J. Phys. Chem. A **2003,** *107,* 10637−10641

Electronic Spectrum of Dicyanoacetylene. 2. Interpretation of the 2800 Å Transition[†]

Gad Fischer,*,[‡] G. Dana Johnson,[§] D. A. Ramsay,[||] and I. G. Ross[‡]

Department of Chemistry, The Faculties, The Australian National University, Canberra ACT 0200, Australia, Chemistry Department, Kansas State University, Manhattan, Kansas 66502, and Steacie Institute of Molecular Sciences, National Research Council, Ottawa, Canada K1A 0R6

Received: April 10, 2003; In Final Form: September 9, 2003

The 2800 Å forbidden $^1\Sigma_u^- \leftarrow {}^1\Sigma_g^+$ transition of dicyanoacetylene shows conventional vibronic origins due to the two π_g vibrations and a third involving the lower π_u vibration. For the latter we argue against a magnetic dipole mechanism and propose that the intensity is electric dipole, involving coupling to a $\pi^* \leftarrow$ n state of reduced point symmetry ($C_{\infty v}$ or less). The strongest band in the spectrum may be another such origin, but there is a competing assignment and neither meets expectations of intensities in related bands. While the vibrational structure is emphatic that the excited-state remains linear, the rotational constants extracted from the principal bands, all double-headed and violet-degraded (ΔB_0 positive), present problems. The apparent contraction or bending of the molecule thus indicated can be countered by large corrections that yield negative values of the equilibrium constant ΔB_e. The size of these corrections and further B values extracted from sequence bands indicate that rotational constants are not uniformly linear in the quantum numbers of the bending vibrations.

Introduction

We embarked on this study of dicyanoacetylene (N≡C−C≡C−C≡N), a molecule since found to be of astronomical interest,[1] in the 1960s. We had every expectation that the ultraviolet spectrum would yield to a conventional analysis. There were precedents in the classic interpretations of the linear molecules HC≡CH [2] and HC≡N [3] (which bend in certain excited states) and later work on N≡C−C≡N (cyanogen, remains linear)[4] and HC≡C−C≡N (cyanoacetylene, bends).[5] Further, Miller and Hannan[6] had recorded the spectrum of NCCCCN at moderate resolution and on theoretical grounds had offered tentative assignments (with which we agree) of the first two excited states, observed in the vapor at 2800 and 2680 Å. They gave a basic vibrational analysis of the second transition. The first was not analyzed. They noted also that there was a possibility that the molecule might bend but for the higher (2680) transition considered that it remained linear.

The measurements we made addressed the first transition, but, notwithstanding the greater detail observed, we were initially unable to propose an analysis.

The more elaborate versions of open-shell molecular orbital (MO) calculations, when applied to linear molecules, for a long time met convergence difficulties. In more recent programs these problems are much mitigated, and they have predictive value for vibrational frequencies in excited states. We have therefore revisited this spectrum, starting with such calculations.

In the preceding paper[7] (part 1) those calculations are reported, not only for NCCCCN but also, as a successful check on their predictive reliability, for HCCCCH, HCCCN, NCCN, HCCCCCCH, and HCCCCCN. For NCCCCN the predicted geometry and vibration frequencies in the excited-state enable us to propose an extensive, if not complete, explanation of the 2800 Å transition.

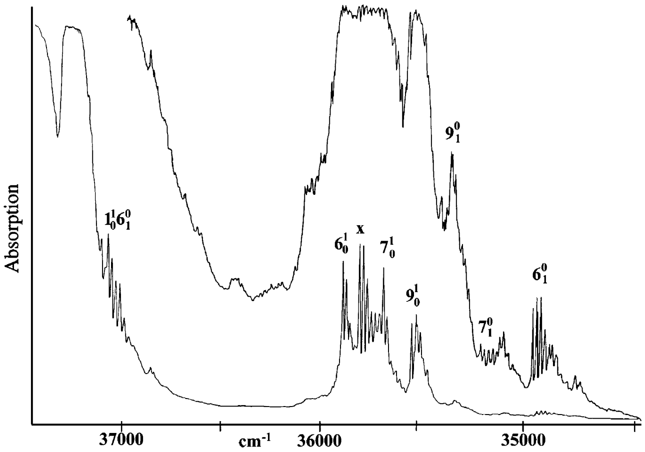

Figure 1. Microphotometer traces of the 2800 Å absorption spectrum of dicyanoacetylene. The band marked X is the 0+340 cm^{-1} band of uncertain assignment.

