Sub-millimeter Wave Spectra of Cyanoacetylene and Revised Ground State Constants

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Sixteen new rotational transitions of cyanoacetylene in the ground vibrational state have been measured in the frequency region from 570 GHz to 710 GHz by the Cologne sub-millimeter wave spectrometer. The observed transition frequencies were analyzed together with unpublished millimeter wave data of our group and with the data available in the literature. Precise rotational constant and the quartic and sextic centrifugal distortion constants have been determined; B = 4549.058224(37) MHz, D = 0.544110(19) kHz, and H = 0.0345(21) mHz.

Cyanoacetylene, HCCCN, a fairly rigid linear molecule, is of great astrophysical interest. The laboratory spectra of this molecule in the ground vibrational state were studied intensively by Creswell et al. [1] and by de Zafra [2] in the microwave (MW) and millimeter wave (mmW) region. Recently, in the course of a high-resolution infrared study of the $2\nu_5$ band [3], we have remeasured the ground state rotational spectra in the sub-millimeter wave (sub-mmW) region, in order to supply accurate rotational and centrifugal distortion constants which should be valuable not only for the laboratory spectroscopy in the infrared but also for astrophysical observations, particularly for molecular line searches.

The sub-mmW spectrometer used in the present work is equipped with backward-wave-oscillators (BWO) made by ISTOK, Russia. For details of the spectrometer see e. g. [4]. A 4.4 m long free-space cell of Duran glass was filled with the sample gas of about 3 Pa. The transmission intensity was measured by a liquid-He-cooled InSb detector. The frequency of the BWO was stabilized by locking to the output of a mmW synthesizer-sweeper by a phase-lock-loop. The accuracy of the measurement is better than ± 10 kHz [5].

About ten years ago, two graduate students in our laboratory, Wolfgang Klebsch and Manfred Bester, measured the pure rotational transitions of this molecule in the mmW region by a spectrometer based on phase-locked klystrons and Gunn-oscillators equipped with frequency multipliers. Their measurements, 13 lines in the frequency range from 218 GHz to 450 GHz, have not yet been published. We have included these data in the present analysis, and also the data available in the literature, i. e. the work of Creswell et al. [1], of de Zafra [2], and the recent sub-mmW data of Chen et al. [6], who measured the spectra between 580 and 1100 GHz by a far-infrared (FIR) laser sidebands spectrometer.

Table 1 lists the transitions used in the present analysis together with the calculated complete rotational spectrum up to 700 GHz, which is intended to facilitate astronomical line identifications. In the present work, many of the transitions reported by Chen et al. have been remeasured with considerably higher accuracy: an uncertainty of the order of 1 MHz is presently the experimental limitation for FIR laser sideband measurements. Weighted least-squares fits were carried out; the weights were assumed to be reciprocally proportional to the square of estimated experimental uncertainties, which are listed in Table 1. The uncertainty in the present and our previous unpublished measurement is assumed to be ± 10 kHz. Four high frequency measurements of Chen et al. were included in the final fit with the assumed uncertainty of ± 2 MHz. For the other lines we just accepted the uncertainties quoted in the original papers. Accurate rotational and centrifugal distortion

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Table 1. Observed and Calculated Frequencies of HCCCN in the Ground Vibrational State.

