

Collision Induced Absorption in Compressed Gaseous Cyanogen and Comparison with the Liquid Phase Absorption in the region 20-120 cm^{-1}

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The far infra-red bimolecular collision induced absorption of compressed gaseous cyanogen has been studied in the region 20-120 cm^{-1} , at pressures of up to 33.5 bar, together with the liquid spectrum at 301 K in the same region. From the integrated intensity of the gaseous absorption an apparent quadrupole moment of $\pm(14.7 \pm 2.0) \times 10^{-26}$ e.s.u. was computed. A MO calculated value of -9.0×10^{-26} e.s.u. has been quoted (McLean). For the liquid an apparent molecular quadrupole moment of $\pm(6.9 \pm 1.0) \times 10^{-26}$ e.s.u. was deduced, the much lower value reflecting *inter alia* the reduced efficacy of multi-molecular collisions in generating induced dipoles.

This work aims to study the molecular interactions which cause far infra-red absorptions in compressed gaseous and liquid cyanogen $(\text{CN})_2$, a non-dipolar species. It is established that compressed non-dipolar gases (e.g., CO_2)^{1a} show an absorption which grows as the square of the pressure and which appears also in non-dipolar liquids where again its principal source is bimolecular collision interaction.^{1b} However, careful studies by Birnbaum *et al.*¹ on compressed carbon dioxide have shown that at a high enough pressure, a term proportional to the cube of pressure appears, indicating the role of triple molecular collisions.

Colpa and Ketelaar² calculated the absorption to be expected on bimolecular collisions of non-dipolar molecules possessed of a quadrupole moment. The assumptions they made that the normal rotation of an individual molecule is undisturbed by the collision becomes less valid as the molecules to which the treatment is applied become larger, and the quadrupolar interaction increases and becomes more angle-dependent.³ From their treatment, however, an effective quadrupole moment can be derived for the non-dipolar gas, and this can be compared with that calculated in the same way from liquid data. The liquid state apparent value will provide some measure of the resultant induced dipole moment in that phase.

For these studies, cyanogen has the advantage of a large quadrupole moment which facilitates measurement of the relevant induced band at moderate pressures (of up to 33.5 bar) where triple collisions are unlikely to occur. Furthermore, cyanogen is a larger molecule than the diatomics (H_2 , N_2) with which the equation of Colpa and Ketelaar is most successful, and consequently provides an opportunity to study the difference between the predicted line spectrum of this theory and the observed band and to draw conclusions about other (shorter range) interactions from the way in which these differ.

EXPERIMENTAL

The spectra, from 20 cm^{-1} to 120 cm^{-1} , have been obtained by Fourier spectrometry⁴⁻⁶ using an NPL-Grubb Parsons interferometer at an instrumental resolution of 4 cm^{-1} ,

this being sufficient for the broad bands observed. The sample was contained in a high pressure cell having 7 mm *z* cut crystalline quartz windows, and with an adjustable path length, fully described elsewhere.⁵ In each case, the spectrum of the compressed gas in equilibrium with the (heated) liquid was obtained at pressures up to 33.5 ± 0.3 bar. The gaseous spectra were obtained by taking the ratio of the mean of a number of sample interferograms to the mean of several background (1 atm dry air) interferograms, using the maximum available path length of 13.2 mm. The liquid spectra were obtained by a standard⁵ procedure using the ratio of a thick path length to a thin path length of liquid at room temperature.

The normal purity of the commercial sample (Matheson and Co. Ltd.), used was 98.6 % w/w having the following specified impurities, whose dipole moments are appended: HCN (0.1 %, 2.98 D); CO₂ (0.5 %, 0 D); Cl₂ (0.1 %, 0 D); CNCl (0.8 %, 2.82 D); H₂O (0.0 %, 1.85 D); N₂ (trace, 0 D); HCl (0.0 %, 1.08 D). The HCN could be removed by passage through AgNO₃ solution, and the CNCl frozen out in glass spirals immersed in a CO₂(s)+acetone bath at 258 K, which also acted as preliminary removers of moisture. The gas then passed through two drying towers containing freshly baked (673 K) type 3A zeolite, and was condensed in a dried and nitrogen-filled cold finger condenser, protected from atmosphere moisture by a drying tube of the same zeolite.

