

Vibrational Raman spectroscopic study of cyanogen

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Received 22 January 1997; accepted 26 February 1997

Abstract

The vibrational Raman spectra of cyanogen have been obtained in the gas, liquid and solid states. The three Raman active fundamentals, ν_1 , ν_2 and ν_4 , have been identified in all three phases; whereas the spectra are consistent with $D_{\infty h}$ molecular symmetry for the gaseous and liquid phases, the solid state spectrum clearly shows the presence of the infrared active and Raman-forbidden ν_3 mode. This is possibly indicative of a breakdown of the centro-symmetric structure in the solid state in contradiction of the X-ray diffraction results. © 1997 Elsevier Science B.V.

Keywords: Raman spectroscopy; Vibrational analysis; Cyanogen

1. Introduction

Cyanogen has been the subject of several vibrational spectroscopic investigations, particularly in the gas phase, which have served to clearly establish the centrosymmetric molecular symmetry point group as $D_{\infty h}$. Of especial relevance have been the pure rotational Raman spectra [1–3] of cyanogen and cyanogen- $^{14}\text{N}_2$ and the vibration–rotational infrared spectra of fundamentals and combination bands [4–6].

The C_2N_2 molecule in the gas phase has a linear, symmetrical NCCN structure with five fundamental vibrations (Fig. 1) of which two non-degenerate stretching modes (ν_1 and ν_2) are Raman active (σ_g^+) and one, ν_3 , is IR-active (σ_u^+). The two doubly-degenerate bending vibrations (ν_4 and ν_5) are the Π_g Raman-active and Π_u IR-active deformations, respectively. The unsymmetrical molecules, $^{12}\text{C}^{13}\text{CN}_2$ and $^{12}\text{C}_2^{14}\text{N}^{15}\text{N}$, have only small isotope shifts (Table 1) and their fundamentals, normally distinguished with a prime to denote the isotopic

substitution, are similarly numbered. It is noteworthy that the wave number values of the Raman-active fundamentals ν_1 and ν_2 for $^{12}\text{C}_2^{14}\text{N}_2$ listed in Table 1 have not been obtained from Raman spectroscopy but indirectly from the infrared analyses of the combination bands $\nu_1 + \nu_3$ and $\nu_2 + \nu_3$ [4,6] using the appropriate anharmonic constants. The value of ν_5 has also not been based on direct observation in the infrared but from measurements of the combination band $\nu_1 + \nu_5$ [4,6].

As a result of the measurements in the gas phase, the rotational constants, centrifugal distortion constants and $\tilde{\nu}_0$ band centre values were determined; the $r_o(\text{C–C})$ and $r_o(\text{C–N})$ bond distances were calculated from the rotational constants of the $^{14}\text{N}_2$ – and $^{15}\text{N}_2$ – cyanogen species and provided much more precise values than had been obtained hitherto from X-ray diffraction [7] and electron diffraction [8,9] experiments (Table 2).

In contrast, the vibrational spectroscopy of cyanogen in the liquid and solid states has not been well

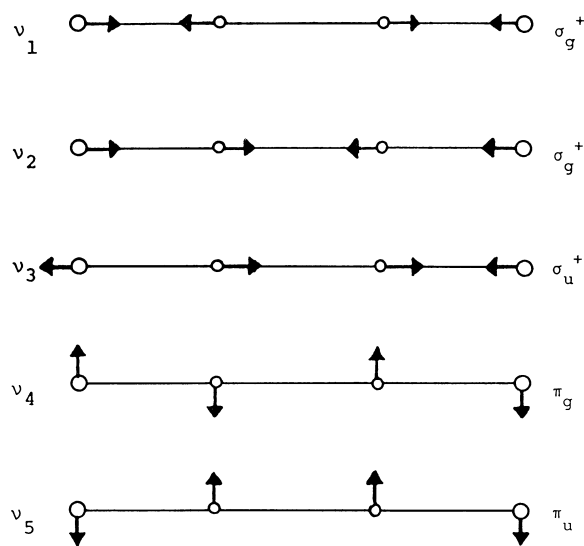


Fig. 1. Vibrational modes of cyanogen, $\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$, $D_{\infty h}$ symmetry; ν_1 , ν_2 and ν_4 , are Raman-active and ν_3 , ν_5 are infrared active.