Experimental Section

Dicyanoacetylene was prepared by the dehydration of acetylene dicarboxamide.[8] $C_4{}^{15}N_2$ was similarly prepared, employing $^{15}NH_3$. Spectra were studied using a 3.4 m Jarrell-Ash Ebert spectrograph at the Australian National University and a 7.3 m Ebert spectrograph at the National Research Council in Ottawa. Pressures ranged from 1 to 80 Torr, path lengths from 1 cm to 8 m, and temperatures from 0 to 70 °C. Figure 1 shows two microphotometer traces of the overall spectrum: relative intensities, other than of adjacent bands, can be deceptive. Table 1 lists the significant bands. The P−Q head spacings are considered to be accurate to ±0.2 cm^{-1}. The isotope shifts are included for the record only. It transpired that they were of no

---

[†] Part of the special issue "Charles S. Parmenter Festschrift".

* To whom correspondence should be addressed. Telephone: +61 2 6125 2935. Fax: +61 2 6125 0760. E-mail: Gad.Fischer@anu.edu.au.

[‡] The Australian National University.

[§] Kansas State University (deceased).

[||] National Research Council.

10.1021/jp034967b CCC: $25.00

TABLE 1: Q Head Measurements for the 2800 Å Transition of Dicyanoacetylene and Their Assignments[a]

freq[b]	from 0−0	P-Q spacing	^{15}N−^{14}N	assignment
37 071.9	+1610.6		−9.6	$1^1_0 6^0_1$
37 051.6	+1590.3		−8.2	$1^1_0 6^0_1 9^1_1$
37 030.5	+1569.2		−6.8	$1^1_0 6^0_1 9^2_2$
37 005.9	+1544.6			$1^1_0 6^0_1 9^3_3$
36 981.8	+1520.5			$1^1_0 6^0_1 9^4_4$
35 883.3	+422.0	1.5	−3.6	6^1_0
35 860.8	+399.5	1.5		$6^1_0 9^1_1$
35 801.1	+339.8	1.8	−1.0	8^1_0 or 6^2_1
35 781.1	+319.8			$8^1_0 9^1_1$ or $6^2_1 9^1_1$
35 765.8	+304.5			$8^1_0 9^2_2$ or $6^2_1 9^2_2$
35 684.5	+223.2	1.6	−0.9	7^1_0
35 667	+205.7	1.5		$7^1_0 9^1_1$
35 548.4	+86.9	1.3	−0.2	9^1_0
35 529.2	+67.9			9^2_1
(35 461.3)[c]	0			0^0_0
35 200.1	−261.2	3.6	+4.1	7^0_1
35 182	−279.3	3.2	+4.3	$7^0_1 9^1_1$
35 163	−298.3		+5.2	$7^0_1 9^2_2$
35 140	−321.3			$7^0_1 9^3_3$
35 109	−352.3			$6^1_1 7^0_1$
34 956.8	−504.5	3.2	+3.5	6^0_1
34 938.1	−523.2	2.8	+3.7	$6^0_1 9^1_1$
34 918.8	-542.5	2.5	+4.0	$6^0_1 9^2_2$
34 899.8	-561.5	2.6	+4.4	$6^0_1 9^3_3$

[a] Other weaker or less clearly defined bands and their assignments are at +973 cm^{-1} ($3^1_0 6^1_0$), +774 ($3^1_0 7^1_0$), −73 ($6^2_2 9^1_0$), −106 (9^0_1), −202 ($3^0_1 6^1_0$), −308 (7^1_2), −368 ($7^0_1 8^1_1$?), −594 (6^1_2), −609 ($6^0_1 8^1_1$?), −673 (6^2_3). [b] All frequencies in cm^{-1}. [c] See text.

assistance in the analysis, given the difficulty of determining band origins with sufficient precision: among the four critical bending modes, the predicted isotope shifts in both states are all between 1.0 and 2.1 cm^{-1}.

