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A far infrared study of propyne in the compressed gaseous, liquid, and solution states

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Abstract—The spectrum of propyne (CH_3—$C{\equiv}C$—H) has been studied in the frequency range 10–200 cm^{-1}, in the gaseous phase at two number densities; in the liquid phase at three temperatures [293K, 309K, 320K]; and in dilute carbon tetrachloride solutions. The observed gaseous contours are in good agreement with theoretical predictions. There is a considerable shift in $\bar{\nu}_{max}$ from 18 cm^{-1} in the gas at 5·1 bar and 296K to 81 cm^{-1} in the liquid at 293K. This shift is interpreted as being due to the change from free, to strongly hindered rotation. A plateau at 20 ± 2 cm^{-1} in the liquid spectra is interpreted as being that before the 'inertial fall off' of the Debye dipole relaxation process. An estimate has been made of the extent of dipole induction in liquid phase propyne–carbon tetrachloride collisions.

INTRODUCTION

RECENT studies in the far infrared have shown that all polar liquids have a notable broad absorption extending from 10 cm^{-1} upwards associated with a more or less hindered molecular rotational mode. In some instances it has been possible to compare the liquid absorption with the corresponding rotational spectrum of the gaseous state and to evaluate not only the total effective dipole moment participating but also to estimate the quadrupole moment which appears to contribute. Propyne ($CH_3 . C{\equiv}CH$) has been chosen for study in this context partly for its near linear character, its modest dipole moment and significant polarisability, and its readily accessible critical state. Measurements have been made on the vapour, the liquid, and in carbon tetrachloride solutions.

EXPERIMENTAL

The spectra, from 10 cm^{-1} to 200 cm^{-1}, were obtained by Fourier spectrometry [1–3] using an N.P.L./Grubb–Parsons interferometer at an instrumental resolution of 4 cm^{-1}, sufficient for the pressure broadened bands observed. Both gaseous and liquid samples of the pure propyne were contained in a high pressure, variable path length cell with *Z* cut, crystalline quartz windows, which has been fully described elsewhere [4]. The spectra of solutions of propyne in CCl_4 were taken in a variable path length R.I.I.C. VC–01 liquid cell, with TPX (poly-4-methyl pent-1-ene) windows. Pressures of up to 25·3 bar in the gas were obtained by heating the liquid in the drying chamber of the cell up to 376K, the body being maintained at least 10K higher to prevent condensation of propyne on the inside of the windows. All individual spectra were obtained by ratioing three transformed interferograms at a long path length to three at a shorter path length. For the

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[1] H. A. GEBBIE and R. Q. TWISS, *Rept. Progr. Phys.* **46**, 396 (1966).
[2] A. I. BAISE, Thesis, University of Wales (1971).
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liquid, this prevents effects arising from refractive index changes inherent in ratioing sample to background [5].

The nominal purity of the commercial sample used (from Matheson and Co. Ltd.) was 96·0 mole % minimum, a typical analysis being: propyne: 97·9 mole %; ethyne 0·1 mole %; dimethyl ether 1·2 mole %; dimethyl ethyne 0·1 mole %; allene 0·5 mole %; unidentified impurities (including moisture) 0·2 mole %. Since water absorbs strongly in this region, it was removed by passing the gas through a drying tower containing freshly baked type 3*A* zeolite. The dried stream was then condensed over the same zeolite at about 243K in a vessel protected from atmospheric moisture. The condensate was then distilled into the drying chamber of the cell. Dimethyl ether is the other polar impurity present in significant amounts: as the integrated absorptions will be, to a good approximation in the ratio of the $N\mu^2$ terms (N = molecular number density in molecules cm^{-3}, μ the permanent dipole moment) we can estimate that the presence of 1·2 mole % of dimethyl ether will increase the absorption by 2·1 per cent above the value to be found were it replaced by propyne.

The propyne/CCl_4 solutions were prepared by bubbling the dried gas into spectroscopic grade carbon tetrachloride over type 3A zeolite, and thence through a drying tube outlet. N(propyne) in carbon tetrachloride was estimated immediately before, during, and after the six interferometric runs using the reaction [6].

$$2\mathrm{H{-}C{\equiv}C{-}Me} + \mathrm{K_2H_gI_4} + 2\mathrm{KOH} \rightarrow (\mathrm{Me{-}C{\equiv}C{-}})_2\mathrm{H_g}\downarrow + 4\mathrm{KI} + 2\mathrm{H_2O}$$

An excess of 0·5 M solution of the alkali was added to the sample containing the mercury complex (0·979 mmole) and titrated immediately with 0·25 M sulphuric acid. Three analyses gave the accepted (mean) concentration. Losses by outgassing of propyne during the time needed to complete six interferograms were negligible. The VC — 01 cell was hermetically sealed as a further precaution.