characterised; however, X-ray diffraction studies [7] clearly show that in the solid at 178 K the cyanogen molecule retains its centre of symmetry and linearity. There appear to have been three early studies of liquid cyanogen [9–11]; although the state has not been specified in the most recent of these [9], a Raman spectroscopic study, it has been assumed to be that of the liquid for subsequent force-constant calculations [12–14]. In the most recent force-constant analysis, Schultz and Eggers [14] were able to calculate values of all six force constants required for the complete SVFF determination from the five fundamentals of $^{12}\text{C}_2^{14}\text{N}_2$ and ν'_1 , ν'_2 and ν'_3 of $^{12}\text{C}^{13}\text{C}^{14}\text{N}_2$ (Table 3); all three interaction constants

are negative and $k(\text{CN},\text{CN})$ has the largest magnitude. Since the calculations of Schultz and Eggers, better values of the anharmonic fundamentals ν_1 , ν_2 , ν_3 , ν_4 and ν_5 (especially ν_2 , ν_4 and ν_5), all of which relate to the gas phase, have become available (Table 1) and rather more is known about isotopically substituted cyanogen molecules. Improved force-constant calculations could thus be performed using revised anharmonic fundamentals but sufficient information is not yet available for the calculation of all the harmonic fundamentals.

The IR spectrum of liquid cyanogen has been reported by Thomas and Orville-Thomas [15]. Twenty-seven bands were observed in the range $4000\text{--}250\text{ cm}^{-1}$ of which ten were assigned. There is one possible coincidence between the Raman and IR spectrum but, in any event, the observation of the broad diffuse feature at ca. 240 cm^{-1} in the Raman spectrum and its assignment as ν_5 implies a relaxation in the liquid state of the selection rules which apparently operate in the gaseous and solid phases. Of the bands not assigned in the IR spectrum, special note should be made of the very strong band at 791 cm^{-1} and the strong bands at 2339 , 1713 , and 766 cm^{-1} . Thomas and Orville-Thomas re-open the debate as to whether ν_5 has a value of $\sim 750\text{ cm}^{-1}$ rather than the generally accepted $\sim 230\text{ cm}^{-1}$. The weight of indirect evidence from gas-phase IR spectra points overwhelmingly to ν_5 at ca. 230 cm^{-1} , although the unassigned bands at 766 cm^{-1} and 791 cm^{-1} in the liquid-phase IR spectrum require explanation. Direct experimental evidence for the occurrence in the IR of the low-frequency band in the $200\text{--}250\text{ cm}^{-1}$ region for the gas, liquid, and solid states is desirable.

Table 1

Anharmonic fundamentals (cm^{-1}) of gaseous $^{12}\text{C}_2^{14}\text{N}_2$, $^{12}\text{C}^{13}\text{C}^{14}\text{N}_2$ and $^{12}\text{C}_2^{15}\text{N}_2$

Vibration	$^{12}\text{C}_2^{14}\text{N}_2$	$^{12}\text{C}^{13}\text{C}^{14}\text{N}_2$	$^{12}\text{C}_2^{15}\text{N}_2$
ν_1, ν'_1	2329.94(15) ^{a,b,d}	2298(2) ^c	–
ν_2	845.4 ^c	–	–
ν_3, ν'_3	2157.8271(5) ^{b,d}	2131(2) ^c	2124.922(3) ^{a,d}
ν_4, ν'_4	503.33 ^{a,b,d}	495(2) ^c	–
ν_5	233.15(15) ^{a,b,d}	–	–

^aMaki [6].

^bBersellini and Meyer [4].

^cCartwright et al. [12,13].