The Spectrum and the Choice of the Origin. The first transitions in NCCCCN result from a $\pi^* \leftarrow \pi$ promotion which generates the following singlet states: $^1\Sigma_u^+$, $^1\Delta_u$, and $^1\Sigma_u^-$. The only transition allowed by the electronic selection rules is to $^1\Sigma_u^+$, which has been observed at 1600 Å.[9] Neither of the two forbidden transitions can borrow electric dipole intensity from the allowed transition by first-order vibronic coupling, because vibrations of the required symmetry do not exist. They could do so only by the excitation of two vibrations, which is a much less probable process. The spectra are therefore weak ($f \sim 2 \times 10^{-5}$ and 4×10^{-3}).[6] Such intensity as they do show must derive from $\pi^* \leftarrow$ n or $\pi^* \leftarrow \sigma$ transitions. These transitions are obscured as evidenced by the comprehensive correlation between the spectra of dicyanoacetylene and triacetylene;[6] also, we found the solution spectrum of C_4N_2 to be unaltered in 5 M H_2SO_4: $\pi^* \leftarrow$ n transitions typically disappear in acid media because they are shifted to higher frequencies.

Miller and Hannan showed that the vibronic activity in the 2680 Å system is produced by the two π_g vibrations which in the upper state have frequencies $\nu_6 = 458$ cm^{-1} and $\nu_7 = 260$ cm^{-1}. The spectrum consists essentially of four bands—6^1_0, 7^1_0, and hot bands 7^0_1 and 6^0_1—repeated at intervals corresponding to a symmetrical stretching frequency in the excited state ($\nu_1' = 2192$ cm^{-1}).

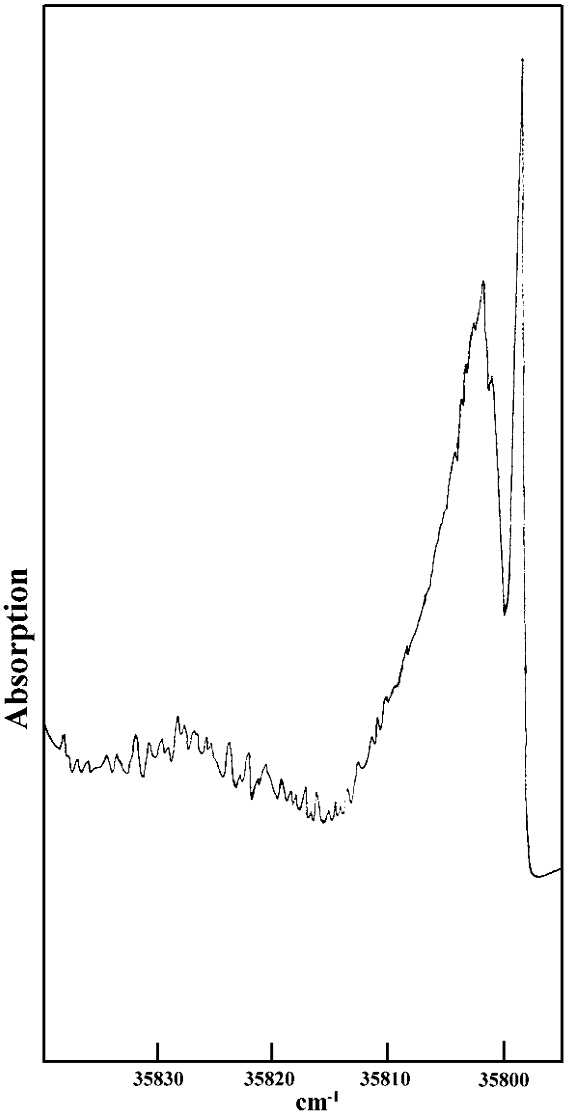

Figure 2. Violet-shaded rotational profile of the 0+340 cm^{-1} band.