The scatter due to noise (electronic, mechanical, heat effects on the Golay detector) in individual values of $\alpha(\bar{\nu})$ (expressed here in neper cm^{-1}) was estimated by taking the standard deviation of several (up to eighteen) computations. Fig. 3 shows the scatter for a liquid absorption. This, together with uncertainties due to extrapolation to $\alpha(\bar{\nu}) = 0$ at high and low $\bar{\nu}$ gives an uncertainty in

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

of approximately ±10%. The uncertainty in the molecular number density N arises in part from the temperature gradient (± 1·5% on the Kelvin scale) between the front and back windows of the cell, and the uncertainty (±0·3 bar) in the pressure reading (as measured by a Budenberg gauge); and in part from the differences in the prediction of N from the Dieterici equation of state and generalised compressibility curves [7]. The overall uncertainty in N was estimated at about ±3 per cent in the compressed gas.

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[5] John Chamberlain, *Infrared Phys.* **12**, 145 (1971).

[6] See for example *Analytical Chemistry* (Edited by C. R. N. Strouts, J. H. Gilfillan and H. N. Wilson), Vol. 1, Chapt 15, pp. 432–433, Oxford University Press (1955).

[7] O. H. Hougen, K. M. Watson, R. A. Ragatz, *Chemical Process Principles Charts*, J. Wiley, New York (1964).

The densities of liquid propyne at the three temperatures studied were estimated using a "rectilinear diameter" plot [8] from the curves of ref. [7], and the equation [9]:

$$\log_{10} P(\text{torr}) = 7{\cdot}7514 - 1230{\cdot}7/\mathbf{K}$$

$$(\mathbf{K} = \text{temperature in } \mathbf{K})$$

to estimate the vapour pressure curve up to the critical point [10], which is at 402·39K and 55·54 ± 0·02 bar, together with a similar equation given in Ref [10]. Literature [11, 12] values of liquid propyne densities up to 273K were used in this estimation.

RESULTS

The experimental observations are summarised in Table 1, and some typical spectra are illustrated in Figs. 1–5. Figure 3 shows a typical liquid phase absorption All the spectra are given as plots of $\alpha(\tilde{\nu})$ in neper cm^{-1} against $\tilde{\nu}$ (cm^{-1}), the wavenumber. The "excess" absorption listed in the last column is defined as $(xA_1/N - A)$cm, where A is the mean of two differently calculated values of the pure dipole rotational integrated intensity per molecule. The first calculation used GORDON'S sum rules [13] which reduce to:

$$A = 2\pi\, \mu_{\text{gas}}^2/3c^2\, \mathrm{I} \tag{1}$$

for a symmetric top molecule such as propyne. I is the moment of inertia perpendicular to the dipole axis; literature [14, 15] values of $\mu_{\text{gas}} = (0{\cdot}781 \pm 0{\cdot}008) \times 10^{-18}$ e.s.u. and $\mathrm{I} = 98{\cdot}16 \times 10^{-40}\,\text{g cm}^{-2}$ give $\mathrm{A} = 14{\cdot}45 \times 10^{-20}$ cm. The second calculation involves summation of the individual $J \rightarrow J + 1$ transition intensities, some of which are given as the bar spectrum (full lines) of Figs. 1 and 2, using the relation [16]

$$A = \frac{\Sigma A(I,J)}{N} = \sum_J \left[\frac{8\pi^3\mu^2\tilde{\nu}(J)}{3hcz_r}\,(1 - \mathrm{e}^{-hc\tilde{\nu}(J)/kT}) \sum_{k=-J}^{J} S(I,K) \times \left(\frac{(J+1)^2 - K^2}{(J+1)}\,\mathrm{e}^{-E(J,K)hc/kT}\right)\right] \tag{2}$$

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[8] J. O. HIRSCHFELDER, C. F. CURTISS and R. B. BIRD, *Molecular Theory of Gases and Liquids*, Chapter 5, p. 362, J. Wiley, New York (1954).

