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Anharmonic Potential Constants and Vibrational and Rotational Parameters for Hydrogen Cyanide

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The general fourth-order potential constants, *f*, for hydrogen cyanide were determined by a least-squares analysis applied to the observed values of the vibrational energies and the rotational constants for six isotopic species, $H^{12}C^{14}N$, $H^{13}C^{14}N$, $H^{12}C^{15}N$, $D^{12}C^{14}N$, $D^{13}C^{14}N$, and $D^{12}C^{15}N$. The normal frequencies, ω_i, the cubic and quartic potential constants, k_{ijk} and k_{ijkl}, the anharmonicity constants, x_{ij}, the vibration-rotation interaction constants, α_i, and the Coriolis coupling constants, $\zeta_{ij}{}^x$ were calculated for the six isotopic species.

The determination of the intramolecular potential function is one of the most important problems in molecular spectrosocpy. Once this has been done, various properties of molecules can be coordinated in a unified way upon this fundamental function. Suzuki, Pariseau, and Overend[1] determined the cubic and quartic potential constants for hydrogen cyanide by means of a least-squares fit to the observed values of the vibrational energies, ν, and the rotational constants, B_v, in various vibrational states. Though they used 87 observed values for two isotopic species, $H^{12}C^{14}N$ and $D^{12}C^{14}N$, the final values of the *nineteen* parameters still have intensive mutual correlations. Accordingly, a further refinement of the potential function is very desirable if one wants to predict various properties based on the potential function. Since the observed values of ν and B_v are available for four other isotopic species, *i. e.*, $H^{13}C^{14}N$, $H^{12}C^{15}N$, $D^{13}C^{14}N$, and $D^{12}C^{15}N$, they are also used in the least-squares analysis in the present study; the number of the observed values has increased to 124.

Another aim of the present study is to obtain the vibrational and rotational parameters, such as ω_i, k_{ijk}, k_{ijkl}, x_{ij}, and α_i and to predict the vibrational energies, ν, and the rotational constants, B_v, in various vibrational states of the six isotopic species. The uncertainties of these predicted values are also estimated on the basis of the probable errors of the potential constants, *f*, and their mutual correlation. It should be noticed that the estimated uncertainties of the calculated values will often become unreasonably large unless the correlations among the *f* constants are taken into account.

Determination of Anharmonic Potential Constants

The method described in our previous paper[2] on the anharmonic potential constants of OCS was applied to the present least-squares calculation as follows.

Observables. The observed values of the vibrational energies, ν, and the rotational constants, $B_v - B_0$, for the six isotopic species used in the least-squares fit are listed in Columns 2 and 6 of Table 1, together with their references.[3-10] The values for higher vibrational levels with $v_1 + \frac{1}{2}v_2 + v_3 > 4$ were not used in the analysis in order to avoid the influence of higher-order terms and accidental perturbations.

Parameters. The variable parameters to be determined were the nineteen potential constants, *f*, up to the fourth order in the expansion formula of:

$$V = \frac{1}{2} f_R \Delta R^2 + f_{Rr} \Delta R \Delta r + \frac{1}{2} f_r \Delta r^2 + \frac{1}{2} f_\alpha \Delta\alpha^2 + f_{RRR} \Delta R^3 + f_{RRr} \Delta R^2 \Delta r + f_{Rrr} \Delta R \Delta r^2 + f_{rrr} \Delta r^3 + f_{R\alpha\alpha} \Delta R \Delta\alpha^2$$

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Table 1. Observed and calculated values of ν and B_v