The cell was prepared by first purging repeatedly with dry nitrogen at up to 50 bar; followed by evacuation to a few millibars, together with heating to >373 K in order to remove adsorbed moisture. The heating and evacuation were continued for 24 h before admission of the purified material. This was carried out by distillation from the cold finger condenser onto a large amount of dry zeolite contained in the cell sample chamber, which was immersed in a CO₂(s)+acetone bath at 247 ± 1 K.

A sample of gas taken from the cell failed to show any trace of CNCl by mass spectrometric analysis. Moisture analysis on a similar sample, using a microtitration technique with Karl-Fischer reagent (B.P. Chemicals (Int.) Ltd., Baglan Bay) revealed a content of 0.05 % w/w: this would contribute only very slightly to the measured absorption (see Appendix). Any significant absorption by polar molecule contamination would itself provide a contribution linearly dependent on the total pressure: the departures from the experimental pressure squared dependence are too small to provide any evidence of this.

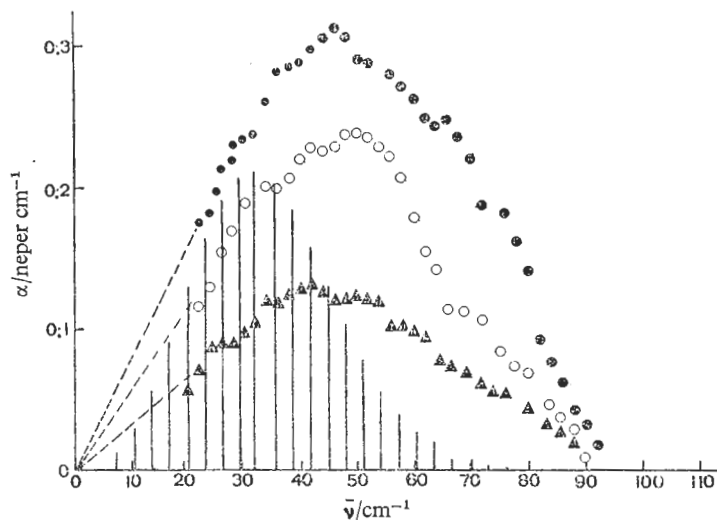


FIG. 1.—(A) (●) Mean of the Fourier transform of several ratios of sample interferograms over the mean of three background (dry air) interferograms. Pressure = 33.5 ± 0.3 bar, temperature = 383 K. (B) (○) As for (A), pressure = 28.4 ± 0.2 bar, temperature = 381 K. (C) (▲) As for (A), pressure = 24.0 ± 0.2 bar, temperature = 348 K. The bar spectrum gives the frequencies and relative integrated intensities for some of the quadrupole induced ($J \rightarrow J+2$) transitions.

The scatter due to noise (electronic, mechanical, and heat effects on the Golay detector) in individual runs caused an uncertainty (about the plotted mean of many interferogram ratios) of at most $\pm 10\%$ in the value of each $A_1 = \int_{\text{band}} \alpha(\bar{\nu}) d\bar{\nu}$; (usual notation); one of the sources of uncertainty is in the extrapolation to $\bar{\nu} = 0$ from $\bar{\nu} = 20 \text{ cm}^{-1}$; (see fig. 1). The uncertainty in the molecular number density N arises in part from the temperature gradient between the front and back windows of the cell which produces an uncertainty of $\pm 1.5\%$ on the Kelvin scale. The pressure, as monitored by a Budenberg gauge, was constant to ± 0.3 bar once equilibrium of the cell heating systems was obtained (ca. 4 h). Another uncertainty arises from the difference in the values of N as obtained from generalised compressibility curves⁷ and from the Berthelot equation (ca. 2%). All these factors provide a total uncertainty in N of $\pm 3.5\%$.

The density of the liquid was estimated from the relation^{8,9}:

$$p = 0.91506(1 - 0.00203T) \quad (T \text{ in } ^\circ\text{C, units: gm cm}^{-3}).$$

Pressures of up to 33.5 ± 0.3 bar were obtained by heating the liquid in the drying chamber of the cell up to 373 K, the absorption cell being maintained at least 10 K higher, to prevent condensation of cyanogen on the inside of the windows. It was implicit in the method of obtaining the vapour spectra that at each different pressure, a new sample of vapour was used, thus producing a check on the efficiency of the purification technique judging from the reproducibility of the liquid spectra.

