The infrared and Raman spectrum of dicyanoacetylene. The ν_9 fundamental¹

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Abstract

The Raman spectrum of liquid dicyanoacetylene, NC-C \equiv C-CN, was reinvestigated and ν_3 found at 617 cm⁻¹. The Fermi resonance between ν_1 and $2\nu_5$ is explained, considering the isotopic species NC-¹³C \equiv C-CN. The high resolution infrared spectrum of the lowest frequency fundamental ν_9 has been recorded for the first time, and the rotational constants for several states with $\nu_9 \leq 9$ have been determined.

Introduction

The infrared and Raman spectra of dicyanoacetylene have been known since 1953 [1,2], but only recently have new attempts been made to investigate this molecule [3–8], partly because C_4N_2 has now been detected in the atmosphere of Saturn's moon Titan [3]. As outlined in ref. 6, infrared astronomy may be expected to find molecules of this class in future.

Most of the fundamentals and several combination bands of C_4N_2 have been assigned with certainty, but some doubt exists concerning the Raman-active vibrations ν_1 , ν_2 and ν_3 , assigned differently in refs. 2 and 3. Therefore, we have recorded the Raman spectrum of a pure sample



of liquid dicyanoacetylene with 1064 nm excitation and a spectral slit width of 2 cm^{-1} . The results

and conclusions are given in this paper.

The lowest frequency bending vibration ν_9 has never been measured directly in the far-infrared. An approximate position of 107 cm^{-1} has been deduced from difference bands, however. In the gas phase, ν_9 turned out to be a band of medium intensity (like $\nu_7 + \nu_8$ or $\nu_6 + \nu_9$) with a strong, broad *Q*-branch, corresponding to a $\Pi_u \leftarrow \Sigma_g^+$ transition with many overlapping hot bands. From a high resolution spectrum several of these and the main band could be analyzed, as described later.

Experimental

Dicyanoacetylene was prepared from acetylenedicarboxylic acid dimethyl ester in two steps:



(1) A mixture of ester and methanol was added to liquid ammonia at -50° C with continuous stirring until the white diamide was formed. The mixture was then allowed to warm up to room temperature, whereby superfluous ammonia

¹ Dedicted to Donald McKean and Lindsay Duncan.

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Fig. 1. Raman spectrum of liquid dicyanoacetylene. Ordinate in uncorrected intensity units. Note that there is just one peak between 600 and $700 \,\mathrm{cm}^{-1}$. Assignments are given in Table 1.

evaporated. After washing the precipitate with methanol, the yield was about 95%.

(2) To improve the yield of dicyanoacetylene with respect to heating the solid diamide with P_2O_5 , the dehydration was carried out in a slurry of P_2O_5 in sulfolane-m (a mixture of 95% tetramethylene sulfone and 5% 3-methyl tetramethylene sulfone to lower the melting point) [9]. The slurry was prepared by slowly adding 0.2 mol P_2O_5 to 100 ml sulfolane-m in a reaction vessel, with stirring, at room temperature. A mixture of 0.05 mol diamide and 25 ml sulfolane-m was placed in a flask with a movable connection to the reaction vessel so that the mixture could be added slowly in vacuo.

The system was then flushed with N_2 or Ar and heated to 110°C at a pressure of about 60 hPa. Care

was taken to remove oxygen from the reaction vessel before adding the diamide slurry. The addition was made during about 30 min and the evolving dicyanoacetylene was condensed in one or two traps at -78° C. After the diamide addition, the temperature of the reaction mixture was raised to 120°C for another 30 min to complete the evaporation of dicyanoacetylene. To remove traces of sulfolane or other impurities, the product was redistilled into another trap. The yield amounts to 25-50%.

Because dicyanoacetylene reacts with oxygen and hydrocarbon-based grease, care should be taken to prevent air entering the reaction vessel, and silicone grease should be used for all joints.