[9] *Handbook of Chemistry and Physics*, (Edited by R. C. WEAST), Vol. 52, D–153, The Chemical Rubber Co. (1972).

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Table 1. Experimental observations of far infrared spectra of propyne systems

Temperature (K)	Pressure (bar)	$10^{-20} N$ (molecules cm^{-3})	$10^{-20} N_1$ (molecules cm^{-3})	$10^{-20} N_2$ (molecules cm^{-3})	α_{max} (neper cm^{-1})	$\bar{\nu}_{max}$ (cm^{-1})	Weighted mean refractive index in solution	Polo–Wilson Factor (x)	A_1 (neper cm^{-2})	$10^{20} \frac{xA_1}{N}$ (cm)	10^{20} × 'excess' (cm)
296 ± 1	5·1 ± 0·3	1·40 ± 0·05			0·90 ± 0·02	18 ± 1		1·00	20·4 ± 1·0	14·6 ± 1·1	Zero within experimental error
376 ± 3	25·3 ± 0·3	6·2$_3$ ± 0·2			3·2$_3$ ± 0·5	21 ± 1		1·00	87.$_8$ ± 5·0	14.$_1$ ± 1·0	
293 ± 0·5	Liquid	92·0 ± 0·9			33·$_5$ ± 1·0	81 ± 3		0·82	2700 ± 150	23.$_8$ ± 1·2	9·1 ± 1·2
309 ± 1	Liquid	88·4 ± 0·9			28.$_0$ ± 1·0	75 ± 3		0·83	2400 ± 200	22.$_5$ ± 2·1	7·8 ± 2·1
320 ± 2	Liquid	85·8 ± 0·9			27.$_2$ ± 1·0	73 ± 3		0·83	2200 ± 200	21.$_5$ ± 2·0	6.$_8$ ± 2·0
293 ± 0·5	Solution		59·7 ± 1·2	3·95 ± 0·08	2·9$_5$ ± 0·05	54 ± 2	1·485	0·76	236 ± 24		
293 ± 0·5	Solution		57·7 ± 1·2	6·91 ± 0·14	3·9$_0$ ± 0·10	60 ± 2	1·480	0·76	342 ± 34		

N = number density of gaseous or liquid propyne.
N_1 = molecules of CCl_4 per cm^3 in solution with propyne.
N_2 = molecules of propyne per cm^3 in solution with CCl_4.

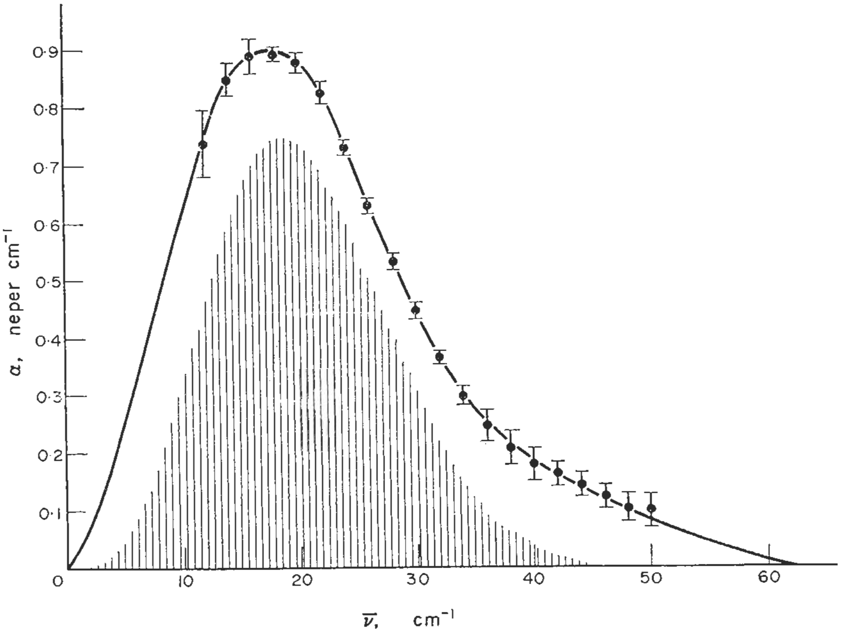

Fig. 1. Far infrared spectrum of gaseous propyne at 5·1 bar and 296K. The uncertainty bars represent standard deviations about the mean points of at least nine computations. The vertical lines give the frequencies and *relative* integrated intensities for all of the pure rotational ($J \rightarrow J + 1$) transitions up to $J = 87$.