RESULTS

The observations are summarised in table 1. The spectra are represented in fig. 1 and 2 as α (neper cm^{-1}), the absorption coefficient, against $\bar{\nu}$ (cm^{-1}).

The spectrum¹⁰ of fig. (1), denoted by bars, gives the frequencies and *relative*

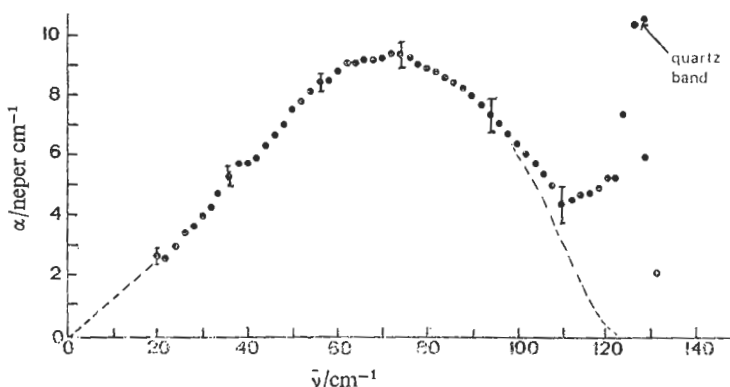


FIG. 2.—Spectrum of liquid cyanogen at 301 K. The results of several runs are represented by the dots, with error bars to denote the experimental uncertainty.

TABLE 1.—PRESSURE DEPENDENCE OF THE FAR INFRA-RED ABSORPTION IN $(\text{CN})_2$

state	tempera- ture/K	pressure/ bar	$10^{-21} \times$ no. density (N)/ molecule cm^{-3}	Polo and Wilson factor (y)	A_1 / neper cm^{-2}	$y \cdot A_1$ / neper cm^{-2}	$10^{-42} \times N^2$ / molecule ² cm^{-6}
gas	348	24.0	0.67 ± 0.02	1.00	7.9 ± 0.8	7.9 ± 0.8	$0.4_5 \pm 0.02$
gas	381	28.4	0.72 ± 0.02	1.00	11.6 ± 1.0	11.6 ± 1.0	$0.5_2 \pm 0.03$
gas	383	33.5	0.90 ± 0.03	1.00	18.1 ± 2.0	18.1 ± 2.0	$0.8_1 \pm 0.04$
liquid	301	—	10.0	0.84	610 ± 30	510 ± 20	100.0

integrated intensities of *some* of the quadrupole induced ($J \rightarrow J+2$) transitions as given by the equation² of Colpa and Ketelaar (see discussion). The experimental absorption in the region $20\text{--}100\text{ cm}^{-1}$ consists of a band of width at half peak height 50 cm^{-1} for the compressed gas, and 65 cm^{-1} for the liquid. The $\bar{\nu}_{\text{max}}$ moves very little in the gas, but shifts from its value there of $47 \pm 3\text{ cm}^{-1}$ to $75 \pm 3\text{ cm}^{-1}$ in the liquid at 301 K.

The experimental A_1 values have been corrected for internal field effects by the Polo-Wilson¹¹ factor, $y = 9 n_{\text{ir}} / (n_{\text{ir}} + 2)^2$, using as a good approximation to the infra-red refractive index n_{ir} , that calculated from the densities and the Lorenz-Lorentz equation. Since yA_1 is experimentally proportional to N^2 for the gas (fig. 3), the origin of the absorption is taken as bimolecular collision. As is also found^{1, 5, 12} for carbon dioxide and nitrous oxide, the yA_1 value for the liquid lies below the straight line plot of yA_1 against N^2 for the compressed gas.

