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The Infrared Spectrum of C_2N_2 in the Region of the Bending Fundamental ν_5

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The high resolution infrared spectrum of C_2N_2 in the region 200–270 cm^{-1} has been studied with a Fourier transform spectrometer. In addition to ν_5, the "hot" bands $2\nu_5^0 \leftarrow \nu_5^1$, $2\nu_5^2 \leftarrow \nu_5^1$ and $3\nu_5^3 \leftarrow 2\nu_5^2$ have been analysed. Polynomial fits have been applied to obtain the vibrational term values and the rotational constants for the levels involved.

1. INTRODUCTION

Cyanogen (C_2N_2) is a stable, symmetric linear molecule. It has five fundamental vibrations. There are two bending modes, of which one is infrared active ($\nu_5 = 234$ cm^{-1}) and the other Raman active ($\nu_4 = 503$ cm^{-1}). The three stretching vibrations are the Raman active fundamentals $\nu_1 = 2331$ cm^{-1} and $\nu_2 = 846$ cm^{-1} and the infrared active fundamental $\nu_3 = 2157$ cm^{-1}. High-resolution spectroscopic studies of this molecule are relatively few (*1–7*). The results concerning the lowest fundamental ν_5 are clearly incompatible. Accordingly, this investigation was undertaken to get accurate results for the ν_5 band and, at the same time, to obtain some information on the associated "hot" bands, too.

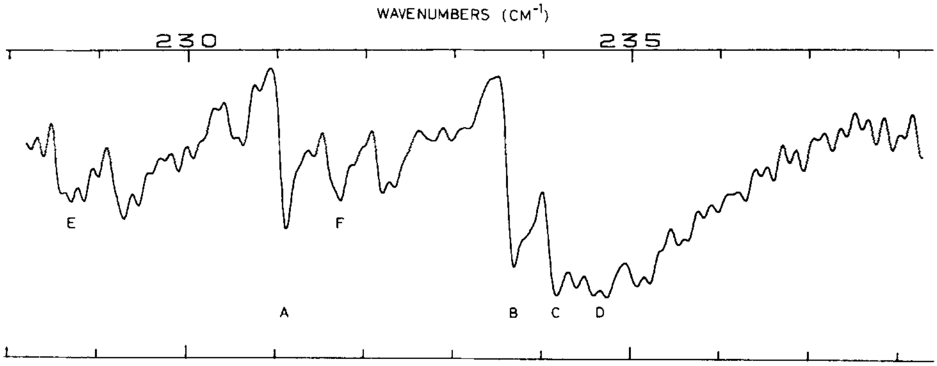

FIG. 1. The Q-branch region of ν_5 of C_2N_2 with low resolution. Absorption downward. The Q branches of the analyzed bands are marked as follows: (A) $0000^0 2^0 \leftarrow 0000^0 1^1$; (B) $0000^0 1^1 \leftarrow 0000^0 0^0$; (C) $0000^0 2^2 \leftarrow 0000^0 1^1$; and (D) $0000^0 3^3 \leftarrow 0000^0 2^2$. The Q-branch E was tentatively attributed to ($0000^0 3^1 \leftarrow 0000^0 2^2$) and the Q branch F to ($0000^0 3^1 \leftarrow 0000^0 2^0$).

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TABLE I

Analyzed Bands of C_2N_2

Transition	J_{MAX} P/R or Q	Measured lines	Standard deviation $[10^{-4}\ cm^{-1}]$
$0000^{0}1^{1c} \leftarrow 0000^{0}0^{0}$	84/82	81	24
$0000^{0}1^{1d} \leftarrow 0000^{0}0^{0}$	75	26	22
$0000^{0}2^{0} \leftarrow 0000^{0}1^{1c}$	62/59	52	19
$0000^{0}2^{2c} \leftarrow 0000^{0}1^{1c}$	59/59	48	26
$0000^{0}2^{2d} \leftarrow 0000^{0}1^{1d}$	61/61	44	28
$0000^{0}3^{3c} \leftarrow 0000^{0}2^{2c}$	57/60	46	26
$0000^{0}3^{3d} \leftarrow 0000^{0}2^{2d}$	59/57	48	30

2. EXPERIMENTAL DETAILS

The sample gas of cyanogen was prepared by allowing sodium cyanide to act on copper (II) sulfate. The gas pressure in the triple pass cell giving a path of 1