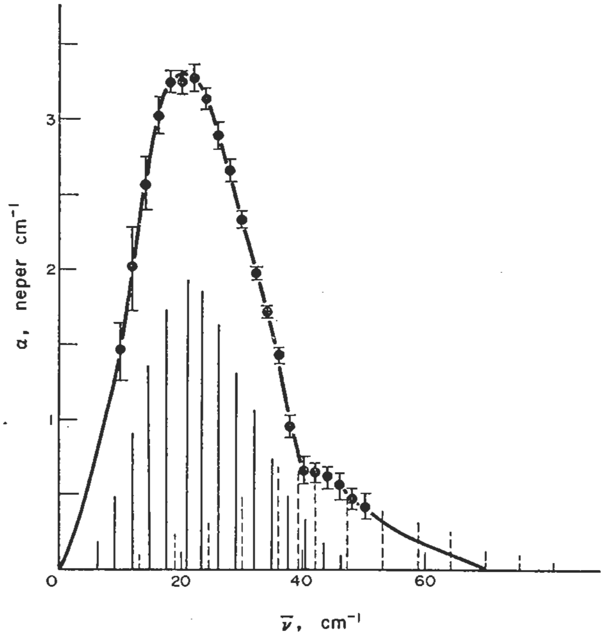

Fig. 2. Far infrared spectrum of gaseous propyne at 25·3 bar and 376K. The continuous vertical lines give the frequencies and *relative* integrated intensities for *some* of the pure rotational transition at 376K and the dotted vertical lines give the frequencies and *relative* integrated intensities for *some* of the quadrupole-induced ($J \rightarrow J + 2$) transitions. The dipole-induced transitions have the same frequencies and *relative* intensities as the pure rotational lines.

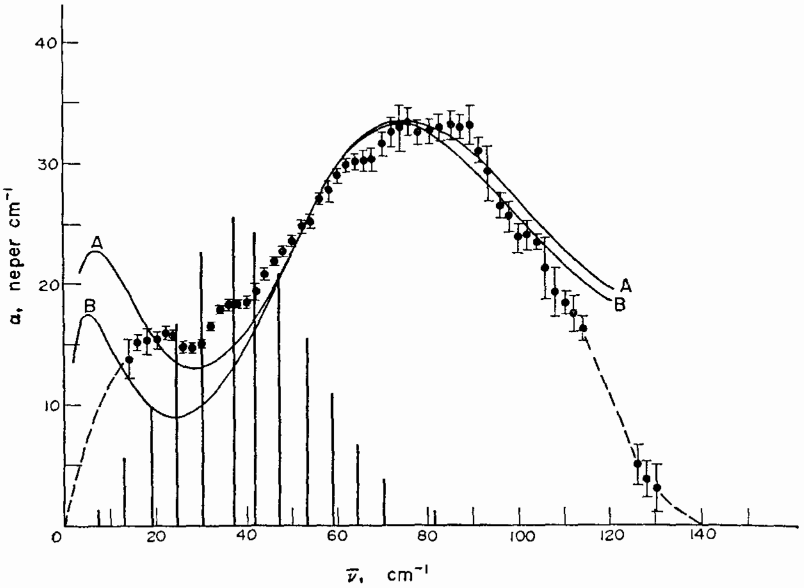

Fig. 3. Far infrared spectrum of liquid propyne at 293K. The dotted section at 120 ± 5 cm^{-1} represents an estimate made necessary by a quartz absorption in this region. The vertical lines give the frequencies and *relative* integrated intensities for *some* of the quadrupole-induced ($J \rightarrow J + 2$) transitions calculated with the assumptions stated in the discussion section. (a) Theoretical curve predicted by the Brot–Larkin model, (b) theoretical curve predicted by the Wyllie–Larkin model.