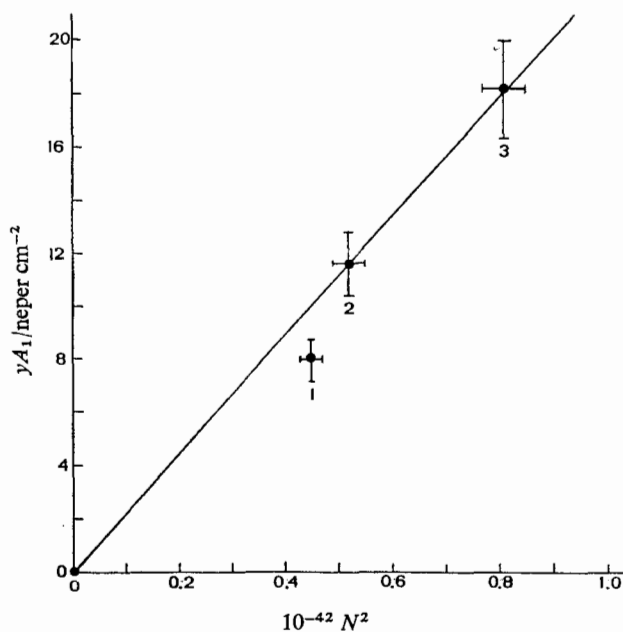


FIG. 3.—A graph of yA_1 against N^2 for the compressed gas. (1) 24.0 ± 0.3 bar, 348 K; (2) 28.4 ± 0.4 bar, 381 K; (3) 33.5 ± 0.5 bar, 383 K. The derivation of the error bars is described in the text.

Despite the experimental uncertainties, fig. 3, is a reasonable straight line plot through the experimental points and the origin. The data have consequently been interpreted on the assumption of a bimolecular collisional mechanism of quadrupole induced dipolar absorption, from which the effective quadrupole moment in the gas and liquid may be evaluated.

DISCUSSION

The effective quadrupole moments in both compressed gas and liquid phases were computed using^{2, 10}:

$$A_1 = A_Q N^2 \quad (1)$$

where

$$A_Q = \sum_J A_Q(J \rightarrow J+2) \\ = \frac{12\pi^3}{kT} BQ^2 \alpha_p^2 \left[4\pi \int_0^\infty R^{-6} \exp(-E(R)/kT) dR \right] \times \\ \left[\sum_J \bar{\nu} \frac{(J+1)(J+2)}{(2J+3)} \exp(-E_J hc/kT) [1 - \exp(-hc\bar{\nu}_J/kT)] \right] \quad (2)$$

where

$$\bar{\nu}_J = 2B(2J+3) - 4D_J(2J+9)(J+15)(J+9) \\ E_J = BJ(J+1) - D_J(J(J+1))^2.$$

Here B is the rotational constant in cm^{-1} , D_J the centrifugal distortion constant in cm^{-1} , Q the quadrupole moment (in e.s.u.), α_p the mean polarizability (cm^3). The molecular quadrupole moment is defined¹³ as:

$$Q = \frac{1}{2} \sum_i (e_i(3z_i^2 - r_i^2))$$

(using standard notation). The integral in (2) was evaluated using the tables¹⁴ given by Buckingham and Pople, with Lennard-Jones parameters¹⁵ $\epsilon/k = 339 \text{ K}$, $r_0 = 4.38 \text{ \AA}$. The summation was carried out over 150 J -terms, when successive contributions became negligibly small. The values of the other constants which were used are^{16, 17}:

$$B = 0.1571_0 \pm 0.00001 \text{ cm}^{-1}. \quad D_J = (3.01 \pm 0.20) \times 10^{-8} \text{ cm}^{-1}. \\ \alpha_p = 5.01 \times 10^{-24} \text{ cm}^3.$$

The results of the calculations are summarised in table 2.