^d ν_0 values from high-resolution infrared vibration–rotational analyses.

^eSchultz and Eggers [14].

Uncertainty in measurement given in parentheses.

Table 2
Bond lengths in cyanogen

Ref.	Method	r_0 (C–C) (pm)	r_0 (C–N) (pm)	r_0 (N–N) (pm)
[6]	Infrared	139 ± 1	115.4 ± 0.6	369.7 ± 0.3
[1]	Raman	138^a	115.7	–
[3]	Raman	140 ± 1^b	115.0 ± 0.7^b	369.0 ± 0.3^b
		138 ± 2^c	116 ± 1^c	369.9 ± 0.6^c
[9]	Electron diffraction	138 ± 2^d	115 ± 2^d	–

^aNo error limit given.

^bFrom B_{av} values.

^cFrom B_0 values.

^d r_a values.

Nixon and co-workers [16–18] have reported the infrared spectra of $^{12}\text{C}_2^{14}\text{N}_2$ and $^{12}\text{C}_2^{15}\text{N}_2$ at 80 K in the region 4000–500 cm^{-1} and the infrared and Raman spectra of the lattice-vibration region at 77 K. A striking feature of ν_3 in the solid-state infrared spectrum is its weak intensity, being only 5% that of the intensity reported for ν_3 in the gas phase [14]. In $^{12}\text{C}_2^{14}\text{N}_2$ and $^{12}\text{C}_2^{15}\text{N}_2$, ν_3 appears as two distinct peaks separated by 1.7 cm^{-1} in $^{12}\text{C}_2^{14}\text{N}_2$ and 1.8 cm^{-1} in $^{12}\text{C}_2^{15}\text{N}_2$, respectively. The lower-wave number peak is 2.4 and 2.1 times, respectively, more intense than the higher one. Initially, Nixon and co-workers, on the basis of a harmonic model with non-polarizable dipole–dipole coupling, interpreted the two peaks as b_{1u} (more intense) and b_{2u} factor-group components with a third and even less

intense component (b_{3u}) lying either under b_{1u} or b_{2u} or elsewhere but undetected. The site- and factor-group symmetries are C_i and D_{2h} . Such a model, even including mutual polarization effects, does not, however, lead to a splitting as substantial as that observed. In order to obtain a calculated splitting of the right order and sense, Nixon and co-workers subsequently invoked a complex atom–atom potential function involving six constants. However, as the authors have themselves pointed out, the apparent inadequacy of the dipole–dipole model to account quantitatively for the observed bands casts some doubt upon the original assignment of the ν_3 components. Some success has also been achieved in the interpretation of the frequencies and intensities of the lattice modes.

Table 3
Force-constant (N m^{-1}) analysis of the vibrational fundamentals (cm^{-1}) of cyanogen

$k(\text{CN}) = 1609.9$	$k(\text{CN,CN}) = -164.4$	
$k(\text{CC}) = 791.6$	$k_{\delta} = 18.5$	
$k(\text{CC,CN}) = -19.1$	$k_{\delta\delta} = -0.21$	
Fundamental	Observed	Calculated
ν_1	2328.5 ^a	2328.5
ν_2	850.6 ^a	850.6
ν_3	2159(2) ^b	2159.0
ν_4	507.2 ^a	502.8
ν_5	240 ^a	240.0
ν_1'	2298(2) ^b	2298.0
ν_2'	–	846.8
ν_3'	2131(2) ^b	2131.3
ν_4'	495(2) ^b	495.0
ν_5'	–	237.4

^aLangseth and Møller [9].

^bSchultz and Eggers [14].

The infrared spectrum of solid cyanogen at an unspecified temperature has also been published independently [15] and six new features are reported but not assigned. Acceptance of the data and assignments leads to the deduction of the following *approximate* values of the unobserved fundamentals of solid $^{12}\text{C}_2^{14}\text{N}_2$: $\nu_1 = 2346$, $\nu_2 = 847$, $\nu_4 = 509$, and $\nu_5 = 246$ and 236 cm^{-1} ; ν_3 was directly observed at 2165 cm^{-1} (average of split components).