$$\begin{aligned} \text{where } S(\text{I}, K) &= \tfrac{1}{3}(2I + 1)(4I^2 + 4I + 3) && \text{for } K = 0 \\ &= \tfrac{1}{3}(2I + 1)(4I^2 + 4I + 3) && \text{for } K \neq 0\ , K = \text{multiple of 3} \\ &= \tfrac{1}{3}(2I + 1)(4I^2 + 4I) && \text{for } K \neq 0,\ K \neq \text{multiple of 3} \\ E(J, K) &= BJ(J \pm 1) + (A - B)K^2 \\ \bar{\nu}(J) &= 2B(J + 1) \\ zr &= \sum_{J} \sum_{K=-J}^{J} g(J, K) e^{-hcE(J,K)/kT} \\ g(J, K) &= (2J \pm 1)\, S\,(I, K) \end{aligned}$$

Here, $S(I, K)$ is the nuclear spin factor, I being the nuclear spin quantum number. The rotational partition function zr was evaluated on a computer, to give 21,217 at 296K; whence A is $14{\cdot}49 \times 10^{-20}$ cm.

$$\therefore \qquad A_{\text{mean}} = (14{\cdot}47 \pm 0{\cdot}02) \times 10^{-20}\ \text{cm}.$$

It can be seen from the line spectra of Figs. 1 and 2 that the theoretical $\bar{\nu}_{\text{max}}$ at 296K is $17{\cdot}8\ \text{cm}^{-1}$ as derived from equation (2), and $21{\cdot}9\ \text{cm}^{-1}$ at 376K. These compare with the observed $\bar{\nu}_{\text{max}}$ of $(18 \pm 1)\ \text{cm}^{-1}$ at 296, and $(21 \pm 1)\ \text{cm}^{-1}$ at 376K.

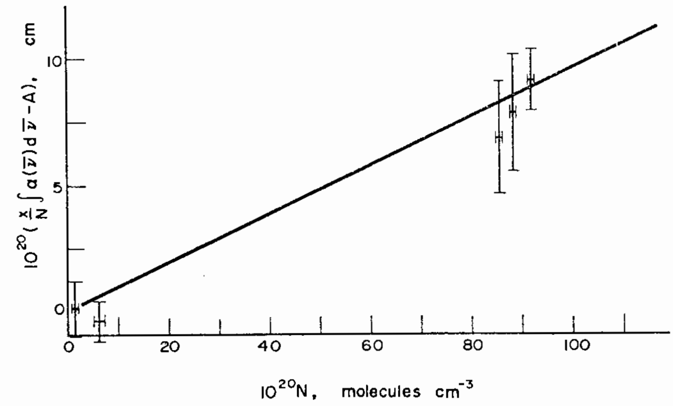

Fig. 4. The "Excess" absorption as a function of number density.

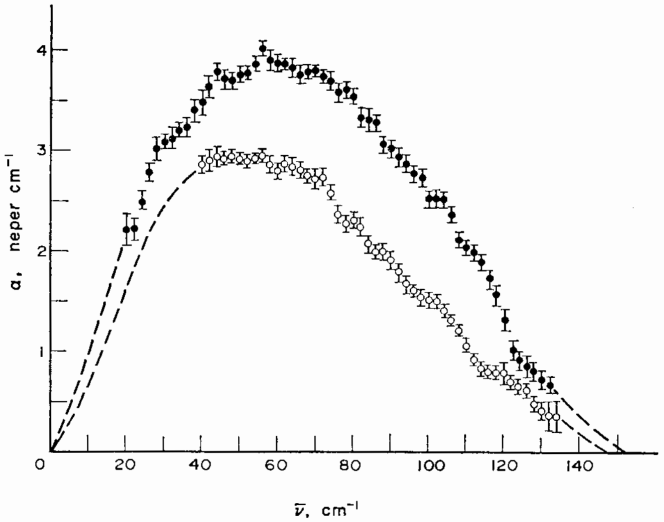

Fig. 5. ● Far infrared spectrum of a dilute solution of propyne in CCl_4. Number density of propyne in solution = 6·9 × 10^{20} molecules cm^{-3}. ○ Far infrared spectrum of a dilute solution of propyne in CCl_4. Number density of propyne in solution = 3·95 × 10^{20} molecules cm^{-3}.

The experimental A_1 values have been corrected for internal field effects by the Polo–Wilson [17] factor $x = 9n/(n^2 + 2)^2$, where, ideally, $n = f(\bar{\nu})$, but is approximated by the value n_D of the liquid propyne, and, by a mean solution refractive index:

$$n_{\mathrm{soln}} = n_1x_1 + n_2x_2 \tag{3}$$

where n_1 and x_1 etc. are the refractive index and mole fraction respectively of the components. *At these concentrations* the use of the mole fraction rather than the number density fraction, as a measure of molecular concentration introduced a negligible change in n_{soln}.