TABLE 2.—QUADRUPOLE MOMENTS IN THE GAS AND LIQUID STATES OF $(\text{CN})_2$

phase	temperature/ K	$\nu A_1/\text{neper}$ cm^{-2}	$A_Q/Q^2 \times 10^{-9}/$ cm^4	$10^{26} Q /\text{e.s.u.}$
gas	348	7.9 ± 0.8	1.02	13.0 ± 2.0
gas	381	11.6 ± 1.0	0.93	15.5 ± 2.2
gas	383	18.1 ± 2.0	0.93	15.5 ± 2.2
liquid	301	510 ± 20	1.08	6.9 ± 1.0

The selection rules and dipole matrix elements were derived by Colpa and Ketelaar on the basis that the normal quantized state of each molecule participating in a bimolecular collision is undisturbed by the interaction with its partner. The first molecule, it is assumed, continues to rotate, but with an induced dipole moment from the quadrupole field of the second. The quadrupole field is expanded in spherical harmonics, but in linear molecules, such as cyanogen, the interactions are large and angle-dependent³ which makes the assumption inherent in the theory that the normal rotation of the individual molecule is undisturbed during a collision, a rather doubtful one. No account is taken, either, of pure translational absorption (where the absorption of a photon changes the relative kinetic energy of the two molecules, with no change in rotational energy, $\Delta J_1 = \Delta J_2 = 0$), but this is not likely⁵ to contribute above 10 cm^{-1} , although the induced rotational band has been separated from the translational band for hydrogen.¹⁸

The factor most likely to account for the discrepancy between the experimental gas phase values of the quadrupole and the preliminary molecular orbital theory value¹⁹ of -9.0×10^{-26} e.s.u. is the neglect in this treatment of the quadrupole-

quadrupole interaction energy, UQQ. Bose and Cole²⁰ have demonstrated its importance when considering the interaction potential of strongly quadrupolar molecules, where its inclusion requires the Lennard-Jones potential $ULJ(R)$ to be replaced by $ULJ(R) + UQQ(R, \theta, \phi, Q)$ where:

$$UQQ(R, \theta, \phi, Q) = (3Q^2/16R^5)(1 - 5 \cos^2 \theta_A - 5 \cos^2 \theta_B - 15 \cos^2 \theta_A \cos^2 \theta_B + 2(\sin \theta_A \sin \theta_B \cos(\phi_A - \phi_B) - 4 \cos \theta_A \cos \theta_B)^2). \quad (3)$$

θ_A and θ_B are the angles formed by molecules A and B with the line joining their centres, and ϕ_A and ϕ_B are the corresponding azimuthal angles. Since this term should be included in $E(R)$ of eqn (2), it would necessitate a lengthy numerical integration (such as that of Bose and Cole for CO_2) if its effect on the quadrupole moment were to be assessed for cyanogen where this correction could be larger than in CO_2 owing to the increased quadrupole moment.

The data show a variation with temperature of Q (apparent) which is in the same sense as that observed by Harries from the compressed CO_2 studies before his inclusion of the Bose and Cole correction. In units of 10^{-26} e.s.u., he found for $Q(CO_2)$ the uncorrected values 6.6 (200 K) and 8.1 (373 K), which become 4.3 (200 K) and 4.8 (373 K) on correction.²¹ The variation of 0.13 per cent per K in Harries' uncorrected values is increased to perhaps 0.5 per cent per K in those for cyanogen. Accordingly the present $Q(CN)_2$ values must be regarded as preliminary until the Bose and Cole computation can be repeated for cyanogen.

The quadrupole moment derived from the compressed gaseous data is about twice the value derived in the same way from the liquid data, and the mean of the gas phase values, i.e., $\pm(14.7 \pm 2.0) \times 10^{-26}$ e.s.u. is 1.6 times as great as a calculated¹⁹ value of -9.0×10^{-26} e.s.u. These results are compared with those^{1, 3, 10} for carbon dioxide and nitrous oxide in table 3.

TABLE 3.—QUADRUPOLE VALUES FOR LINEAR MOLECULES IN THE GAS AND LIQUID STATES

molecule	$10^{26} Q_{gas} / \text{e.s.u.}$	$10^{26} Q_{liq} / \text{e.s.u.}$	$10^{26} Q_c / \text{e.s.u.}$	Q_{gas}/Q_c	Q_{gas}/Q_{liq}
$(CN)_2$	14.7 ± 2.0	6.9 ± 1.0	9.0	1.6	~ 2
N_2O	8.0 ± 0.7	4.0	3.7	2.2	~ 2
CO_2	$(8.1 \pm 0.5)^*$	about 5 times less ^{1a}	4.1	2.0	~ 5

* At 373 K (Harries)²¹ uncorrected for quadrupole-quadrupole interaction; Q_c = quadrupole moment measured by the induced birefringence technique or calculated using molecular orbital theory.