Species State	Vibrational energy ν (cm^{-1})				Rotational constant B_v-B_0(10^{-3} cm^{-1})			
	Obsd	Calcd	O-C	Weight[a]	Obsd	Calcd	O-C	Weight[b]
H^{12}C^{14}N								
00^00					1478.219 i	1478.205	0.014	12.5
10^00	2096.85 c	2096.85	0.00	5.0	-10.0_7 c	−10.068	-0.0_{02}	12.3
02^00	1411.43 d	1412.08	−0.65	0.078	7.59_8 c	7.385	0.21_3	0.78
00^01	3311.48 e	3311.45	0.03	5.0	-10.42_1 e	−10.418	-0.00_3	12.5
20^00	4173.07 e	4172.79	0.28	0.078		−20.135		
12^00	3502.13 c	3501.70	0.43	0.059	−2.748 c	−2.683	−0.065	0.595
04^00	2802.85 c, k	2804.63	−1.78	0.0012		14.770		
10^01	5393.70 e	5393.69	0.01	1.25	−20.286 e	−20.486	0.200	4.2
02^01	4684.32 e	4685.57	−1.25	0.059	-2.37_7 c	−3.033	0.65_6	0.595
00^02	6519.61 e	6519.48	0.13	0.078	−21.151 e	−20.836	−0.315	0.78
22^00	5571.89 f, k	5570.41	1.48	0.0195		−12.750		
12^01	6761.33 e	6760.59	0.74	0.0446		−13.101		
10^02	8585.57 e	8587.11	−1.54	0.059	−30.82 e	−30.904	0.08_4	0.595
00^03	9627.02 g	9624.08	2.94	0.0068	−32.21 e	−31.255	-0.95_5	0.154
12^02	9914.41 g	9916.05	−1.64	0.016	−24.02 g	−23.519	-0.50_1	0.219
10^03	11674.46 e	11677.11	−2.64	0.0061	−41.61 e	−41.322	-0.28_8	0.137
00^04	12635.90 e	12625.25	10.65	0.0012	−43.794 e	−41.673	−2.121	0.064
01^10	711.98 h	712.35	−0.37	2.5	3.549 c	3.693	−0.144	6.25
11^10	2805.58 c	2805.59	−0.01	0.83	−6.657 c	−6.375	−0.282	3.12
03^10	2113.46 c	2114.66	−1.20	0.0068	11.35_9 c	11.078	0.28_1	0.152
01^11	4004.17 e	4004.83	−0.66	0.83	-6.65_9 e	−6.726	0.06_7	3.12
21^10	4878.27 e	4877.93	0.34	0.056	-16.9_0 f	−16.443	-0.4_{57}	0.568
13^10	4201.29 e	4200.67	0.62	0.0060		1.010		
11^11	6083.35 e	6083.47	−0.12	0.38	−16.639 e	−16.793	0.154	1.79
03^11	5366.86 e	5369.19	−2.33	0.0060		0.659		
01^12	7192.75 e	7193.89	−1.14	0.056	−17.097 e	−17.144	0.047	0.568
11^12	9256.11 g	9257.92	−1.81	0.042	−26.82 g	−27.212	0.39_2	0.446
01^13	10280.30 g	10279.53	0.78	0.0060	−27.72 g	−27.562	-0.15_8	0.136
02^20	1426.53 c	1427.55	−1.02	0.039		7.385		
12^20	3516.88 c	3517.21	−0.33	0.0303	-3.52_6 c	−2.683	-0.84_4	0.338
04^20	2818.16 c	2820.07	−1.91	0.0012		14.770		
02^21	4699.21 e	4701.08	−1.87	0.0303		−3.033		
H^{13}C^{14}N								
00^00					1439.988 e	1439.978	0.010	12.5
10^00		2063.05				−9.741		
00^01	3293.51 e	3293.46	0.05	5.0	−9.63 d	−9.648	0.01_8	12.3
10^01	5343.66 e	5343.62	0.04	1.25	−19.19 e	−19.389	0.19_9	4.15
02^01	4655.86 e	4657.19	−1.33	0.059	−3.09 e	−3.058	-0.03_2	0.595
00^02	6483.28 e	6483.17	0.11	0.078	−19.55 e	−19.296	-0.25_4	0.78
10^02	8519.24 e	8520.43	−1.19	0.059		−29.037		
00^03	9571.73 j	9569.13	2.60	0.0068	−29.2 j	−28.944	-0.2_{56}	0.154
10^03	11591.42 j	11593.50	−2.08	0.0061	−38.8 j	−38.685	-0.1_{15}	0.137
00^04	12561.84 j	12551.35	10.49	0.0012	-40.6_6 j	−38.593	-2.0_{68}	0.064
01^10	707.39 e	706.34	1.05	2.5	3.20 e	3.295	-0.09_5	6.25
11^10	2765.32 c	2765.27	0.05	0.83		−6.446		
01^11	3982.22 e	3981.44	0.78	0.83		−6.353		
11^11	6028.79 e	6027.47	1.32	0.38		−16.094		
01^12	7153.07 e	7152.78	0.29	0.056	−15.949 e	−16.001	0.052	0.568
02^21	4675.03 e	4672.41	2.62	0.0303	−2.79 e	−3.058	0.26_8	0.338
H^{12}C^{15}N								
00^00					1435.27 d	1435.226	0.04_4	11.1
10^00		2064.35				−9.655		
00^01	3310.09 d	3310.13	−0.04	5.0	-10.02_8 d	−10.020	-0.00_8	12.3
01^10		711.41				3.541		