The Raman spectra were recorded at a spectral slit width of 2 cm^{-1} with a Bruker IFS 66 FT spec-

| Assignment | Symmetry | This work ^a | Miller et al. [2] | Khanna et al. [3] |
|-------------------------------|---|------------------------|---------------------|-------------------|
| $2\nu_5 + \nu_3$ F.r. | Σ_{μ}^{+} | 2950 | | |
| $v_1 + v_2$ F.r. | Σ_{a}^{B} | 2882 | 2886vw ^b | |
| $2\nu_5$ F.r. | Σ_{α}^{5+} | 2335 | 2333vs | 2304 ^c |
| $2\nu_5$ F.r. ¹³ C | $\Sigma^{\frac{5}{4}}$ | 2307 | 2309vw ^b | |
| ν_1 F.r. | Σ^+_{o} | 2268 | 2267vs | 2333 |
| ν_1 F.r. ¹³ C | Σ^{+} | 2247 | | |
| $\nu_4 - \nu_9$ | $\Sigma_{\mathrm{u}}^{+} \leftarrow \Pi_{\mathrm{u}}$ | 2137 | 2137w | |
| ν_{γ} | Σ_{g}^{+} | 2121 | 2119m | 2267 ^d |
| - | 0 | | 2070w | |
| $2\nu_6$ - | Σ_{g}^{+} | 1013 | 1018vw | |
| - | 8 | | | 980 |
| | | | 759w | |
| ν_3 | Σ_{g}^{+} | 617 | 692m | 640 |
| | e e | | 618vw | |
| | | | 570w | |
| ν_6 | $\Pi_{\mathbf{g}} \leftarrow \Sigma_{\mathbf{g}}^+$ | 505 | 504vs | 504 |
| ν_7 | $\Pi_{g}^{} \leftarrow \Sigma_{g}^{}$ | 263 | 263w | 263 |

Table 1 Raman spectrum of liquid NC-C \equiv C-CN (cm⁻¹)

Abbreviations: F.r. = Fermi resonance; ${}^{13}C$ = isotopomer NC $-{}^{13}C \equiv C-CN$; w = weak m = medium, s = strong, v = very. ^a Frequency accuracy $\pm 2 \text{ cm}^{-1}$.

^b Not assigned.

^c Solid state frequency.

^d Khanna et al. [3] consider 2137 and 2119 cm⁻¹ to be impurity bands.

trometer with Nd/YAG laser excitation. Low resolution IR spectra were obtained from a Perkin-Elmer model 325 grating spectrometer at about 1.5 cm^{-1} slit width. The far-infrared spectra with resolutions of up to 0.0016 cm^{-1} were measured with a Bruker IFS 120 HR instrument. An absorption path of 300 cm was used with a pressure of 0.5 hPa.

Results and discussion

Low resolution spectrum

The Raman spectrum of liquid dicyanoacetylene is shown as Fig. 1. The spectrum is different from those of refs. 2 and 3 as summarized in Table 1. The assignment of the lowest frequency stretching vibration ν_3 has been disputed because several bands appeared in the Raman spectrum between 900 and 600 cm⁻¹. However, our spectrum of what we believe to be a very pure sample shows just one band in this region. This band must be ν_3 . The assignment is confirmed by the combination bands $\nu_1 + \nu_3$ and $2\nu_5 + \nu_3$ near 2900 cm⁻¹ having a reasonable anharmonicity of about -3 cm^{-1} .

Miller et al. [2] discuss thoroughly the possible assignments of the three Raman bands at 2335, 2307 and 2268 cm⁻¹, concluding that the first and the last are a "resonance pair". This is in agreement with our observation of *two* combination bands near 2900 cm⁻¹ involving ν_3 .

The difficulty with the weak Raman peak at 2307 cm^{-1} which caused Khanna et al. [3] to change the assignment of ν_1 and ν_2 can now be removed. We have observed an additional peak of low intensity at 2247 cm^{-1} in the liquid phase. Because of overlapping, its intensity is difficult to measure, but it is probably stronger than the 2307 cm^{-1} peak. Our conclusion is that two Fermi resonance systems are seen near 2300 cm^{-1} , one belonging to the main isotopic species and the other belonging to the NC- $^{13}C\equiv C-CN$ isotopomer in its natural abundance of 2.2%.