TABLE II

Observed Line Positions (cm^{-1} in Vacuum) in the Fundamental ν_5 of C_2N_2

$0000^{0}1^{1} \leftarrow 0000^{0}0^{0}$

J	P_{cc} (J)	R_{cc} (J)	Q_{dc} (J)	J	P_{cc} (J)	R_{cc} (J)	Q_{dc} (J)	J	P_{cc} (J)	R_{cc} (J)	Q_{dc} (J)
5	232.1663	-	-	31	-	-	-	57	-	253.3905	-
6	-	-	-	32	-	244.5711	234.4116	58	216.9283	253.7567	-
7	231.5461	-	-	33	-	244.9143	-	59	216.6701	254.1148	-
8	-	-	-	34	223.5238	-	234.4994	60	216.4038	-	263.0733
9	230.9312	-	-	35	-	-	-	61	-	-	-
10	230.6261	237.2383	-	36	-	-	-	62	-	255.2132	-
11	230.3192	-	-	37	222.6739	246.2949	-	63	-	-	-
12	-	237.8922	-	38	222.3916	246.6472	-	64	-	-	-
13	-	238.2178	-	39	-	246.9868	-	65	215.1017	-	-
14	-	238.5468	-	40	-	-	234.7892	66	-	256.6867	-
15	229.1025	238.8714	-	41	-	-	-	67	-	-	-
16	-	239.2016	233.9040	42	221.2700	248.0410	234.8961	68	-	257.4189	236.7292
17	-	239.5312	-	43	-	248.3916	-	69	-	-	236.8135
18	228.2023	239.8580	-	44	-	248.7398	235.0098	70	213.8114	-	236.9056
19	227.9017	-	-	45	-	249.0934	235.0697	71	-	-	-
20	227.6051	240.5222	234.0010	46	-	-	235.1283	72	213.3098	-	237.0784
21	-	240.8568	-	47	-	-	-	73	-	-	-
22	-	241.1902	-	48	-	250.1598	-	74	212.8081	259.6631	-
23	226.7161	241.5252	234.0888	49	219.3413	-	-	75	-	260.0434	237.3604
24	226.4255	-	-	50	219.0727	-	235.3756	76	212.3015	260.4225	-
25	-	-	234.1510	51	-	251.2263	-	77	-	-	-
26	225.8361	242.5287	234.1825	52	218.5281	251.5874	235.5039	78	211.8113	261.1726	-
27	-	242.8715	234.2184	53	218.2637	251.9468	-	79	-	-	-
28	-	243.2051	234.2586	54	217.9958	252.3075	235.6427	80	211.3145	261.9366	-
29	224.9629	243.5497	234.2923	55	217.7294	252.6670	235.7085	82	210.8258	262.6972	-
30	224.6729	243.8901	-	56	-	253.0286	235.7824	84	210.3398	-	-

m was about 300 Pa. The measurements were performed on the Fourier spectrometer at the University of Oulu (*8*, *9*). The resolution attained was better than 0.02 cm^{-1}. The wavenumber scale was calibrated with the aid of water vapor lines (*10*), which were simultaneously recorded.

3. RESULTS AND ANALYSIS

The term values of a linear molecule may be written as

$$T_v = G_v + B_v[J(J+1) - l^2] \pm (1/2)q_vJ(J+1) - D_v[J(J+1) - l^2]^2 \pm (1/2)\mu_vJ^2(J+1)^2, \quad (1)$$

where G_v is the vibrational term value, B_v is the rotational constant, D_v is the centrifugal distortion constant, and the *l*-doubling constants q_v and μ_v are the differences of the *B* and *D* constants for the component levels of the *l*-doublets. The upper sign in Eq. (1) applies to the *d* levels and the lower sign to the *c* levels. The polynomial expressions applied to the lines in the *P* and *R* branches as well as in the *Q* branch of rovibrational transitions can be derived from Eq. (1) (*11*).