Table 1. (continued)

Species state	Vibrational energy ν (cm^{-1})				Rotational constant B_v-B_0(10^{-3} cm^{-1})			
	Obsd	Calcd	O-C	Weight[a]	Obsd	Calcd	O-C	Weight[b]
$D^{12}C^{14}N$								
00^00					1207.747 e	1207.692	0.055	25.0
10^00	1925.26 d	1925.24	0.02	6.67	−6.55 d	−6.542	-0.00_8	24.4
02^00	1129.98 d	1130.29	−0.31	0.104	8.87 d	8.783	0.08_7	1.56
00^01	2630.30 d	2630.34	−0.04	6.67	-10.32_9 d	−10.264	-0.06_5	24.4
20^00	3836.35 f	3836.79	−0.44	0.104	−13.63 f	−13.084	-0.54_6	1.56
12^00	3060.67 d	3061.56	−0.89	0.078	1.92_6 d	2.240	-0.31_4	1.19
10^01	4523.27 e	4523.18	0.09	1.67	-16.61_0 e	−16.807	0.19_7	8.26
02^01	3729.12 d	3729.03	0.09	0.078	−0.83 d	−1.482	0.65_2	1.19
00^02	5220.24 d	5219.69	0.55	0.104	−20.69 d	−20.529	-0.16_1	1.56
01^10	569.04 d	569.30	−0.26	3.33	4.34 d	4.391	-0.05_1	12.3
11^10	2497.14 d	2497.56	−0.42	1.11	−2.37 d	−2.151	-0.21_9	6.21
01^11	3183.67 d	3183.85	−0.18	1.11	−5.69 d	−5.873	0.18_3	6.21
21^10	4410.96 f, k	4412.13	−1.17	0.074		−8.693		
13^10	3623.94 d, k	3625.56	−1.62	0.0080		6.632		
11^11	5079.46 e	5079.71	−0.25	0.513	−12.056 d	−12.415	0.359	3.56
01^12	5757.88 d	5757.40	0.48	0.074	−15.79 d	−16.138	0.34_8	1.13
02^20	1137.94 d	1138.59	−0.65	0.052	8.66 d	8.783	-0.12_3	0.782
12^20	3068.63 d	3069.88	−1.25	0.040	1.56 d	2.240	-0.68_0	0.676
02^21	3736.94 d	3737.37	−0.43	0.040	−1.04 d	−1.482	0.44_2	0.676
$D^{13}C^{14}N$								
00^00					1187.073 d	1187.017	0.057	12.5
10^00	1911.84 d	1911.81	0.03	6.67		−6.420		
00^01	2590.07 d	2590.05	0.02	6.67	−9.74 d	−9.648	-0.09_2	24.4
01^10		561.60				4.054		
$D^{12}C^{15}N$								
00^00					1173.0 d	1173.080	-0.0_{79}	7.0
10^00		1900.12				−6.290		
00^01	2621.19 d	2621.22	−0.03	6.67	-10.00_8 d	−9.883	-0.12_5	24.4
01^10		568.06				4.236		

a) Statistical weights in the least-squares analysis, in cm^2 units.
b) Statistical weights in 10^6 cm^2 units.
c) Maki *et al.*, Ref. 3.
d) Maki *et al.*, Ref. 4.
e) Rank *et al.*, Ref. 5.
f) Allen *et al.*, Ref. 6.
g) Douglas *et al.*, Ref. 7.
h) Brim *et al.*, Ref. 8.
i) Burrus *et al.*, Ref. 9.
j) Rank *et al.*, Ref. 10.
k) Only the Q branch has been observed.