| 14010 2 | | | | | | | |
|-----------------|------------------|--------|-------------|-----|----------|-------------|----|
| Calculated | frequency | shifts | (cm^{-1}) | for | ^{13}C | isotopomers | of |
| $NC-C \equiv C$ | -CN ^a | | | | | | |

| | Δu_1 | $\Delta 2 u_5$ | |
|---|----------------|-----------------|--|
| $N^{13}C-C \equiv C-CN$ $NC-^{13}C \equiv C-CN$ | -12.2 -18.9 | -3.2 -33.2 | |

^a Calculated at the HF/6-31G** level [11]; compare ref. 7. In ref. 12, almost the same $\Delta \nu_5$ values are found for the matrix phase.

To show that this explanation is self-consistent, we first calculated the unperturbed positions of ν_1 and $2\nu_5$ for the ¹²C species from the relative intensities of the perturbed bands [10]. Adopting an intensity ratio of 1.84 and assuming the intensity of the unperturbed $2\nu_5$ to be negligible, the unperturbed levels $v_5 = 2$ and $v_1 = 1$ should be at 2311 and 2292 cm⁻¹, respectively. The resonance parameter obtained, $|W_{155}| = 32 \text{ cm}^{-1}$ seems very reasonable in magnitude for a strong resonance.

The calculated isotopic shifts of $N^{13}C-C \equiv C-CN$ and $NC^{-13}C \equiv C-CN$ given in Table 2 have been

Table 3 The Fermi resonance between $2\nu_5$ and ν_1

| Level ^a | Unperturbed ^b | Perturbed ^c | Observed | |
|--------------------|--------------------------|------------------------|--------------|--|
| $v_5 = 2$ | 2311 | | 2335 | |
| $v_1 = 1$ | 2292 | | 2268 | |
| $v_5^{\rm NC}=2$ | 2308 | 2329 | (overlapped) | |
| $v_1^{\rm NC} = 1$ | 2279 | 2259 | (overlapped) | |
| $v_5^{\rm CC} = 2$ | 2278 | 2309 | 2307 | |
| $v_1^{\rm CC} = 1$ | 2275 | 2245 | 2247 | |

^a NC refers to N¹³C-C \equiv C-CN, CC to NC-¹³C \equiv C-CN. ^b Calculated as explained in the text for the main isotopomer, and with the frequency shifts of Table 2 for the ¹³C species.

^c Calculated from the unperturbed frequencies with $|W_{155}| = 32 \text{ cm}^{-1}$.

used to predict the perturbed positions for $2\nu_5$ and ν_1 for both ¹³C isotopomers. Additional assumptions are that x_{55} and W_{155} do not change upon isotopic substitution. The results are given in Table 3, and Fig. 2 depicts our explanation of the Raman spectrum in the 2300 cm⁻¹ region. It should be noted that $2\nu_5$ and ν_1 of N¹³C-C=C-CN are too near the



Fig. 2. The Fermi resonance between ν_1 and $2\nu_5$: on the left, the unperturbed levels as given in Table 3; on the right, the perturbed levels of the three isotopic species with the corresponding transition frequencies in cm⁻¹. NC refers to N¹³C-C=C-CN, CC to NC-¹³C=C-CN as in Table 3.

Table 2

Table 4

| Transition v ₉ | Maximum J'' obs. | | Number of | σ polynom. fit | |
|------------------------------|--------------------|------------------|-----------|-----------------------|--|
| | P-branch | <i>R</i> -branch | nnes m ne | (10 cm) | |
| $(1^1 \leftarrow 0^0)e$ | 144 | 136 | 205 | 1.0 | |
| $(2^2 \leftarrow 1^1)e$ | 124 | 107 | 152 | 2.5 | |
| $(2^2 \leftarrow 1^1)f$ | 140 | 132 | 214 | 2.2 | |
| $(3^3 \leftarrow 2^2)e$ | 124 | 119 | 176 | 2.6 | |
| $(3^3 \leftarrow 2^2)f$ | 120 | 122 | 179 | 2.9 | |
| $(4^4 \leftarrow 3^3)e$ | 127 | 120 | 168 | 2.4 | |
| $(4^4 \leftarrow 3^3)f$ | 116 | 117 | 171 | 3.0 | |
| $(5^5 \leftarrow 4^4)e$ | 122 | 112 | 164 | 1.9 | |
| $(5^5 \leftarrow 4^4)f$ | 119 | 110 | 166 | 2.2 | |
| $(6^6 \leftarrow 5^5)$ | 126 | 105 | 153 | 2.4 | |
| $(7^7 \leftarrow 6^6)$ | 120 | 110 | 153 | 3.1 | |
| $(8^8 \leftarrow 7^7)$ | 112 | 112 | 99 | 2.3 | |
| $(9^9 \leftarrow 8^8)$ | 110 | 95 | 88 | 3.5 | |