In the present work, the Raman spectra of gaseous liquid and solid cyanogen are reported and the observed wave numbers compared with those deduced from infrared spectroscopic measurements by several groups.

2. Experimental

Cyanogen samples were prepared in an all-glass

vacuum line by the thermal decomposition [19,20] of silver cyanide, which had itself been prepared from potassium cyanide. AgCN (2.6 g; 0.02 mol), dried at 100°C, produced C₂N₂ in 75% yield based on the original KCN after heating to 350°C under vacuum; the major loss of cyanogen in this preparation arises from the production of paracyanogen, (CN)_x, as an involatile brown deposit in the vacuum line. Alternative methods of preparation of cyanogen which have been proposed in the literature involve either decomposition of metal cyanides, e.g. Hg(CN)₂ at higher temperatures, with a consequent increase in paracyanogen or reaction of an alkali metal cyanide with copper(II) sulphate solution, which yields a rather impure product.

The cyanogen was stored in break-seal ampoules and used as required to fill a cruciform cell of volume 11 cm³ at 400 torr for the vapour phase experiments, and temperature-controlled cells for the liquid and solid phases. Cyanogen has a narrow liquid range; the melting and boiling points of cyanogen are 245 and 252K, respectively [19].

Raman spectra of cyanogen were recorded in the gas phase (293 K; 400 torr), liquid phase (250 K; at which the vapour pressure is about 600 torr) and solid phase (240 K). Temperature control was effected using cold nitrogen gas flow and vacuum-jacketed cells. Spectra were excited using the 488.0 nm and 514.5 nm lines of a Spectra-Physics Model 2020 argon laser, with nominal powers of 1500 mW in each line, and recorded using a Spex Industries 1401 0.75 m double monochromator with ITTFW130 photon-counting detection and having a reciprocal linear dispersion of 20 cm⁻¹ mm⁻¹ in the first order of diffraction at 500 nm. Spectral resolution was normally 2 cm⁻¹ and calibration was effected using the emission lines of neon and thorium hollow-cathode lamps and comparison with interferometrically measured wavelengths [21]. Spectral data accumulation and spectrometer scanning control were carried out using a Thorn-EMI system and multiple scanning over prescribed wave number units. Normally, between 5 and 10 scans of each wave number region was required to effect suitable signal-to-noise enhancement for the solid and liquid phase spectra, but up to 25 scans were required for the vapour-phase spectra.

3. Results and discussion

The band wave numbers observed in the Raman spectra of gaseous, liquid and solid cyanogen are given in Table 4, which also contains reference to the previously observed infrared and Raman spectra in the literature. As mentioned previously, the Raman spectroscopic study of Langseth and Møller [9], although not actually defining the phase, has been assumed here to refer to the liquid.

The infrared spectra demonstrate a richer number of modes in comparison with the Raman spectra; this has enabled the calculation of the Raman-active ν_1 , ν_2 and ν_4 fundamentals from infrared-active overtones and combination bands. Also, the hitherto unobserved infrared-active ν_5 mode has been calculated from infrared-active combination bands to be near 235 cm⁻¹[6].