Similar activity is evident in the 2800 Å band system (Figure 1). All the best defined bands are double-headed and violet-degraded. Figure 2, which shows the 0+340 cm^{-1} band discussed below, is an example. At the long-wavelength end of the spectrum there are two distinct systems of bands plus accompanying sequence bands, and the first members of these sequences of bands are separated by 243.3 cm^{-1} (compare $\nu_6'' - \nu_7'' = 243.61$ cm^{-1} [10]). The first members may therefore be assigned as 6^0_1 and 7^0_1, and the origin of the band system is confidently calculated to lie at 35461.3 cm^{-1}. The sequences built on these two bands extend to several members and must involve the lowest frequency vibration ν_9 ($\nu_9'' = 107.29$ cm^{-1} [10]). Since the average spacing in the sequences is ~19 cm^{-1}, we deduce that $\nu_9' \sim 88$ cm^{-1} (calc,[7] 91 cm^{-1}).

Bands at +422, +223, and +87 cm^{-1} and Stretching Modes. On the high-frequency side of the origin there are *four* prominent bands at +422, +340, +223, and +87 cm^{-1} together with associated sequence structure. Two of these bands can be assigned as 6^1_0 and 7^1_0 (π_g) by comparison with the frequencies found in the next transition (+458 and +260 cm^{-1}) and with the calculations of part 1 (415 and 236 cm^{-1}), which also explain, through the effect of reorientation of the normal coordinates, the relative intensities of these vibrations as cold and as hot bands—that is, why 6^0_1, despite a less favorable

Boltzmann factor, is stronger than 7^0_1. A Σ^-_u state with π_g vibrations must derive intensity from a Π_u state and be polarized perpendicularly to the molecular axis: the presence of Q branches confirms the polarization.

However, assignment of all four bands provides a major difficulty in the interpretation of the 2800 Å band system. There are no vibrations other than π_g type that can induce intensity in a conventional way, yet there is no doubt that the 0+87 cm^{-1} band is 9^1_0, close to the two independently predicted values above. The hot band 9^0_1 is also present but somewhat overlapped by unassigned structure, at approximately 0−106 cm^{-1}. Formally, 9^1_0 could be a magnetic dipole band, *vibronically induced*, but it contributes perhaps a tenth of the total intensity; i.e., it has $f \sim 0.2 \times 10^{-5}$. The upper limit of an allowed magnetic dipole transition in molecules of this type is $\sim 1 \times 10^{-5}$. Allowed magnetic dipole transitions, though hard to see because weak, have been observed in many molecular electronic spectra. As far as we know, no vibronically induced magnetic dipole transition has yet been proposed in an analysis, and we are reluctant to do so here. The source of the intensity would need to be a $^1\Pi_g$ state. Whether this state is close or distant, the matrix element needed to transfer some 20% of the allowed intensity to the coupled state would be so large that the coupling vibration ν_9' would be rendered strongly anharmonic.[11] In fact its sequence bands show that ν_9' is regularly harmonic. The alternative is that the intensity is, or is largely, of electric dipole character obtained vibronically from a higher state which, since 9^1_0 is a perpendicular band, must be a Π state. If the molecular point group remains $D_{\infty h}$, the coupling needs to be of second order, involving a further quantum of a σ^+_u vibration. Since this is not the case, we envisage that the coupling is to a noncentrosymmetric excited state, of point symmetry $C_{\infty v}$ (or less) whose displacement along a σ^+_u coordinate embodies the mixing of the Π_g and Π_u states and consequently accommodates a first-order connection with the ν_9' level of the $^1\Sigma^-_u$ state. The calculations of part 1, though not convergent for higher states, indicate that the lowest ($\pi^* \leftarrow$ n) Π states are energetically very close and most likely have geometries displaced from $D_{\infty h}$. These states, though not necessarily the perturbing states responsible for the appearance of 9^1_0, are nevertheless the most obvious candidates. The failure to see similar activity in the 2680 Å transition, which is 50 times stronger, is readily understood if the intensity achieved is similar in magnitude.