Summary of assigned bands in the ν_9 system of dicyanoacetylene

main bands to be observed under our experimental conditions.

After our work had been completed, a paper by A.M. Smith et al. [12] appeared with an investigation of the matrix spectrum of dicyanoacetylene. From a study of the visible fluorescence and a force constant calculation including some isotopic shifts, our assignments above have been independently confirmed.

The ν_9 band system

Because our high resolution spectrum was recorded at room temperature, a very large number of hot bands are seen overlapping the main $\Pi_u \leftarrow \Sigma_g^+$ transition. Its *Q*-branch was not resolved. It obscured the central part of the *P*and *R*-branches, below *J* of about 20 for the main band. However, by means of an efficient interactive Loomis-Wood program ([13]; compare refs. 9 and 10 in ref. 6), most line series could be followed across the central gap, and nine bands have been evaluated. Figure 3 illustrates the line density in the ν_9 band system and shows some of the assignments.

From ref. 6, B_0 and B_9 were known, so that the $v_9(1 \leftarrow 0)$ and $(2 \leftarrow 1)$ transitions could be identi-

fied by comparing the rotational constants, thereby also obtaining the correct J-numbering as described in ref. 6. The assignments were confirmed by the 2:1 line intensity alternation due to nuclear spin statistics [14]. For example, in the $\Delta_g \leftarrow \Pi_u$ band, $v_9(2 \leftarrow 1)$, the *e* component is strong for odd J", and the *f* component is strong for even J".

A series of relatively unperturbed hot bands has been found, obviously belonging to $v_9(n + 1 \leftarrow n)$ transitions. Because the series is so unperturbed it is believed to arise from transitions with the highest |l| possible, and with $\Delta l = +1$. A similar band series has been observed in the otherwise strongly perturbed $\nu_6 + \nu_9$ system having the same lower state rotational constants [15]. This confirms the *J* assignment, as B_0 and B_9 do for the $v_9(1 \leftarrow 0)$ and $(2 \leftarrow 1)$ bands. So far, the bands from the lower *l* states $(v_9 > 1)$ have not been identified. Thus only effective constants for the various v_9 levels are given in this present paper.

A total number of almost 2000 lines has been observed. To save space the 13 line series are described by the polynomials given in Table 5. It should be noted that the polynomial coefficients may change outside the *J*-range given in Table 4. A complete list of all measured lines has been deposited under TNA 30 in the University Library



Fig. 3. Loomis–Wood representations of the ν_9 band system. The ordinate range is 0.15 cm^{-1} , abscissa approximately 27 cm^{-1} . Each line in the spectrum is given by one point. (On the monitor each point is colour-coded according to the line intensity). The central gap is due to unresolved Q-branches. The upper part of the figure shows all lines, the lower part just the transitions $A: 2^2 \leftarrow 1^1, B: 3^3 \leftarrow 2^2, C: 4^4 \leftarrow 3^3, D: 5^5 \leftarrow 4^4$ and $E: 6^6 \leftarrow 5^5$. The decreasing $q_v = B_{\text{eff}}(f) - B_{\text{eff}}(e)$ is clearly seen. Series E is no longer split into an e and f component.