Generally, there is a good agreement between the calculated and previously observed Raman-active fundamental wave numbers and those observed in the present comprehensive study. Hence, the ν_1 wave number value in the gas phase found here at 2332.2 cm⁻¹ matches very well the 2327.9 cm⁻¹ value in the liquid state and the 2327 cm⁻¹ band found in the solid. The Raman spectra, particularly in the region of the ν_1 fundamental near 2330 cm⁻¹ for the gas phase, exhibit some 'hot' bands arising from the contribution of the ν_4 and ν_5 molecular states. It has previously been shown [3] that the pure rotational Raman spectra of ¹²C₂¹⁴N₂ and ¹²C₂¹⁵N₂ are complicated by the presence of molecules in the ν_5 (Π_u) and ν_4 (Π_g) states at 235 and 502 cm⁻¹, respectively; at 300 K the occupancy of the vibrational states ν_5 , $2\nu_5$ and ν_4 relative to the vibrationless ground state (100%) are 66%, 32% and 30%, respectively. Hence, the observed Raman spectrum of cyanogen molecules in the gas phase should consist not only of the transitions arising from the ground vibrational state (0000°0°) but also from the molecules existing in the ν_5 (0000°1°), $2\nu_5$ (0000°2) and ν_4 (0001°0°) vibrational states. Contributions from molecules in other excited vibrational states can be neglected because of their smaller populations at the experimental temperatures used.

In a study of the Raman spectrum of cyanogen in the gas phase [22], a similar progression of 'hot' bands near the Raman-active ν_1 fundamental was

Table 4
Raman and infrared vibrational band wave numbers (cm^{-1}) for cyanogen, $^{12}\text{C}_2^{14}\text{N}_2$

IR Gas [17]	Raman This work	IR Liquid [15]	Raman Liquid [9]	This work	IR		Raman This work	Assignment
					Solid [15]	Solid [16]		
		3000 vw				3012.9 w		$\nu_2 + \nu_3$
2663 s		2663 s			2668 s	2673.4 m } 2670.1 m }		$\nu_3 + \nu_4$
2563 s	2556 m				2581 m } 2569 m }	2588.7 m } 2573.8 m }		$\nu_1 + \nu_5$
	2332.2 s 2329.8 2323.7 2326.8		2328.5 vs	2327.9 vs			2327 vs	ν_1 $\nu_1 + \nu_5 - \nu_5$ $\nu_1 + \nu_4 - \nu_4$ $\nu_1 + 2\nu_5 - 2\nu_5$
2157.6 s ^a		2158 vs	2149 m		2163 s	2166.7 m } 2164.9 m }		ν_3
2092 w		2089 vw						$\nu_1 - \nu_5$
					1714 m 1387 vw 1367 w			
		1262 vw				1265.6 vw } 1255.6 vw }		$2\nu_4 + \nu_5$
		1092 vw			1226 w 1184 vw 1088 vw	1088.0 vw		$\nu_2 + \nu_5$ $2\nu_4$
	858.8 w 854.8 w 850.8 w 846.5 ms 838.4 w		1028.5 w				850 w	ν_2 $\nu_2 + \nu_5 - \nu_5$
		791 mw 766 s	850.6 m 841 w	850.5 m	791 w		847 s	
732 s		741 vs	750 vw	745.0 s	754 m } 744 m }	755.5 s } 745.6 vs }		$\nu_4 + \nu_5$
		612 w						$\nu_2 - \nu_5$ $2\nu_4 - \nu_5$ $2\nu_4 - \nu_4$ ν_4 (S-branch maximum)
	507.4 mw		561.4 vw 521.4 w					ν_4 (O-branch maximum)
	502.6 ^b 497.7 mw		507.2 s				505 s	
	492.1 vw							$2\nu_5$ ν_5
			~475 vw ~240 w				234.5 mw	

^a $\bar{\nu}_0$ value from Ref. [6], $2157.849 \pm 0.005 \text{ cm}^{-1}$.

^bBand centre, $\bar{\nu}_0$, calculated from observed O,S branch maxima.

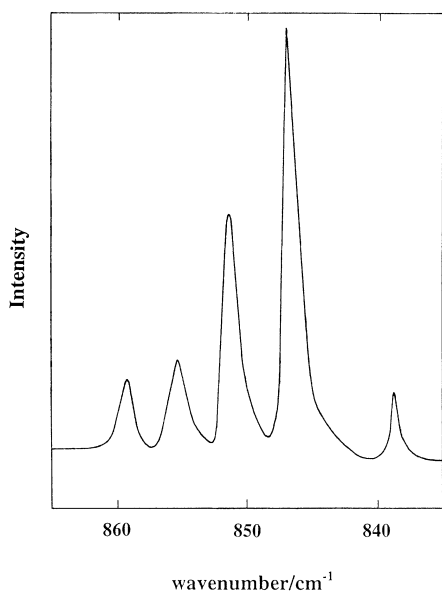


Fig. 2. ν_2 region of cyanogen in the gas phase Raman spectrum at 393 K. Excitation wavelength 488 nm, laser power 1200 mW. Slit width 1 cm^{-1} .