For 1000 cm^{-1} beyond the four strong band groups there is little absorption, but within it we can identify very weakly the stretching frequency ν_3' (calc, 577 cm^{-1}; obs, 551 cm^{-1}) built on 6^1_0 and 7^1_0, and ν_1' comes in more strongly as a hot band $1^1_0 6^0_1$ (calc, 2211 cm^{-1}; obs, 2115 cm^{-1}) on the rising shoulder of the next transition. A wide difference between the intrinsic intensities of these two stretching frequencies was predicted in part 1.

Band at +340 cm^{-1}. Marginally the strongest in the spectrum, the band at +339.8 cm^{-1} (Figure 2) could be assigned as the self-sequence band 6^2_1 (predicted: $2 \times 422.0 - 504.5 = 339.5$ cm^{-1}). Its theoretical intensity relative to 6^1_0 may be calculated, by generalizing to a doubly degenerate mode a general treatment[12] of self-sequence intensities and ignoring the change in frequency, as $(v_< + 1)(v_< + 2)(\exp(-v''h\nu''/kT)$, with $v_<$ (the lesser of the vibrational quantum numbers) $= v'' = 1$. The result, 26% at 300 K, is too small to account for most of the observed intensity. Also, among the hot bands, 6^1_2 should have the same intensity relative to 6^0_1 as 6^2_1 has to 6^1_0; a band at the expected position assigned as 6^1_2, which is only about 25% as intense as 6^0_1, also argues against the assignment of +340 cm^{-1} as purely 6^2_1. Moreover 6^2_1 is not seen in the 2680 Å transition, and the P−Q head spacing is anomalous (see later). We therefore consider whether this band can be assigned otherwise, and particularly as 8^1_0 (calc,[7] 424 cm^{-1}), the most serious counterargument to which is that the predicted hot band 8^0_1 at 34 989 cm^{-1}, with a Boltzmann factor of 20%, is not seen in the clear notch between 7^0_1 and 6^0_1 (nor, at 0+208 cm^{-1}, is 8^2_1). Reorientation of the π_u normal coordinates on excitation is negligible[7] and cannot account for these absences. An alternative value for ν_8', from otherwise unassigned sequence bands on 7^0_1 and 6^0_1 parent bands, is 365 cm^{-1}.

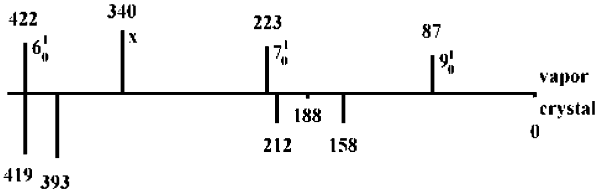

Figure 3. Schematic representation of the vapor and neat crystal spectra of dicyanoacetylene at 4 K. The very weak crystal-induced origin is at 33 912 cm^{-1}. Adapted from Robey.[13]

Band 6^2_1 is a hot band, and 8^1_0 is not, but the temperature range over which we measured the spectra was insufficient to discriminate between them. The choice might be resolved via a low-temperature spectrum. The simplification of low-temperature beam spectroscopy is not easily available: fluorescence is not observed, and photodecomposition is. Robey,[13] however, obtained a spectrum of the polycrystalline neat solid at 4 K, the onset of which is reproduced here as Figure 3 (about 15 further mainly diffuse lines follow). Unfortunately this spectrum can be interpreted in two ways. The crystal is monoclinic, space group $P2_1/a$,[14] and degenerate vibrations are expected to split. Vibronically induced bands will respond to the crystal-induced changes in the spacing of the energy levels and will shift and trade intensity.[15] Large-amplitude bending frequencies such as ν_9 may increase due to steric hindrance. The two simple interpretations are as follows: (1) four main bands in the vapor become the four strong bands in the crystal, so all are true cold bands, or (2) the degenerate 422 (ν_6) and 223 cm^{-1} (ν_7) bands are each split and the latter pushed to lower frequencies; weaker ν_9 is equivocal, and 0+340 cm^{-1} (vapor) is a hot band. The evidence of the low-temperature spectrum could thus be taken to accommodate either assignment of the 0+340 cm^{-1} band, and we are obliged to include them in Table 1 as alternatives.