TABLE III

Results from the Analysis of the Fundamental ν_5

		This work		
		P and R branch	Q branch	Literature
ν_{BC}	$[cm^{-1}]$	233.7271(5)	233.7279(12)	
$B'' = B_o$	$[cm^{-1}]$	0.157124(7)		0.157124(12) [1] 0.15712 [4] 0.157115(50) [6] 0.157135(10) [7]
$B' - B''$	$[10^{-3}\ cm^{-1}]$	0.42855(46)	0.65205(109)	
$B' = B^c(\nu_5^1)$	$[cm^{-1}]$	0.157553(7)		
$B' = B^d(\nu_5^1)$	$[cm^{-1}]$		0.157776(8)*	
$D'' = D_o$	$[10^{-8}\ cm^{-1}]$	2.63(8)		3.01(20) [1] 2.7(5) [6] 2.50(8) [7]
$D' - D''$	$[10^{-8}\ cm^{-1}]$	0.085(7)	0.268(19)	
$D' = D^c(\nu_5^1)$	$[10^{-8}\ cm^{-1}]$	2.72(8)		
$D' = D^d(\nu_5^1)$	$[10^{-8}\ cm^{-1}]$		2.90(9)**	
q_5	$[10^{-5}\ cm^{-1}]$	22.59(9)		22.43(18) [5]
μ_5	$[10^{-9}\ cm^{-1}]$	-2.2(3)		

* Calculated with the aid of $B_o = 0.157124(7)\ cm^{-1}$.

** Calculated with the aid of $D_o = 2.63(8) \cdot 10^{-8}\ cm^{-1}$.

The central part of the spectrum with low resolution is shown in Fig. 1. This spectrum has been transformed from a small part of the interferogram points only to visualize better the *Q* branches.

Table I presents an overall summary of the different bands analyzed. For each of these, the observed maximum *J* value, the number of measured lines, and the standard deviation of the data for the whole band are given.