noted and confirmed as arising from contributions from cyanogen molecules in the ν_5 state using rotational constants from a previous infrared high-resolution study [6]. However, it was predicted that a Q-branch from the $10010 \leftarrow 00010$ transition would be expected to occur around 2323 cm^{-1} ; this $\nu_1 + \nu_5 - \nu_5$ band is observed in the present work at 2323.7 cm^{-1} . Also, from the infrared-active $10001 \leftarrow 00000$ transition at 2561.3 cm^{-1} [6], the wave number of the hitherto unobserved ν_5 fundamental was estimated at 233.7 cm^{-1} in the gas phase [22]. In the present work, using the directly observed Raman spectroscopic value for ν_1 at 2332.2 cm^{-1} and the infrared combination band $\nu_1 + \nu_5 = 2561.3$ [6], a gas phase value for $\nu_5 = 229.1 \text{ cm}^{-1}$ is found. This is in very good agreement with that found by Langseth and Møller of $\sim 240 \text{ cm}^{-1}$ in the liquid phase and 234.5 cm^{-1} found for the solid phase in the current work.

The ν_2 region near 845 cm^{-1} in the Raman spectrum of the gas phase is also complicated by 'hot' bands (Fig. 2). Using the rotational and vibrational constants derived from the infrared spectra by Maki [6], a good fit to the Raman spectrum is achieved with the confirmation of the ν_2 fundamental as the strongest Q-branch at 846.5 cm^{-1} (in good agreement with the

infrared calculated value for ν_2 of 845.5 cm^{-1} from the combination band analyses).

The Raman-active ν_4 band exhibits strong O- and S-band unresolved vibration-rotational structure, with a separation of the maxima of 9.7 cm^{-1} . The band centre is estimated at 502.6 cm^{-1} in the present work, which is in fair agreement with the only other reported value for ν_4 of 507.2 cm^{-1} from the liquid phase Raman spectrum [9]. The very weak feature at 492.1 cm^{-1} is assignable to the $2\nu_5$ overtone. The value of ν_4 found here is in excellent agreement with the values of 502.7 cm^{-1} [22] and 502.8 cm^{-1} [13] proposed from infrared measurements of combination bands.

Depolarisation measurements of the fundamentals in the gas-phase Raman spectra gave the following results:

ν_1 (2332.2 cm^{-1})	: $\rho = 0.37 \pm 0.01$
ν_2 (846.5 cm^{-1})	: $\rho = 0.33 \pm 0.01$
ν_4 (502.6 cm^{-1})	: $\rho = 0.83 \pm 0.01$

These values are in the range of those expected for polarised and depolarised bands for σ_g^+ and Π_g symmetry and confirm the band assignments.

In contrast to the gas-phase studies, the previous spectroscopic work on the liquid phase of cyanogen has been rather contradictory. The earliest study of Petrikaln and Hochberg [10] was followed by that of Langseth and Møller [9] (assumed liquid phase) and more recently by Thomas and Orville-Thomas [15]. A very strong band in the infrared spectrum of liquid cyanogen [15] at 2158 cm^{-1} is assigned to ν_3 ; surprisingly, Langseth and Møller observed a band at 2149 of medium intensity in the Raman spectrum of the liquid which was assigned to ν_3 , forbidden in the Raman spectrum for $D_{\infty h}$ molecular symmetry. No band was observed near 2150 cm^{-1} in the Raman spectrum of liquid cyanogen in the present work; however, the very strong band at 2327.9 cm^{-1} observed in the present work is in good agreement with that reported at 2328.5 cm^{-1} by Langseth and Møller [9].