| v_9^l | $\nu_{\rm c}~({\rm cm}^{-1})$ | $c_1 \times 10^2$ | $c_2 \times 10^5$ | $c_{3} \times 10^{9}$ | $c_4 \times 10^{12}$ | $c_6 \times 10^{16}$ |
|--------------------------|-------------------------------|-------------------|-------------------|-----------------------|----------------------|----------------------|
| $(1^1 \leftarrow 0^0)e$ | 107.24424(2) | 8.92516(2) | 7.6738(5) | -4.34(2) | -35.2(3) | _ |
| $(2^2 \leftarrow 1^1)e$ | 107.30107(5) | 8.94456(8) | 11.504(4) | -1.84(10) | 2136(7) | 555(3) |
| $(2^2 \leftarrow 1^1)$ f | 107.30086(4) | 8.94816(5) | 7.6843(10) | -4.60(4) | -38.1(6) | - |
| $(3^3 \leftarrow 2^2)e$ | 107.35742(6) | 8.96579(7) | 9.617(4) | -0.98(7) | 1476(7) | 356(3) |
| $(3^3 \leftarrow 2^2)f$ | 107.35735(6) | 8.96508(8) | 9.580(4) | -2.37(9) | 821(8) | 99(4) |
| $(4^4 \leftarrow 3^3)e$ | 107.41332(5) | 8.98494(6) | 9.590(4) | -2.89(7) | -73(6) | 170(3) |
| $(4^4 \leftarrow 3^3)f$ | 107.41305(6) | 8.98473(8) | 9.652(5) | -1.76(9) | -249(9) | -128(5) |
| $(5^5 \leftarrow 4^4)e$ | 107.46883(4) | 9.00388(5) | 9.604(3) | -2.53(7) | -28(6) | -74(3) |
| $(5^5 \leftarrow 4^4)f$ | 107.46888(5) | 9.00401(6) | 9.611(4) | -2.98(8) | -95(7) | 38(4) |
| $(6^6 \leftarrow 5^5)$ | 107.52381(5) | 9.02315(7) | 9.629(2) | -3.01(9) | -77(2) | - |
| $(7^7 \leftarrow 6^6)$ | 107.57854(5) | 9.04231(9) | 9.638(2) | -3.04(10) | -74(2) | _ |
| $(8^8 \leftarrow 7^7)$ | 107.63331(5) | 9.06075(9) | 9.634(3) | -0.89(10) | -82(2) | _ |
| $(9^9 \leftarrow 8^8)$ | 107.68714(9) | 9.07844(15) | 9.678(4) | -2.3(2) | -95(4) | _ |

Description of the observed line frequencies $\nu(m)^a$

Table 5

 $\nu(m) = \nu_c + \Sigma c_i m^i$, c_5 could not be determined significantly and was always fixed to zero. One standard error in units of the last digit is given in parentheses.

^a m = -J for *P*-branch and m = J + 1 for *R*-branch lines.

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From the polynomial coefficients given in Table 5, effective rotational constants and the position of the vibrational levels have been calculated as follows. Including the present measurements, improved values of B_0 and D_0 were obtained from weighted means of B'' and D'' for the most accurately observed bands, ν_8 , ν_9 , $\nu_6 + \nu_9$ and

 $\nu_7 + \nu_8$. B_{9f} and D_{9f} were calculated from the corresponding hot bands in ref. 6 and from the transition $(2^2 \leftarrow 1^1)f$ of this work. The equations used are

$$B'' = 1/2(c_1 - c_2 + c_4 - 3c_6)$$

$$D'' = 1/4(-c_3 + 2c_4 - 6c_6) \quad \text{(for } c_5 = 0)$$
(1)