TABLE 2. FOURTH-ORDER POTENTIAL CONSTANTS f OF HCN DETERMINED BY LEAST-SQUARES METHODS

Potential constant	Suzuki *et al.*[a]	This work	Unit
f_R(CN)	18.776 ±0.17	18.707 ±0.016	md/Å
f_{Rr}	−0.216 ±0.08	−0.211 ±0.006	md/Å
f_r(CH)	6.230 ±0.03	6.244 ±0.003	md/Å
f_α	0.2592±0.003	0.2598±0.0004	md·Å
f_{RRR}	−19.227±0.36	−20.846 ±0.16	md/Å^2
f_{RRr}	−1.335±0.40	0.046 ±0.22	md/Å^2
f_{Rrr}	−0.322±0.27	−0.496 ±0.11	md/Å^2
f_{rrr}	−6.085±0.15	−5.626 ±0.07	md/Å^2
$f_{R\alpha\alpha}$	−0.272±0.05	−0.328 ±0.02	md
$f_{r\alpha\alpha}$	−0.134±0.07	−0.054 ±0.03	md
f_{RRRR}	17.52 ±6.9	27.09 ±1.2	md/Å^3
f_{RRRr}	4.71 ±7.7	0.73 ±1.2	md/Å^3
f_{RRrr}	1.17 ±3.0	1.07 ±0.4	md/Å^3
f_{Rrrr}	1.05 ±2.0	1.35 ±0.4	md/Å^3
f_{rrrr}	8.79 ±0.7	6.38 ±0.3	md/Å^3
$f_{RR\alpha\alpha}$	−0.189 ±0.46	−0.010 ±0.10	md/Å
$f_{Rr\alpha\alpha}$	0.196 ±0.43	0.138 ±0.06	md/Å
$f_{rr\alpha\alpha}$	0.201 ±0.23	−0.110 ±0.07	md/Å
$f_{\alpha\alpha\alpha\alpha}$	0.0029±0.004	0.0014±0.0007	md·Å
$\hat{\sigma}^2$		0.130	

a) Ref. 1. Table 3, Column (iii).

Table 3. Correlation factors among the f constants ($\times 10^{-2}$)

	f_R	f_{Rr}	f_r	f_α	f_{RRR}	f_{RRr}	f_{Rrr}	f_{rrr}	$f_{R\alpha\alpha}$	$f_{r\alpha\alpha}$	f_{RRRR}	f_{RRRr}	f_{RRrr}	f_{Rrrr}	f_{rrrr}	$f_{RR\alpha\alpha}$	$f_{Rr\alpha\alpha}$	$f_{rr\alpha\alpha}$	$f_{\alpha\alpha\alpha\alpha}$
f_R																			
f_{Rr}	−44																		
f_r	−51	71																	
f_α	2	−1	1																
f_{RRR}	−8	−11	−10	−16															
f_{RRr}	−7	19	−19	20	−86														
f_{Rrr}	12	−29	−26	−20	59	−75													
f_{rrr}	−3	11	12	21	−85	92	−87												
$f_{R\alpha\alpha}$	−10	27	29	40	−34	37	−44	38											
$f_{r\alpha\alpha}$	11	−31	−32	−39	29	−38	43	−38	−95										
f_{RRRR}	−73	30	32	16	−55	55	−46	55	36	−32									
f_{RRRr}	0	−70	−44	−12	48	−56	56	−50	−38	42	−22								
f_{RRrr}	−51	3	5	−8	59	−60	32	−52	−24	27	6	52							
f_{Rrrr}	38	−43	−22	10	−32	36	−62	56	13	−9	−8	1	−35						
f_{rrrr}	13	−22	−24	−21	84	−93	87	−99	−42	42	−61	55	47	−47					
$f_{RR\alpha\alpha}$	−2	−8	−5	−50	32	−35	38	−37	−87	81	−35	30	18	−14	38				
$f_{Rr\alpha\alpha}$	2	−8	−10	27	−5	9	−17	15	31	−35	14	−29	−6	−3	−17	−51			
$f_{rr\alpha\alpha}$	−8	26	25	39	−18	26	−32	26	93	−98	26	−37	−20	1	−30	−83	44		
$f_{\alpha\alpha\alpha\alpha}$	−7	20	25	−56	−7	11	−14	10	34	−41	11	−16	−9	0	−12	−25	1	37	