Rotational Analysis. The 9^1_0 band is the only band that shows measurable rotational structure. Assignments for the R-branch lines of the 9^1_0 band are given in Table 2. Lines with even-J have twice the statistical weight of lines with odd-J. Fitting these lines to the equation

$$R(J) = \nu_0 + B'(J+1)(J+2) - B''J(J+1)$$

with $B'' = B_0'' = 0.044\,587$ cm^{-1} [10] gives $\nu_0 = 35\,548.20 \pm 0.04$ cm^{-1} and $B'(9^1) = 0.046\,20 \pm 0.000\,07$ cm^{-1}. If the J numbers are decreased by two, then the band origin is increased by 0.38 cm^{-1} and the B' value increased by 0.000 05 cm^{-1}.

A value for B_0' can be deduced from the P−Q head separations (Table 1) of the 6^0_1 and 7^0_1 bands, using the rotational constants for the lower state levels from infrared spectroscopy.[10] In this way we obtain $B_0' = 0.045\,25 \pm 0.000\,02$ cm^{-1} from the 6^0_1 band and $B_0' = 0.045\,23 \pm 0.000\,02$ cm^{-1}

TABLE 2: Rotational Assignments for the 9_0^1 Band of Dicyanoacetylene[a]

J	*R*(*J*)	obs − calc	*J*	*R*(*J*)	obs − calc	*J*	*R*(*J*)	obs − calc
30	35 552.61	+0.05	54	35 558.07		78	35 565.44	
32	35 553.03	+0.07	56	35 558.59	−0.04	80	35 566.21	+0.06
34	35 553.34	-0.02	58	35 559.17		82	35 566.94	+0.08
36	35 553.79		60	35 559.72	−0.03	84	35 567.67	+0.08
38	35 554.21		62	35 560.27	−0.06	86	35 568.40	+0.08
40	35 554.65		64	35 560.91	−0.02	88	35 569.07	
42	35 555.10		66	35 561.48	-0.06	90	35 569.87	+0.04
44	35 555.60	+0.04	68	35 562.15	−0.01	92	35 570.62	
46	35 556.08	+0.05	70	35 562.73	−0.06	94	35 571.34	−0.06
48	35 556.53		72	35 563.42		96	35 572.17	−0.04
50	35 557.02	−0.01	74	35 564.05	−0.04	98	35 573.01	−0.01
52	35 557.48	−0.07	76	35 564.74	−0.03	100	35 573.85	+0.01

[a] Wavenumbers (cm^{-1}) with no difference values are calculated.

TABLE 3: Vibrational Term Values and Rotational Constants for Levels in the Ground and Excited States of Dicyanoacetylene

ground[a] $^1\Sigma_g^+$				excited $^1\Sigma_u^-$			
level	freq[b]	B_v''	B_v'' - B_0''	level	freq[b]	B_v''	B_v' - B_0'
6_1	504.66	0.044 6467	0.000 0597	6^1	422.0	0.045 98	0.000 74
				6^2?	2 × 422.0	0.045 77	0.000 53[c]
7_1	261.05	0.044 6747	0.000 0877	7^1	223.2	0.045 86	0.000 62
8_1	471.57	0.044 647	0.000 060	8^1?	339.8	0.045 71	0.000 47[c]
9_1	107.29	0.044 6830	0.000 0960	9^1	86.9	0.046 20	0.000 96
0_0	0.00	0.044 5870	0.0	0^0	0.0	0.045 24	0.0

[a] From ref 10. [b] All frequencies in cm^{-1}. [c] From alternative assignments for the 0+339.8 cm^{-1} band.

from the 7_1^0 band. Taking the mean value we obtain $B_0' = 0.045\,24\ \mathrm{cm}^{-1}$, and $B_0' - B_0'' = 0.000\,65\ \mathrm{cm}^{-1}$.