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DISCUSSION

The agreement, within experimental uncertainties, of xA_1/N and A at the two gaseous number densities studied, indicates that the absorption is the pressure broadened, unresolved band made up of the individual $J \rightarrow J + 1$ lines from the rotation of the permanent dipole with very little induced dipolar contribution. As can be seen from Figs. 1 and 2, the agreement between the observed contour, and the bar spectrum of equation (2) of the results section is good at both gaseous densities.

BAISE [18] showed that in the weakly dipolar nitrous oxide, collision induced dipolar absorption can, at a sufficiently high pressure, become more important in this region, than that due to the permanent dipole. In the more strongly dipolar propyne however, it is clear that this induced absorption which has been treated [19] in terms of a bimolecular collision mechanism will not become important until much higher gas densities than those measured are reached.

The difference $[xA_1/N - A]$ becomes appreciable at liquid densities (Table 1) as is the case [20, 21] for all dipolar liquids, where dipoles are induced by multi-body interactions, and where the librational [22] (i.e. torsional oscillatory) mechanism of whole molecule absorption becomes important. An estimate of an effective quadrupole moment of propyne is possible on the basis of this experimental "excess" liquid absorption, but with the following assumptions:

(a) that in calculating the quadrupole-induced dipole, propyne is treated as an approximately linear molecule;

(b) that the sum rules of Gordon used in the first calculation of A, can be applied to the liquid phase;

(c) that collision involving a number greater than two molecules can be neglected.

Clearly the assumption (b) and (c) are over-simplifications as shown by BAISE [2, 4] on nitrous oxide, where the apparent quadrupole moment in the liquid is one half the value found for the compressed gas; this discrepancy is attributed to a cancellation by symmetry of the inducing fields due to multi-body collisions in the liquid phase.

The value of A is strictly valid only for the gas phase; in the liquid the librational motion is the equivalent of a gas phase rotation heavily damped by collisions. With these limitations the quadrupole can be estimated from:

$$\frac{xA_1}{N} - A = A'N \qquad (1)$$

where the coefficients $A'\,\mathrm{N}^2 = A^{\mu} + A^{Q}$ are defined by BAISE [18] and represent theoretical predictions of the dipole and quadrupole induced dipole intensities respectively. The integrals in the coefficients A^{μ} and A^{Q} were evaluated using

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Table 2. Brot and Wyllie parameters for liquid propyne at 293 ± 0·5K

τ_D (psec) (estimated)	τ_r (psec)	τ_j (psec)	τ_i (psec)	Barrier height (V) (kJ mole^{-1})	*Brot model* ξ (rads)	10^{40} I (g cm^2)	α (calc)/α(obs)	Curve shape broadening factor	ϵ_0 (estimated)	ϵ_∞ ($\approx 1{\cdot}07 n_D^2$)
2·8	2·9	0·25	0·69	6·2	0·524	98·1	0·30	2·0	2·95	2·04

Wyllie model

τ_D (psec) (estimated)	$\zeta/2kT$ (psec)	Barrier height (kJ mole^{-1})	10^{40} I (g cm^2)	α (cals)/α(obs)	Broadening factor for curve shape	ϵ_0 (estimated)	ϵ_∞ ($\approx 1{\cdot}07 n_D^2$)
2·8	3·5	5·1	98·1	0·34	0·15	2·95	2·04

tables given by BUCKINGHAM and POPLE [23], and the values of the molecular constants needed were taken from the literature [14, 15, 24, 25] as:

$$B = 0{\cdot}2854\ \mathrm{cm}^{-1}, \qquad D_J = 1{\cdot}37 \times 10^{-7}\ \mathrm{cm}^{-1}.$$

Mean molecular polarisability, $\alpha_{\mathrm{mean}} = 5{\cdot}98 \times 10^{-24}\ \mathrm{cm}^3$; Lennard–Jones parameters $\epsilon/k = 261K$, $\sigma = 4{\cdot}742 \times 10^{-8}$ cm. Dipole moment $\mu = (0{\cdot}781 \pm 0{\cdot}008) \times 10^{-18}$ e.s.u. Using these data A^μ and A^Q were computed as:

$$A^\mu = (1{\cdot}59 \pm 0{\cdot}04) \times 10^9\, N^2 Q^2\ \mathrm{cm}^{-2} \text{ in the range } (293\text{–}320)K$$

$$A^Q = (7{\cdot}0 \pm 0{\cdot}17) \times 10^{-43}\, N^2\ \mathrm{cm}^{-2} \text{ in the range } (293\text{–}320)K$$

where Q is the molecular quadrupole moment.