TABLE IV

Observed Line Positions of the "Hot" Bands

	$0000^02^0 \leftarrow 0000^01^1$		$0000^02^2 \leftarrow 0000^01^1$				$0000^03^3 \leftarrow 0000^02^2$				
J	P_{cc} (J)	R_{cc} (J)	P_{cc} (J)	R_{cc} (J)	P_{dd} (J)	R_{dd} (J)	P_{cc} (J)	R_{cc} (J)	P_{dd} (J)	R_{dd} (J)	J
4	229.8999	-	-	-	-	-	-	-	-	-	4
5	229.5890	-	232.6328	-	-	-	-	236.5850	233.0942	236.5850	5
6	229.2808	-	-	-	-	236.4243	232.7816	236.9053	232.7787	236.9053	6
7	228.9734	-	-	236.7607	-	-	-	-	-	-	7
8	-	-	-	-	-	-	232.1570	-	-	-	8
9	-	234.3760	231.4068	237.4180	-	-	-	237.8819	-	237.8819	9
10	-	-	-	-	231.0796	-	231.5465	-	231.5465	-	10
11	-	235.0315	230.8014	238.0766	-	-	-	-	-	-	11
12	-	-	-	238.4044	230.4623	-	230.9312	238.8714	-	238.8714	12
13	-	-	230.1949	238.7407	-	238.7027	-	239.2016	-	239.2016	13
14	-	-	229.8999	239.0767	229.8531	-	-	-	-	-	14
15	-	-	229.6030	-	229.5454	-	-	-	-	-	15
16	-	236.7091	229.3064	239.7489	-	239.6832	-	-	-	-	16
17	225.9705	-	229.0101	240.0831	-	240.0129	-	-	-	-	17
18	-	237.3862	-	240.4282	-	-	-	-	-	240.8749	18
19	-	-	228.4268	240.7667	228.3412	240.6783	-	241.2109	228.8369	241.2109	19
20	-	-	-	241.1054	-	-	228.5347	241.5436	228.5347	-	20
21	224.8008	238.4044	-	-	-	241.3517	228.2386	-	228.2386	241.8924	21
22	-	-	-	241.7980	227.4521	241.6891	227.9419	-	-	-	22
23	224.2310	239.0936	227.2764	-	-	-	227.6482	242.5651	-	-	23
24	-	-	-	-	-	-	-	242.9075	227.3643	-	24
25	-	239.7865	-	-	226.5663	242.6952	227.0585	-	227.0746	-	25
26	-	-	226.4255	-	-	243.0358	-	243.5900	226.7805	243.6084	26
27	223.0935	240.4877	-	-	-	-	-	-	226.4923	243.9457	27
28	-	-	-	-	-	-	226.1945	-	226.2105	-	28
29	222.5294	-	225.5918	-	-	-	-	-	225.9248	244.6517	29
30	-	241.5436	-	244.6077	225.0963	244.3979	-	244.9788	-	-	30
31	-	-	-	-	-	244.7376	-	-	-	-	31
32	-	-	224.7674	-	-	-	225.0524	-	-	-	32
33	-	-	224.4932	-	-	245.4265	224.7674	-	-	-	33
34	221.1471	242.9630	-	-	-	-	-	246.3794	-	-	34
35	220.8717	243.3250	-	246.4162	-	246.1126	-	246.7329	224.2310	246.7638	35
36	220.6051	-	-	-	-	-	-	247.0785	-	247.1110	36
37	220.3327	244.0440	-	247.1449	223.0935	-	-	-	-	247.4752	37
38	220.0592	-	-	247.5112	222.8027	247.1582	-	-	-	-	38
39	219.7891	244.7641	-	-	-	-	-	-	223.1266	248.1953	39
40	219.5247	-	222.6320	248.2457	-	247.8615	-	248.5022	-	248.5560	40
41	219.2570	-	-	248.6180	-	-	222.5294	248.8606	-	248.9097	41
42	-	-	-	-	-	248.5560	-	-	-	-	42
43	218.7281	246.2236	-	-	221.3965	248.9097	221.9796	249.5811	222.0461	249.6449	43
44	218.4630	-	-	-	-	249.2583	221.7042	-	221.7714	-	44
45	218.2001	246.9557	221.3452	-	-	-	-	-	221.5147	250.3815	45
46	217.9386	-	221.0916	250.5063	-	249.9652	221.1672	-	-	-	46
47	217.6794	-	-	-	-	-	220.8927	-	-	-	47
48	217.4154	248.0665	220.5879	-	220.0131	-	-	251.3862	-	-	48
49	217.1592	248.4386	-	251.6472	219.7383	-	-	251.7520	-	251.8542	49
50	216.9028	-	-	252.0317	219.4669	-	220.0783	252.1155	220.1998	252.2296	50
51	-	249.1821	219.8577	252.4271	219.1929	-	219.8163	-	219.9404	252.6045	51
52	-	249.5555	219.6090	-	218.9221	-	-	252.8434	219.6801	-	52
53	-	249.9325	-	-	218.6543	-	219.2869	-	219.4280	253.3612	53
54	-	250.3053	-	-	-	-	219.0230	-	219.1655	-	54
55	-	-	-	253.9807	218.1140	253.1888	-	-	-	-	55
56	-	-	218.6543	-	-	253.5509	218.4963	-	-	-	56
57	-	251.4321	218.4212	254.7758	-	-	218.2293	-	-	254.8803	57
58	-	251.8110	-	-	-	254.2761	-	255.0665	218.1624	-	58
59	214.6105	252.1879	217.9580	255.5764	-	-	-	-	217.9170	-	59
60	-	-	-	-	216.7792	255.0015	-	255.8044	-	-	60
61	214.1116	-	-	-	216.5127	255.3689	-	-	-	-	61
62	213.8596	-	-	-	-	-	-	-	-	-	62

3.1. *The Fundamental* ν_5

The observed line positions of the fundamental ν_5 are listed in Table II. The molecular constants from unconstrained polynomial fits are given in Table III. The error limits quoted in this table as well as in all the others are standard deviations in the units of the last digits given. The l-doubling constants q_5 and μ_5 were determined from the relation

$$F_{5d}(J) - F_{5c}(J) = q_5 J(J+1) + \mu_5 J^2(J+1)^2. \tag{2}$$

The values of $F(J)$ were calculated from the line positions given in Table II, and from the results for B_0 and D_0 obtained in this work. The results have been compared with selected literature data. The ground-state rotational constants B_0 and D_0 and the l-doubling constant q_5 are in good agreement with the literature values. The result for ν_5 is greater than the calculated literature values 233.0722(15) cm^{-1} (*5*) and 233.15(15) cm^{-1} (*1*, *4*). The calculated value 233.7 cm^{-1} reported by Jones (*12*), however, is consistent with the present result. Wang *et al.* (*7*) observed ($1000^0 0^0 \leftarrow 0000^0 0^0$) at 2330.512(2) cm^{-1} and Picard (*6*) measured 2096.765(1) cm^{-1} for the difference transition ($1000^0 0^0 \leftarrow 0000^0 1^1$). These values yield ν_5 = 233.747(3) cm^{-1}, which is reasonably near to the present result, although the difference is larger than the error limits would allow.