The standard error of c_2 in Table 5 is always about

Table 6 Calculated ΔB . ΔD and ΔH values^a in cm⁻¹

| Transition v_9^l | $(B'_{\rm eff}-B''_{\rm eff})	imes 10^4$ | | $(D'_{\rm eff} - D''_{\rm eff}) \times 1$ | 10 ¹² | $(H'_{\rm eff}-H''_{\rm eff})	imes 10^{16}$ | |
|---------------------------------|--|-------------|---|------------------|---|---------|
| | e | f | e | f | e | f |
| $1^1 \leftarrow 0^0$ | 0.76738(5) | b | 35.2(3) | b | _ | |
| $2^2 \leftarrow 1^1$ | 1.1504(4) | 0.76843(10) | -2137(7) | 38.1(6) | -555(3) | pprox 0 |
| $3^3 \leftarrow 2^2$ | 0.9617(4) | 0.9580(4) | 1476(7) | -821(8) | 356(3) | 99(4) |
| $4^4 \leftarrow 3^3$ | 0.9590(3) | 0.9652(5) | 73(6) | 249(9) | 170(3) | -128(5) |
| $5^5 \leftarrow 4^4$ | 0.9604(3) | 0.9611(4) | 28(6) | 95(7) | -74(3) | 38(4) |
| $6^6 \leftarrow 5^5$ | 0.9629(2) | | 77(2) | | | |
| 7 ⁷ ← 6 ⁶ | 0.9638(| 2) | 74(2 | 2) | - | |
| $8^8 \leftarrow 7^7$ | 0.9634(| 2) | 82(2 | 2) | - | |
| $9^9 \leftarrow 8^8$ | 0.9678(| 4) | 95(4 |) | - | |

^a One standard error in units of last digit given.

^b Not observed.

| v9 | Vibrational level | $B_{\rm eff} 	imes 10^4$ | | | $D_{\rm eff} 	imes 10^{12}$ | | |
|----------------|-----------------------------|---------------------------|--------------|---------------------------|-----------------------------|----------------------|--|
| | | e | | f | e | f | |
| 00 | Ground state | 445.8715(10) ^a | | _ | 1057(4) ^a | | |
| 11 | 107.24424(2) ^{a,b} | 446.6389(10) | | 447.0242(11) ^a | 1092(4) | 1130(5) ^a | |
| 2 ² | 214.54518(4) | 447.7893(11) | | 447.7926(11) | -1045(8) | 1168(5) | |
| 3 ³ | 321.90257(6) | 448.7510(11) | | 448.7506(12) | 431(11) | 347(10) | |
| 4 ⁴ | 429.31578(7) | 449.7099(12) | | 449.7158(13) | 504(12) | 596(13) | |
| 5 ⁵ | 536.78463(8) | 450.6704(12) | | 450.6769(13) | 532(14) | 691(15) | |
| 6 ⁶ | 644,30844(9) | | 451.6362(9) | | 683(| (10) | |
| 7^{γ} | 751.88698(10) | 452.6000(9) | | | 757(| (10) | |
| 8 ⁸ | 859.52029(12) | 453.5634(10 | | | 839 | (11) | |
| 9 ⁹ | 967.20743(15) | | 454.5313(11) | | 934 | (11) | |

Table 7 Calculated vibrational levels and rotational constants for the ν_9 system (cm⁻¹)

^a Constants from which the rest of the values have been calculated by means of Tables 5 and 6.

^b Not including a calibration error of the same order of magnitude.

one order of magnitude less than c_1 . The same is valid for c_4 versus c_3 . Thus ΔB and ΔD were calculated from the expressions

$$B'_{\rm eff} - B''_{\rm eff} = c_2 - c_4 + 3c_6$$

$$D'_{\rm eff} - D''_{\rm eff} = -c_4 + 3c_6$$
 (2)

The results are given in Table 6. By addition of these values to the accurately known B_0 , D_0 , B_{9f} and D_{9f} obtained above, the constants of Table 7 have been found. It should be noted that the agreement between this calculation and B and D calculated directly from Eq. (1) (and analogous equations for the upper state) is excellent except for the $v_9 = 8^8$ and 9^9 levels. The discrepancy may be due to unrealistic low errors of the polynomial fit, possibly originating in misassignments in the very weak P-branches of the two highest transitions.

From the $v_9(1^1 \leftarrow 0^0)$ band, it could only be confirmed that $H_0 < 5 \times 10^{-16} \text{ cm}^{-1}$. Thus, no attempt to calculate H_{eff} for the levels of Table 7 has been made. However, it is pleasing to note that the sums of ΔH_{eff} for both *e* and *f* series of Table 6 are close to zero, even if the formal error limits given must be underestimated.

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