$$+ f_{r\alpha\alpha}\Delta r\Delta\alpha^2 + f_{RRRR}\Delta R^4 + f_{RRRr}\Delta R^3\Delta r + f_{RRrr}\Delta R^2\Delta r^2 + f_{Rrrr}\Delta R\Delta r^3 + f_{rrrr}\Delta r^4 + f_{RR\alpha\alpha}\Delta R^2\Delta\alpha^2 + f_{Rr\alpha\alpha}\Delta R\Delta r\Delta\alpha^2 + f_{rr\alpha\alpha}\Delta r^2\Delta\alpha^2 + f_{\alpha\alpha\alpha\alpha}\Delta\alpha^4, \quad (1)$$

where ΔR and Δr denote the stretching displacements of the CN and CH bonds respectively, and $\Delta\alpha$, the bending displacement. The force constants obtained by Suzuki, Pariseau, and Overend¹⁾ were used as the initial values for the least-squares refinement. No account was taken of the resonance interactions, such as the Fermi resonance ($\omega_1 \sim 2\omega_2$ and $\omega_3 \sim 2\omega_2$) and a third-order anharmonic resonance ($3\omega_1 \sim 2\omega_3$). The equilibrium bond lengths were assumed to be $R_e(\text{CN}) = 1.15313$ Å and $r_e(\text{CH}) = 1.06593$ Å, according to Rank, Skorinko, Eastman, and Wiggins.⁴⁾

Statistical Weights. The weights of ν and B_v in the least-squares analysis were evaluated by taking into account the uncertainties due to higher-order terms as well as the experimental uncertainties, according to the procedure suggested in our preceding paper.²⁾ The uncertainties of the former type were estimated on the basis that $\sigma_\nu{}^2 = 0.20$ (cm^{-1})^2 and $\sigma_\Gamma{}^2 = 0.08 \times (10^{-3}\ \text{cm}^{-1})^2$ for HCN, and $\sigma_\nu{}^2 = 0.15 \times (\text{cm}^{-1})^2$ and $\sigma_\Gamma{}^2 = 0.04 \times (10^{-3}\ \text{cm}^{-1})^2$ for DCN. In Columns 5 and 9 of Table 1 the weights thus evaluated are shown in units of (cm^{-1})$^{-2}$ and (10^{-3} cm^{-1})$^{-2}$ respectively.

The calculation was carried out by using the computer program described in our preceding paper²⁾ on the HITAC 5020E computer at the Computer Centre, The University of Tokyo.

The general fourth-order portential constants determined are shown in Column 2 of Table 2, while their correlation factors are given in Table 3. The potential constants obtained in the present study are essentially the same as those obtained by Suzuki, Pariseau, and Overend,¹⁾ but they are more precise than the latter, as may clearly be seen from the probable errors listed in Table 2. The calculated values of ν and $B_v - B_0$ are tabulated in Columns 3 and 7 of Table 1, and the deviations, in Columns 4 and 8.

Potential Constants in the Normal-Coordinate System and the Vibrational and Rotational Parameters

On the basis of the force constants, f, determined above, the potential constants, ω_i, k_{ijk}, and k_{ijkl}, in the normal-coordinate representation were calculated for the six isotopic species; the results are shown in Table 4. These calculated values have the advantage that the isotopic relations among them are fully taken into account. The standard errors for ω and k were evaluated according to Eq. (20) of Ref. 2, with account taken of the correlations among the f constants. The ω and k constants vary to a large extent for different isotopic species as a result of the change in normal coordinates. Table 5 shows the contributions of the f constants to the k constants; the main term is underlined for each k constant. One can see that the contributions of *bond-stretching* f constants are predominant in the cubic and quartic k constants, including even those related to the *bending* vibration. The contributions of the *cross* terms are much smaller

TABLE 4. POTENTIAL CONSTANTS IN THE NORMAL-COORDINATE SYSTEM (cm^{-1})