3.2. *The "Hot" Bands*

All the "hot" bands analyzed are listed in Table I. The observed line positions are presented in Table IV. Table V shows the results obtained from the fits where the B'' and D'' constants were constrained to the values given by the present findings. In the error limits for the B and D of the upper state, the uncertainty of the constrained value has been added to the standard error (one standard deviation) given by the fit. The rotational constants B of the levels $0000^0 v_5^l$ (with $l = v_5$ and v_5 = 0, 1, 2, 3) grow regularly as v_5 increases. The values were fitted according to the expression

TABLE V

Results from the "Hot" Bands of C_2N_2

Transition	ν_{BC} [cm^{-1}]	B' [cm^{-1}]	B'' [cm^{-1}]	B' - B'' [10^{-3} cm^{-1}]	D' [10^{-8} cm^{-1}]	D'' [10^{-8} cm^{-1}]	D' - D'' [10^{-8} cm^{-1}]
$0000^0 2^0 \leftarrow 0000^0 1^{1c}$	231.1524(7)	0.158198(8)	0.157553	0.6455(9)	4.27(10)	2.72	1.555(23)
$0000^0 2^{2c} \leftarrow 0000^0 1^{1c}$	234.1926(8)	0.158201(8)	0.157553	0.6480(14)	1.75(12)	2.72	-0.967(40)
$0000^0 2^{2d} \leftarrow 0000^0 1^{1d}$	234.1923(11)	0.158205(10)	0.157776	0.4288(15)	3.12(13)	2.90	0.220(39)
$0000^0 3^{3c} \leftarrow 0000^0 2^{2c}$	234.6628(9)	0.158721(10)	0.158201	0.5199(14)	2.48(16)	1.75	0.728(40)
$0000^0 3^{3d} \leftarrow 0000^0 2^{2d}$	234.6626(10)	0.158731(11)	0.158205	0.5256(16)	2.32(18)	3.12	-0.801(49)

B'' and D'' constrained (this work).

TABLE VI

Some Vibrational Term Values (cm^{-1}) of C_2N_2

Level	$G_0(v)$ [cm^{-1}]
$0000^0 1^1$	233.8849(7)
$0000^0 2^0$	464.8796(13)
$0000^0 2^2$	468.5526(15)
$0000^0 3^3$	704.0110(23)

$$B(0000^0 v_5^l) = B_0 - \alpha_5^0 v_5 + (\gamma_{55}^0 + \gamma_{ll}) v_5^2 \,. \tag{3}$$

The fit resulted in $\alpha_5^0 = -0.548(5) \times 10^{-3}$ cm^{-1} and $\gamma_{55}^0 + \gamma_{ll} = -0.45(15) \times 10^{-5}$ cm^{-1}.

The levels $2\nu_5^0$ and $2\nu_5^{2c}$ perturb each other through *l*-type resonance, while the $2\nu_5^{2d}$ state is unperturbed (*13*). The effect of the resonance appears in the $(D' - D'')$ values obtained from the fits in the $2\nu_5 \leftarrow \nu_5$ bands. The values of $(D' - D'')$ in the resonance diad are roughly equal in absolute value, but have opposite signs, as shown in Table V.

The absorption at 228.7 cm^{-1}, (E) in Fig. 1, was tentatively attributed to $(0000^0 3^1 \leftarrow 0000^0 2^2)$ and, respectively, the absorption (F) at 231.7 cm^{-1} to $(0000^0 3^1 \leftarrow 0000^0 2^0)$. Some rotational lines could be assigned in accordance with these assumptions, but the results remained so dubious that they will not be reported.

3.3. Vibrational Term Values

The determined term values, as listed in Table VI, were obtained by combining the band centers, *B* values and *q* values and by employing the following expression (*14*) for a band center:

$$\nu_{BC} = G_0(v') - G_0(v'') - B'l'^2 + B''l''^2 \pm (1/2)(q'l'^2 - q''l''^2), \tag{4}$$

where the different ν_{BC} values were weighted with the inverses of their estimated errors squared. The uncertainties in Table VI are the sums of the uncertainties of the various components included in the determinations.

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