions (p.d.f.'s) are developed for the angular velocity as a Gaussian but non-Markovian variate. A numerical method is developed for computing the p.d.f. of \underline{u} the dipole unit vector reorienting in 3-D space.

The calculated p.d.f.'s are discussed in terms of molecular motion and interaction in fluids of geometrically isotropic and anisotropic molecules, ranging from sub-critical liquid fluoroform on the one hand to nematic methoxybenzylidene-*p*-*n*-butyl aniline on the other. It is concluded that the p.d.f. is a much more incisive probe of molecular statistics in fluids than its integral over the appropriate space, the autocorrelation function.