$J' \leftarrow J''$	Observed[a]	Calculated[a]	O–C[a]	σ[b]	Energy[c]	Ref.[d]	$J' \leftarrow J''$	Observed[a]	Calculated[a]	O–C[a]	σ[b]	Energy[c]	Ref.[d]
1← 0	9098.1152	9098.1143	0.0009	0.0002	0.00000	Z	42← 41		381959.6698			261.24290	
2← 1	18196.226	18196.2155	0.0105	0.01	0.30348	G	43← 42		391045.9955			273.98370	
3← 2	27294.289	27294.2906	–0.0016	0.01	0.91044	G	44← 43		400131.7600			287.02759	
4← 3	36392.324	36392.3265	–0.0025	0.01	1.82088	G	45← 44		409216.9503			300.37455	
5← 4		45490.3102			3.03480		46← 45		418301.5533			314.02456	
6← 5	54588.247	54588.2286	0.0184	0.005	4.55219	Z	47← 46		427385.5560			327.97759	
7← 6	63686.052	63686.0686	–0.0166	0.01	6.37306	Z	48← 47		436468.9454			342.23364	
8← 7	72783.822	72783.8173	0.0047	0.015	8.49740	Z	49← 48	445551.722	445551.7085	0.0135	0.01	356.79268	K1
9← 8		81881.4614			10.92520		50← 49		454633.8321			371.65468	
10← 9	90979.023	90978.9881	0.0349	0.02	13.65648	G	51← 50		463715.3034			386.81964	
11← 10	100076.392	100076.3841	0.0079	0.015	16.69121	Z	52← 51		472796.1092			402.28751	
12← 11	109173.634	109173.6365	–0.0026	0.004	20.02940	Z	53← 52		481876.2365			418.05829	
13← 12		118270.7323			23.67104		54← 53		490955.6724			434.13196	
14← 13	127367.666	127367.6582	0.0078	0.03	27.61612	G	55← 54		500034.4037			450.50847	
15← 14		136464.4014			31.86465		56← 55		509112.4175			467.18783	
16← 15	145560.946	145560.9487	–0.0027	0.03	36.41661	G	57← 56		518189.7007			484.16999	
17← 16	154657.284	154657.2871	–0.0031	0.001	41.27200	Z	58← 57		527266.2404			501.45494	
18← 17	163753.389	163753.4035	–0.0145	0.015	46.43082	Z	59← 58		536342.0235			519.04265	
19← 18	172849.300	172849.2848	0.0152	0.04	51.89304	G	60← 59		545417.0369			536.93309	
20← 19	181944.923	181944.9181	0.0049	0.04	57.65867	G	61← 60		554491.2678			555.12624	
21← 20	191040.299	191040.2903	0.0087	0.05	63.72770	G	62← 61		563564.7030			573.62208	
22← 21	200135.392	200135.3882	0.0038	0.022	70.10012	Z	63← 62	572637.329	572637.3295	–0.0005	0.01	592.42058	K2
23← 22	209230.234	209230.1989	0.0351	0.030	76.77592	G	64← 63	581709.129	581709.1344	–0.0054	0.01	611.52170	K2
24← 23	218324.723	218324.7093	0.0137	0.01	83.75509	K1	65← 64	590780.096	590780.1047	–0.0087	0.01	630.92543	K2
25← 24	227418.905	227418.9064	–0.0014	0.01	91.03762	K1	66← 65	599850.227	599850.2272	–0.0002	0.01	650.63173	K2
26← 25		236512.7770			98.62349		67← 66	608919.484	608919.4891	–0.0051	0.01	670.64058	K2
27← 26		245606.3082			106.51271		68← 67	617987.876	617987.8773	–0.0013	0.01	690.95195	K2
28← 27	254699.500	254699.4869	0.0131	0.01	114.70526	K1	69← 68	627055.378	627055.3788	–0.0008	0.01	711.56581	K2
29← 28	263792.308	263792.3001	0.0079	0.01	123.20112	K1	70← 69	636121.978	636121.9807	–0.0027	0.01	732.48212	K2
30← 29		272884.7346			132.00028		71← 70	645187.669	645187.6698	–0.0008	0.01	753.70087	K2
31← 30		281976.7775			141.10273		72← 71	654252.426	654252.4333	–0.0073	0.01	775.22201	K2
32← 31	291068.427	291068.4157	0.0113	0.01	150.50847	K1	73← 72	663316.257	663316.2581	–0.0011	0.01	797.04553	K2
33← 32	300159.647	300159.6362	0.0108	0.01	160.21747	K1	74← 73	672379.131	672379.1312	–0.0002	0.01	819.17137	K2
34← 33	309250.430	309250.4259	0.0041	0.01	170.22971	K1	75← 74	681441.039	681441.0397	–0.0007	0.01	841.59953	K2
35← 34		318340.7717			180.54520		76← 75	690501.975	690501.9705	0.0045	0.01	864.32995	K2
36← 35	327430.671	327430.6607	0.0103	0.01	191.16390	K1	77← 76	699561.919	699561.9107	0.0083	0.01	887.36262	K2
37← 36	336520.084	336520.0797	0.0043	0.01	202.08581	K1	78← 77	708620.850	708620.8472	0.0028	0.01	910.69749	K2
38← 37	345609.010	345609.0158	–0.0058	0.01	213.31091	K1	83← 82	753899.700	753900.0213	–0.3213	2.0	1031.90378	L
39← 38		354697.4559			224.83919		87← 86	790104.300	790103.9715	0.3285	2.0	1134.30501	L
40← 39	363785.397	363785.3870	0.0100	0.01	236.67062	K1	110←109	997900.670	997899.3052	1.3648	2.0	1816.75839	L
41← 40	372872.811	372872.7960	0.0150	0.01	248.80520	K1	115←114	1042978.110	1042977.4666	0.6434	2.0	1986.19786	L

[a] Numbers are in MHz. [b] The column σ indicates the assumed experimental uncertainties in MHz. [c] The energy of the lower state is given in cm^{-1}. [d] The column Ref. indicates the references: K1 = the unpublished data of Cologne, K2 = present work, G = data from [1], Z = data from [2], L = data from [6].

constants have been determined from the 52 weighted data with the maximum J quantum number of 115; B = 4549.058224(37) MHz, D = 0.544110(19) kHz, and H = 0.0345(21) mHz with the standard polynomial expression of the rotational energy,

$$E(J) = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3. \quad (1)$$

Cyanoacetylene is a "well-behaved" linear molecule as indicated by the obtained sextic centrifugal constant, which is very small. The polynomial expression given above converges without any problem for J much larger than 115, which is the maximum J of the present data. Thus we can conclude that the present set of constants is the best one available today to calculate the ground state rotational transitions or rotational energies of cyanoacetylene for spectroscopic or astrophysical purposes.

Large discrepancies between the observed frequencies and the calculated ones have been found for the lines measured with the laser sidebands spectrometer, marked with L in Table 1. They are consistent with the expected experimental uncertainties of the laser sideband technique. In comparison, the accuracy achieved with the Cologne sub-mmW spectrometer with phase-locked BWOs is by two orders of magnitude higher in the spectral region around 1 THz.

Interstellar molecular line surveys establish the astrophysical importance of HCCCN. For example in the CSO(Caltech Submillimeter Observatory)-survey (325–360 GHz) of Orion A, the J = 38 – 37 transition

is fairly intense with 4.3 K antenna temperature [7], whereas in the 680–720 GHz CSO-survey an upper limit of $\sim$ 1K was found [8].

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