The region of the ν_2 fundamental in the liquid phase has been the subject of some controversy; Thomas and Orville-Thomas report several features in the infrared spectrum between 700 and 800 cm^{-1} , viz. 791 , 766 and 741 cm^{-1} . It was suggested that one of these features could arise from HCN impurities

($\nu_2 \approx 715 \text{ cm}^{-1}$), but this is hardly tenable as some of these features occur in the gas, liquid and solid phases, and in the infrared and Raman spectra. In Table 4, the assignment of the strongest features near 740 cm^{-1} has been made in accord with combination bands rather than an alternative assignment which invokes the adoption of P- and R- branches for the 766 and 741 cm^{-1} components. A suggestion has also been made [15] that a new assignment of ν_2 be considered to the strongest feature near 741 cm^{-1} ; however, no explanation can be given for the intensity of this infrared-forbidden band or for the combination bands involving a $\nu_4 \approx 503 \text{ cm}^{-1}$ which are generally compatible with this latter assignment, particularly in the gas phase spectra. The observation of a weak feature at $\sim 1028 \text{ cm}^{-1}$ in the Raman spectrum of the liquid [9] has not been confirmed in the current work; Langseth and Møller invoked the occurrence of a Fermi resonance between $2\nu_4$ and ν_2 (whose unperturbed levels are separated by 150 cm^{-1}) to explain the appearance of this band in their Raman spectrum. Support for the Fermi resonance idea is provided by the infrared work of Maki [6], who has derived some band constants.

The Raman spectrum of solid cyanogen at 240 K reported here is again much more simple than the corresponding infrared spectrum; the most characteristic feature is the strong band at 2327 cm^{-1} which is the ν_1 fundamental, displaced some 6 cm^{-1} from its gas-phase value. The ν_2 and ν_4 fundamentals are also clearly seen as strong bands at 847 and 505 cm^{-1} , respectively. However, a medium intensity band at 234.5 cm^{-1} observed in the solid-state Raman spectrum in the current work is clearly a new feature, which does not appear in our gas-phase or liquid-phase studies. The assignment of this band to the infrared-active ν_5 fundamental, which has not been recorded directly but whose wave number value is well known from combination band measurements, is quite realistic. However, the interesting conclusion which can then be made is the breakdown of $D_{\infty h}$ molecular symmetry in cyanogen in the solid state which gives rise to this feature. The strongest infrared-active band in $D_{\infty h}$ symmetry is the ν_3 mode near 2160 cm^{-1} ; no evidence for this mode is observed in the Raman spectrum of the solid state here. However, Langseth and Møller [9] have reported a weak feature at $\sim 240 \text{ cm}^{-1}$ in their Raman spectrum

of liquid cyanogen and this is also consistent with its assignment as ν_5 . Since the ν_5 fundamental involves a lateral displacement of the nitrogen atoms relative to the carbon atoms out of the molecular axis (Fig. 1), it is tempting to suggest that in the solid (and, perhaps, also in the liquid phase) cyanogen molecules are subject to molecular interactions at right angles to the molecular axis. This would facilitate the dynamic creation of 'bent' C_2N_2 molecules and cause activation of the ν_5 mode in the Raman spectrum and would explain the band observed at 234.5 cm^{-1} in the present work. This conclusion conflicts with the X-ray diffraction results [7] on solid cyanogen, but a possible contributory factor to the discrepancy could be the temperature at which the solid state Raman spectrum was obtained viz. 240 K , just below its melting point. At this temperature, the population of the lowest vibrational state, ν_5 , is still about 50% that of the ground state and this would favour the observation of a non-linear structure. The temperature of the X-ray diffraction experiment was not defined, but that of the solid-state infrared spectra was 80 K ; at this temperature, the population of the ν_5 state is negligibly small and therefore the linear structure would be in preponderance.

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