A' was calculated from the plot of $(xA_1/N - A)$ against N (Fig. 4) and thus Q was found to be:

$$Q = (7{\cdot}4 \pm 1{\cdot}0) \times 10^{-26}\ \text{e.s.u.}$$

This is a value derived for the liquid state using an essentially gas phase treatment, and its shortcomings can be seen in Fig. 3 where the bar spectrum gives the quadrupole induced $J \rightarrow J + 2$ transitions predicted by Colpa and Ketelaar. The bar spectrum peaks at 38 cm^{-1} whereas the observed liquid band peaks at 81 ± 3 cm^{-1}. This shift to the higher frequencies reflects the transition from free to strongly hindered rotation, the molecules being restrained to librations in potential wells produced by their neighbours. Similar displacements have been recorded for OCS by DARMON *et al.* [26] and for N_2O by BAISE [18]. The extent of the higher frequency absorption which is not bimolecular collision-induced dipole absorption means that the calculated Q value will be too high. The neglect of the quadrupole-quadrupole interaction energy [27, 28] will operate in the same sense.

An independent estimate of Q(propyne) has been made from a S.C.F.M.O. calculation [29]. According to the importance attached by the authors to the role of the π electrons, two possible values of Q_{calc} are: $+5{\cdot}0 \times 10^{-26}$ e.s.u. or $+1{\cdot}4 \times 10^{-26}$ e.s.u. Our estimate is twice the mean of these values, which are calculated [30] about the centre of mass of the molecule.

The Debye dielectric absorption, usually given as ϵ'', is a cooperative molecular process which leads to the form:

$$\epsilon''(\mathrm{limit}) = (\epsilon_0 - \epsilon_\infty)\omega\tau/(1 + w^2\tau^2) \qquad (2)$$

or, for $\omega\tau \gg 1$

$$\epsilon''\ (\mathrm{limit}) = (\epsilon_0 - \epsilon_\infty)/\omega\tau.$$

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On conversion of ϵ'' to α values, this is:

$$\alpha(\text{limit}) = (\epsilon_0 - \epsilon_\infty)/nc\tau$$

which is a constant α value for any liquid [31, 32] at one temperature. This "Debye limit" does not normally appear in the $\alpha(\bar{\nu})$ plot, as the *individual* molecular mode absorption, not envisaged by Debye, appears superposed upon the contour predicted from equation (2). Microwave dielectric measurements of liquid propyne have not been reported and only an indirect estimate of α (limit) can be made for it. The relaxation time τ for CH_3 $C\equiv CH$ can be equated to that [33] for CH_3 $C\equiv N$ i.e. $\tau = 2{\cdot}8 \times 10^{-12}$ sec. For liquid propyne, ϵ_0 may be estimated from $\mu_{gas} = 0{\cdot}78D$ via the Onsager permittivity equation after first scaling μ_{gas} down to an anticipated lower effective value in the liquid by the same ratio as applies to μ_{gas}/μ_{liq} (Onsager) for CH_3 $C\equiv H$ i.e. 3·46/3·92: to give μ (CH_3 $C\equiv CH$) $= 0{\cdot}69D$, which gives in turn $\epsilon_0 = 3{\cdot}95$ at 296K. Bond polarizability values give $n_D{}^2$ (propyne) $= 1{\cdot}90$. These estimates lead to $\alpha(\text{limit}) \approx 18$ neper cm^{-1}. The plateau value near 20 cm^{-1} shown in Fig. 3 and in other plots for the liquid absorption gives $\alpha(\text{limit}) = 16{\cdot}0 \pm 0{\cdot}5$ neper cm^{-1}.