	$H^{12}C^{14}N$	$H^{13}C^{14}N$	$H^{12}C^{15}N$	$D^{12}C^{14}N$	$D^{13}C^{14}N$	$D^{12}C^{15}N$
ω_1	2128.67±0.80[a]	2094.16	2095.12	1952.12±0.63[a]	1938.52	1925.83
ω_2	727.10±0.51	720.71	726.01	579.85±0.41	571.82	578.49
ω_3	3441.16±0.44	3422.04	3439.85	2703.34±0.72	2661.58	2794.30
k_{111}	−106.9 ±0.5	−105.7	−104.6	−84.7 ±0.4	−83.8	−82.9
k_{113}	53.3 ±2.5	50.7	52.1	−3.7 ±2.0	4.4	1.5
k_{122}	96.2 ±1.4	85.0	92.7	184.7 ±1.1	174.4	178.6
k_{133}	−216.3 ±4.6	−198.0	−210.6	−329.6 ±3.3	−315.7	−321.6
k_{223}	608.9 ±1.3	613.7	612.7	269.7 ±1.1	278.3	277.1
k_{333}	−289.0 ±7.9	−291.6	−290.1	−90.1 ±5.5	−100.0	−97.3
k_{1111}	6.47±0.3	6.34	6.29	4.62±0.2	4.53	4.47
k_{1113}	−5.23±0.8	−4.86	−5.06	1.61±0.7	0.49	0.88
k_{1122}	−14.38±0.4	−12.45	−13.66	−37.45±0.6	−34.35	−35.39
k_{1133}	14.00±1.5	12.11	13.36	33.97±1.8	31.74	32.50
k_{1223}	−89.35±1.9	−82.56	−87.51	−90.64±0.6	−88.44	−89.52
k_{1333}	28.74±0.6	26.93	28.16	19.21±0.5	19.93	19.79
k_{2222}	58.97±2.0	59.69	59.56	23.40±2.1	23.62	23.75
k_{2233}	−244.79±4.8	−246.60	−246.30	−93.96±1.9	−95.79	−96.21
k_{3333}	33.14±1.5	33.44	33.29	11.00±0.7	11.39	11.39

a) Standard error calculated by taking into account the correlations among the f constants according to Eq. (20) of Ref. 2.

Table 5. Contributions of the f constants to the k constants (cm^{-1})

(a) Cubic constants of $H^{12}C^{14}N$

	k_{111}	k_{113}	k_{133}	k_{333}	k_{122}	k_{223}
f_R(CN)					33.0	−9.8
f_{Rr}					−10.6	2.3
f_r(CH)					$\underline{135.7}$	$\underline{676.3}$
f_α					−16.2	−57.2
f_{RRR}	$\underline{-104.1}$	$\underline{93.1}$	−27.8	2.8		
f_{RRr}	0.1	0.4	−0.3	0.0		
f_{Rrr}	−0.5	−4.6	−10.5	3.5		
f_{rrr}	−2.4	−35.7	$\underline{-177.8}$	$\underline{-295.3}$		
$f_{R\alpha\alpha}$					−42.5	12.7
$f_{r\alpha\alpha}$					−3.1	−15.3
Total	−106.9	53.3	−216.3	−289.0	96.2	608.9

(b) Cubic constants of $D^{12}C^{14}N$

	k_{111}	k_{113}	k_{133}	k_{333}	k_{122}	k_{223}
f_R(CN)					53.0	−42.3
f_{Rr}					−6.2	3.1
f_r(CH)					$\underline{194.3}$	$\underline{323.5}$
f_α					−23.4	−27.6
f_{RRR}	$\underline{-56.2}$	$\underline{134.5}$	$\underline{-107.3}$	28.5		
f_{RRr}	0.2	0.0	−0.3	0.2		
f_{Rrr}	−2.0	−4.9	−0.2	4.3		
f_{rrr}	−26.7	$\underline{-133.2}$	$\underline{-221.8}$	$\underline{-123.1}$		
$f_{R\alpha\alpha}$					−27.6	22.0
$f_{r\alpha\alpha}$					−5.5	−9.1
Total	−84.7	−3.7	−329.6	−90.1	184.7	269.7