Values for the rotational constants B' for the other upper-state levels can be obtained in a similar way from the P−Q separations and are summarized in Table 3, as well as values for $B' - B_0'$. The value for 8^1, derived from the spacing 1.8 cm^{-1}, is consistent with the other values. The alternative assignment 6_1^2 predicts a P−Q spacing of 0.9 cm^{-1}, which is less than the spacing for the 6_0^1 band (1.5 cm^{-1}).

The values for $B' - B_0'$ are about 10 times larger than the corresponding quantities in the lower state, a difference manifest in the contrast between the P−Q spacings of the hot and the cold bands. Using these values, we obtain a lower limit for $B_e' = 0.042\,45\ \mathrm{cm}^{-1}$. Contributions for the stretching vibrations will increase this estimate by ~0.0003 cm^{-1}, assuming that the contributions are similar to those in the ground state. B_e'', calculated from the infrared data,[10] is 0.044 52 cm^{-1}. Thus, while B_0' represents a 1.5% increase over B_0'' leading to the violet degradation of the bands, B_e' could be as much as 4% less than B_e''. The calculations of part 1 predict little change.

The ν_9 sequences now introduce a new feature. Consider the band 6_1^0 and its first sequence member $6_1^0 9_1^1$. The latter band involves the upper-state level 9^1 with its large vibrational increment (0.000 96 cm^{-1}) to B', and thus should exhibit the drastic narrowing of the P−Q head spacing shown in all the cold bands. This is not observed. Indeed the value of $B(9^1)' - B_0'$ that one deduces from the head spacings (Table 1) in the bands $6_1^0 9_1^1$ and $6_1^0 9_2^2$ is ~0.000 17 cm^{-1}, which is much closer to the ground-state value. The sequences on 7_1^0 are similar, and among the corresponding cold bands once again the expected narrowing is not seen; e.g., the calculated value for the P−Q spacing in $6_0^1 9_1^1$ is 0.8 cm^{-1}, considerably different from the observed 1.5 cm^{-1}. The band 9_1^2 (which is split due to *l*-type doubling) on the other hand does show, qualitatively, the expected narrowing. These results for ν_6 and ν_7 cannot be reconciled if the expansion of B' and B'' in terms of vibrational quantum numbers is confined to linear terms (the α coefficients: for a comprehensive expansion of *B* in a similar molecule—acetylene—see Canè et al.[16]). If quadratic corrections (the γ terms) are included, they can be fitted, but the coefficients γ_{69}, γ_{79} are required to be large and of different signs in the two electronic states.

Discussion

The very weak 2800 Å spectrum of dicyanoacetylene, undoubtedly $^1\Sigma_u^- \leftarrow {}^1\Sigma_g^+$, presents unusual features.

First, there is a securely established perpendicularly polarized vibronic origin involving the π_u vibration ν_9. Such an origin is formally allowed through a vibronically induced magnetic dipole mechanism, but the band is considered to be too intense. We must therefore entertain an electric dipole mechanism. The rotational analysis of the 9_0^1 band does not allow a distinction to be made between electric and magnetic dipole transitions since the *l*-type doubling is not resolved. We propose that the intensity is electric dipole in nature and arises by vibronic mixing with an allowed transition to a $\pi^* \leftarrow$ n state which is of symmetry $C_{\infty v}$ or less. There may be, at 0+340 cm^{-1}, a second such vibronic origin involving ν_8, but we are unable to offer a firm assignment of the relevant band: the alternative is 6_1^2. This band is the strongest in the spectrum on the high-wavenumber side of the origin, but on the low-energy side the hot band 8_1^0 is missing and from the alternative assignment (6_1^2) the band 6_2^1 is observed but without the required intensity. Indeed it is one of the peculiarities of the spectrum that the strong showing of the π_u band or bands to high energy of the origin is so weakly reflected among the hot bands. This may suggest an interplay in the upper state between the π_g and π_u vibrations as a result of their common coupling to the proposed reduced symmetry state.