It has previously been shown [20–22] that when the molecules in the liquid are relatively free to rotate (e.g. for the "spherical" polar molecules $CH_3 . CCl_3$ etc.) the Debye limiting value of α cannot be detected as the quasi-free rotational absorption, with its contour approximating to that of the gas, is superimposed upon it. The fact that the α (limit) can be detected in propyne is a consequence of this pronounced anisotropy of this molecule, whose dipole is along its "needle" axis. The rotation of individual molecules about axes perpendicular to their length is notably hindered by the proximity of other rod-like molecules. This situation leads to the considerable shift of the absorption maximum from *ca.* 18 ± 1 cm^{-1} in the moderately compressed gas to 81 ± 3 cm^{-1} in the liquid, the latter value reflecting the depth and sharpness of the energy well in which the molecules librate in the liquid.

An estimation of a mean barrier height between such wells is possible using two models extended and described by LARKIN [22]. The experimental curve of Fig. 3 has been fitted using a minimum of arbitrary parameters. Both models then suggest values of the barrier height V of 5–6 kJ mole^{-1} which can be compared with a similarly deduced [22] value of 2·8 kJ mole^{-1} for the "pseudo spherical" 2,2 dichloropropane molecule. Other predicted parameters, such as the time of residence in each well, τ_r, are shown in Table 2, where the symbols are defined as in Ref. [22]. Here, τ_D for acetonitrile has been taken as a guide to $\zeta/2kT \approx \tau_D$ of the Wyllie model and $\tau_r \equiv \tau_D$ of the Brot model.

Both predictions (Fig. 3) show the α (limit) value, but at a lower frequency in both models than the observed shoulder at *ca.* 20 cm^{-1}; moreover, each curve is normalised to the maximum α value of the observed curve, and, in Table 2, the ratio $\alpha(\text{calc})/\alpha(\text{obs})$ reflects the failure to predict the correct intensity of absorption in the far i.r. region. This may be due to the effect of induced dipolar absorption,

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internal field effects [17] ,and other limitations in the models discussed by LARKIN [22].

The choice of a well with half angular aperture (ξ) of 30° corresponds to a molecule having, on average, 8–10 nearest neighbours; this figure is supported by the evaluation of the molecular data for propyne based on a recent general treatment [35] of the liquid state.

The absorption intensities reported above for the liquid phase clearly establish that contributions from collisionally induced dipoles can be very significant. This feature can be further examined by a study of the integrated intensities in the carbon tetrachloride solutions. There the solvent absorption is itself principally due to collisional interaction of the non-dipolar molecules and can be represented as $a_1N_1^2$ where N_1 is the number density of the CCl_4 molecules. The dissolved propyne will contribute a total of three further terms: a_2N_2 as its own dipole absorption, $a_2^1N_2^2$ from propyne–propyne collisional interactions; and $a_3N_1N_2$ from propyne–carbon tetrachloride interactions. The terms a_1 and a_2^1 can be determined from the respective pure liquid absorptions with a_2 taken as the Gordon value corrected to the liquid state by the Polo–Wilson factor $9n/(n^2 + 2)^2$. The total intensity anticipated from this propyne carbon tetrachloride solution is thus:

$$A_{\text{soln}} = a_1N_1^2 + a_2N_2 + a_2^1N_2^2 + a_3N_1N_2 \qquad (3)$$

As the term a_2N_2 will be much the largest, any uncertainty in it and the ones in a_1 and a_2 will result in a_3 carrying the accumulated uncertainties. The data in Table 1 lead [34] to:

$$a_1 = (2{\cdot}4 \pm 0{\cdot}2) \times 10^{-42}\ \text{cm}^4$$
$$a_2 = (14{\cdot}47 \pm 0{\cdot}02) \times 10^{-20}\ \text{cm}$$
$$a_2^1 = (9{\cdot}9 \pm 1{\cdot}0) \times 10^{-42}\ \text{cm}^4$$

From these one finds:

$$a_3 = (14 \pm 8) \times 10^{-42}\ \text{cm}^4 \text{ for } N_2 = 3{\cdot}95 \times 10^{20} \text{ molecules cm}^{-3}$$
$$a_3 = (19 \pm 6) \times 10^{-42}\ \text{cm}^4 \text{ for } N_2 = 6{\cdot}91 \times 10^{20} \text{ molecules cm}^{-3}$$

The overlap between the two a_3 values shows these data are not inconsistent with equation (3). Furthermore it is not entirely without significance that a_3 is appreciably larger than a_1 or a_2^1; this implies that the propyne–carbon tetrachloride collisional interactions result in a larger induced moment than the A–A or B–B collisional encounters.

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