The ν_4 Rotation Vibration Band of Dicyanoacetylene

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Z. Naturforsch. **47a,** 1253–1254 (1992);
received October 8, 1992

The ν_4 fundamental band of dicyanoacetylene has been recorded in a 60 m-Herriot cell with a PC-controlled diode laser spectrometer. Transitions were measured in the range from 2232 to 2250 cm^{-1} with a resolution of 0.005 cm^{-1}. Although the upper state is perturbed, $\nu_0 = 2245.374\,(3)$ cm^{-1} and $B' - B'' = -1.016\,(10) \cdot 10^{-4}$ cm^{-1} could be obtained.

Dicyanoacetylene (NC–C≡–CN) was prepared as described in [1] and the ν_4 fundamental was recorded with a diode laser spectrometer in Köln [2]. For the presented measurements, the laser was controlled by a PC and the spectra were digitally recorded. Technical details of the spectrometer will be published elsewhere. The spectral resolution was 0.005 cm^{-1} (limited by Doppler resolution) and the lines were calibrated with N_2O lines from [3].

In order to record the ν_4 band, which is very weak, a Herriot cell with a path length of 60 m was used with a sample pressure less than 100 Pa. The measurements were carried out at room temperature.

Due to the many low lying vibrational levels of dicyanoacetylene, several line series of similar intensity overlap the main band. Thus the expected gap between P and R branch of the $\Sigma \leftarrow \Sigma$ band could not be seen clearly. Consequently the correct J numbering had to be found from the spin statistics and the ground state rotational constants. For the $\Sigma_u^+ \leftarrow \Sigma_g^+$ transition the lines with J'' even are expected to be two times as intense as the odd ones. The ground states constants have been reported in [1]: $B_0 = 445.8699\,(10) \cdot 10^{-4}$ and $D_0 = 10.49\,(4) \cdot 10^{-10}$ cm^{-1}. These values are in good agreement with those found for the ν_4 main band in the present study: $B'' = 445.87\,(2) \cdot 10^{-4}$ and $D'' = 11.3\,(9) \cdot 10^{-10}$ cm^{-1}.

Similar to the ν_5 band, $\Delta B = B' - B''$ is negative in the ν_4 band, as well as in the numerous hot bands seen in the spectrum. From the expected range of B'' values for the lower levels it can be deduced that the band centers of the hot bands are all at lower frequencies

Table 1. ν_4 Band of dicyanoacetylene. Line frequencies in cm^{-1}.

J	R(J)OBS	P(J)OBS	J	R(J)OBS	P(J)OBS
5		2244.9225	66	2250.8747	
6		2244.8328	67	2250.9491	
7		2244.7409	68	2251.0240	2238.8396
8		2244.6519	69		2238.7358
9		2244.5596	70	2251.1723	2238.6317
10		2244.4712	71		2238.5278
11	2246.4268	2244.3781	72		2238.4231
12	2246.5124	2244.2885	74		2238.2147
13		2244.1979	75		2238.1084
16	2246.8576		77		2237.8980
17	2246.9431		84	2252.1866	
18		2243.7359	85	2252.2577	
19	2247.1140		86	2252.3282	
20		2243.5497	87	2252.3992	
24	2247.5378		88	2252.4695	
25	2247.6222		89	2252.5399	
26	2247.7057		90	2252.6095	
27	2247.7889		91	2252.6787	
28	2247.8716	2242.8010	92	2252.7486	2236.2978
29	2247.9555	2242.7059	93	2252.8167	2236.1898
30	2248.0383	2242.6111	94	2252.8875	2236.0813
31		2242.5157	95	2252.9574	2235.9713
32	2248.2034	2242.4194	96	2253.0241	2235.8617
33	2248.2857		97	2253.0922	2235.7540
34	2248.3679		98	2253.1603	2235.6416
35	2248.4472		99	2253.2275	2235.5327
36	2248.5305		100	2253.2965	2235.4224
37		2241.9404	101	2253.3648	
38		2241.8435	102	2253.4309	2235.2022
39	2248.7724	2241.7458	103	2253.4980	2235.0916
40		2241.6490	104	2253.5652	2234.9792
41		2241.5509	105		2234.8680
42	2249.0136	2241.4533	107		2234.6462
43		2241.3563	108		2234.5358
44	2249.1753	2241.2582	112		2234.0868
45	2249.2543	2241.1595	113		2233.9749
46	2249.3343	2241.0614	115		2233.7479
47	2249.4134	2240.9630	116	2254.3475	2233.6352
48	2249.4930		117	2254.4110	2233.5210
50	2249.6470		118	2254.4752	2233.4076
51	2249.7252		119		2233.2943
53		2240.3656	120	2254.6031	2233.1780
54		2240.2651	121		2233.0652
55		2240.1658	122	2254.7298	
56		2240.0621	123	2254.7923	
57		2239.9622	124	2254.8549	
58	2250.2692	2239.8616	125	2254.9161	
59	2250.3458	2239.7607	126	2254.9780	2232.4895
60	2250.4222	2239.6583	128		2232.2598
62	2250.5744		130		2232.0251
65	2250.7994		132		2231.7925

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than the main band. However, the insufficient accuracy of the line positions due to line overlapping did not allow us to identify the hot bands from their B'' values.

A seen in the low resolution spectrum [4], the ν_4 band system is overlapped by another one of approximately the same intensity. Within our frequency range (2232 to 2250 cm^{-1}) we could not detect any line series belonging to the second band system. This suggests that the absorption maximum at 2226 cm^{-1} in the low resolution spectrum must be interpreted as the center Q branch of a perpendicular band. If the observed absorption minimum near 2232 cm^{-1} is the center gap of a parallel band, the R branch of this band should have been observed in our spectrum. The assignment of the 2226 cm^{-1} band, a difference band $2\nu_5-\nu_9$, presumably, shall be discussed in a forthcoming paper [5].

Attempts to fit the lines of the ν_4 band to a low order polynomial were unsuccessful, indicating that the upper state is perturbed, probably by Coriolis coupling with a combination state nearby. The ($v_2=1$, $v_9=1$) state, which is of Π_u symmetry, is the most likely candidate for the interaction partner. Since no transitions to this level have been observed, it was possible to analyze the ν_4 band rigorously.

Table 1 lists the observed lines. We have obtained $\nu_0=2245.374(3)$ cm^{-1} and $B'-B''=-1.016(10)\cdot 10^{-4}$ cm^{-1} from a sixth order polynomial fit of the lines. The errors given are confidence limits, not the standard errors of the fit, which are not realistic in view of the perturbation and the many overlapping hot bands.

Acknowledgement

This work was supported in part by the Deutsche Forschungsgemeinschaft (Grant SFB 301).

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