Next, the bands are violet-degraded which would ordinarily mean that the linear molecule contracts—almost unthinkable for a $\pi^* \leftarrow \pi$ process—or else bends. Theory[7] predicts that it should do neither, and the lack of progressions in any of the four bending vibrations shows that it remains linear. Further, there is no evidence of K structure, dependent on the long-axis rotational constant *A*, though it is conceivable that the higher *K* values are subject to predissociation and thus not readily seen under high resolution. These observations can be compared with the first singlet transition in diacetylene, which is bent and shows a hot band progression in ν_6 and bands involving $K_a = 0$ and 2 in the excited state.[17] The resolution of the problem of the violet degradation appears to reside in the exceptionally large increments to the value of B_0' when the molecule is vibrationally excited. Correcting back to the equilibrium value B_e'' can resolve the anomaly while leaving open the question of why the increments should be so large.

Indeed, the various rotational constants deduced from the spectra are so unexpected that we have been led to consider that the excited state might be marginally quasi-linear, that is, has a potential function with quartic terms in one or more of the bending vibrations. However, no anharmonicities have been observed in the excited-state vibrational levels; indeed the ν_9 levels appear to be reasonably harmonic. Clearly no definitive solution can be given at the present time. It would be interesting in the future to obtain higher resolution spectra, perhaps with sub-Doppler techniques, in an attempt to solve this problem.

Acknowledgment. We thank Dr. Michael Robey for permission to adapt Figure 3 from his thesis.

References and Notes

(1) Khanna, R. K.; Perera-Jarmer, M. A.; Ospina, M. J. *Spectrochim. Acta A* **1987**, *43*, 421.

(2) Ingold, C. K.; King, G. W. *J. Chem. Soc.* **1953**, 2702, 2725.

(3) Herzberg, G.; Innes, K. K. *Can. J. Phys.* **1957**, *35*, 892.

(4) Callomon, J. H.; Davey, A. B. *Proc. Phys. Soc.* **1963**, *82*, 335. Fish, G. B.; Cartwright, G. D.; Walsh, A. D.; Warsop, P. A. *J. Mol. Spectrosc.* **1972**, *41*, 20.

(5) Job, V. A.; King, G. W. *J. Mol. Spectrosc.* **1966**, *19*, 155.

(6) Miller, F. A.; Hannan, R. B. *Spectrochim. Acta* **1958**, *12*, 321.

(7) Fischer, G.; Ross, I. G. *J. Phys. Chem.***,** preceding paper in this issue.

(8) Moureu, C.; Bongrand, J. C. *Ann. Chim.* **1920**, *14*, 5.

(9) Connors, R. E.; Roebber, J. L.; Weiss, K. *J. Chem. Phys.* **1974**, *60*, 5011.

(10) Winther, F.; Schönhoff, M. *J. Mol. Spectrosc*. **1997**, *186*, 54.

(11) See for example pyridine and pyrazine: Chappell, P. J.; Ross, I. G. *Chem. Phys. Lett.* **1976**, *43*, 440.

(12) Ross, I. G.; Hollas, J. M.; Innes, K. K. *J. Mol. Spectrosc*. **1966**, *20*, 312.

(13) Robey, M. J. Ph.D. Thesis, Australian National University, Canberra, 1974, pp 90−95.

(14) Hannan, R. B.; Collin, R. L. *Acta Crystallogr.* **1953**, *6*, 350.

(15) See for example: Fischer, G.; Small, G. J. *J. Chem. Phys*. **1972**, *56*, 5934.

(16) Canè, E.; Cazzoli, G.; Di Lonardo, G.; Dore, L.; Escribano, R.; Fusina, L. *J. Mol. Spectrosc.* **2002**, *216*, 447.

(17) Hardwick, J. L.; Ramsay, D. A. *Chem. Phys. Lett.* **1977**, *48*, 399. Hardwick, J. L.; Ramsay, D. A. Unpublished results.