From this study of carbon dioxide, Birnbaum *et al.*¹ concluded that the high frequency tail of the gas and liquid absorption is due to short range binary interactions, and that the longer range quadrupolar interactions effectively cancel in the liquid state. The bar spectrum of fig. 1 shows that the calculated peak occurs at lower frequencies than the observed $\bar{\nu}_{max}$ in the compressed gas or in the liquid. Therefore it is envisaged that the high frequency contribution in cyanogen due to short-range overlap forces, hexadecapolar-induced dipolar absorption, or due to actual distortion of the molecular framework, is quite considerable. The high frequency part of the spectrum is even more accentuated in the liquid, and this, together with the finding that the apparent quadrupole is approximately halved in the liquid lends support to the second suggestion of Birnbaum *et al.* that the longer-range quadrupolar interactions are effectively cancelled in the liquid by the proximity of interacting neighbours.

However, the bar spectrum will be pressure broadened in reality leading to a

slightly different overall contour, and other deviations from first order expectations will arise from effects such as: (i) the anisotropy of polarisability; (ii) the reaction of the induced dipole moment of molecule (B) back into molecule (A); (iii) the anisotropy of the attractive (dispersion) and repulsive forces appearing in the Lennard-Jones potential.

The shift of 15 cm^{-1} observed in $\bar{\nu}_{\max}$ between gas and liquid can be interpreted in terms of the increased amount of shorter range interaction in the liquid, where computing the molecular dynamics poses a formidable multi-body problem. This shift can be compared with the corresponding ones^{1a, 5} of 25 cm^{-1} in CO_2 , 30 cm^{-1} in N_2O , and 60 cm^{-1} in propyne.²² In each case the half widths increase in the liquid. In the dipolar nitrous oxide and propyne, librational modes of absorption²³ are envisaged in the liquid state, corresponding to a change from free to strongly hindered rotation. Darmon *et al*²⁴ have found a shift in $\bar{\nu}_{\max}$ to higher frequencies in OCS, librational modes contributing at the higher frequency end of the spectrum.

The difference in the ratios $Q_{\text{gas}}/Q_{\text{c}}$ between cyanogen and carbon dioxide may relate to the respective liquid densities (critical density of $\text{CO}_2(\text{l}) = 0.468\text{ gm cm}^{-3}$, density of $\text{C}_2\text{N}_2(\text{l})$ at $301\text{ K} = 0.863\text{ g cm}^{-3}$). It could be that the higher density in cyanogen is the cause of other mechanisms of absorption dependent on the increased frequency of molecular collision. Actual distortion of the molecular framework, producing a temporary dipole, would contribute a purely dipolar absorption besides that due to the induced dipoles.

APPENDIX

The effect of moisture on the integrated intensity of liquid cyanogen can be estimated using the data of Pardoe²⁵ for liquid water:

$$\frac{1}{N_w} \int_0^{200} \alpha_{\omega} d\bar{\nu} = 360 \times 10^{-20} \text{ cm.}$$

In liquid cyanogen the contribution of monomolecularly dispersed water to the observed integrated intensity in the range $0\text{--}120\text{ cm}^{-1}$ will be at most $180 \times 10^{-20} N'_w$, where N'_w is the number of molecules of water per cm^3 of the mixture of cyanogen and water.

A typical analysis gave 0.05% w/w of water in the cyanogen and assuming a density of 0.863 g cm^{-3} for cyanogen liquid at 301 K this amount of water is equivalent to a 26.0 neper cm^{-2} contribution to the integrated intensity of the liquid cyanogen. This is equivalent to an error of $+4.5\%$ in the experimental parameter A_1 , and thus to an error of about 2% in the liquid quadrupole, which is well within the uncertainty (due to other sources) in Q (liquid).

In addition, Pardoe has studied the effect of 0.05% w/w of water in benzene (ref. (25), p. 57), the excess integrated absorption due to water in the region $0\text{--}120\text{ cm}^{-1}$ being 40 neper cm^{-1} .

If this value were applicable for liquid cyanogen, it would give a quadrupole moment too large by about 3% .

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