(c) Quartic constants of $H^{12}C^{14}N$

	k_{1111}	k_{1113}	k_{1133}	k_{1333}	k_{3333}	k_{1122}	k_{1223}	k_{2233}	k_{2222}
f_R						−1.32	0.79	−0.12	0.27
f_{Rr}						0.21	0.96	−0.31	−0.17
f_r						−2.59	−25.82	−64.34	$\underline{70.76}$
f_α						0.59	3.40	7.84	−8.22
f_{RRR}						$\underline{-5.11}$	3.04	−0.45	
f_{RRr}						0.11	−0.34	0.00	
f_{Rrr}						−1.01	−4.76	1.29	
f_{rrr}						$\underline{-7.46}$	$\underline{-74.40}$	$\underline{-185.40}$	
$f_{R\alpha\alpha}$						1.90	6.13	−2.00	−0.70
$f_{r\alpha\alpha}$						0.14	1.17	2.41	−3.20
f_{RRRR}	$\underline{6.27}$	$\underline{-7.47}$	3.34	−0.66	0.05				
f_{RRRr}	0.07	0.31	−0.31	0.10	−0.01				
f_{RRrr}	0.05	0.45	0.90	−0.66	0.10				
f_{Rrrr}	0.03	0.39	1.86	2.70	−0.98				
f_{rrrr}	0.06	1.10	$\underline{8.21}$	$\underline{27.27}$	$\underline{33.97}$				
$f_{RR\alpha\alpha}$						−0.06	0.04	−0.01	
$f_{Rr\alpha\alpha}$						0.36	1.71	−0.54	
$f_{rr\alpha\alpha}$						−0.13	−1.27	−3.17	
$f_{\alpha\alpha\alpha\alpha}$									0.22
Total	6.47	−5.23	14.00	28.74	33.14	−14.38	−89.35	−244.79	58.97

TABLE 5. (Continued)

(d) Quartic constants of $D^{12}C^{14}N$

	k_{1111}	k_{1113}	k_{1133}	k_{1333}	k_{3333}	k_{1122}	k_{1223}	k_{2233}	k_{2222}
f_R						−1.73	2.76	−1.10	1.05
f_{Rr}						0.26	0.22	−0.34	−0.22
f_r						−8.29	−27.61	−22.99	$\underline{29.02}$
f_α						1.42	3.54	2.97	−3.86
f_{RRR}						−6.67	10.65	−4.25	
f_{RRr}						0.06	−0.28	0.01	
f_{Rrr}						−1.24	−1.27	1.33	
f_{rrr}						$\underline{-23.90}$	$\underline{-79.57}$	$\underline{-66.24}$	
$f_{R\alpha\alpha}$						2.22	0.85	−2.10	−1.09
$f_{r\alpha\alpha}$						0.44	1.26	0.87	−1.64
f_{RRRR}	$\underline{2.75}$	$\underline{-8.78}$	$\underline{10.51}$	−5.59	1.12				
f_{RRRr}	0.09	−0.07	−0.19	0.24	−0.08				
f_{RRrr}	0.16	0.27	−0.30	−0.36	0.28				
f_{Rrrr}	0.24	1.02	1.05	−0.49	−0.89				
f_{rrrr}	1.38	$\underline{9.17}$	$\underline{22.89}$	$\underline{25.41}$	$\underline{10.58}$				
$f_{RR\alpha\alpha}$						−0.03	0.05	−0.02	
$f_{Rr\alpha\alpha}$						0.53	0.46	−0.70	
$f_{rr\alpha\alpha}$						−0.51	−1.70	−1.41	
$f_{\alpha\alpha\alpha\alpha}$									0.14
Total	4.62	1.61	33.97	19.21	11.00	−37.45	−90.64	−93.96	23.40

TABLE 6. VIBRATIONAL AND ROTATIONAL ANHARMONIC TERMS (cm^{-1})

	$H^{12}C^{14}N$	$H^{13}C^{14}N$	$H^{12}C^{15}N$	$D^{12}C^{14}N$	$D^{13}C^{14}N$	$D^{12}C^{15}N$
x_{11}	−10.45 ±0.38[a]	−10.27	−10.13	−6.84 ±0.29[a]	−6.80	−6.69
x_{12}	−3.61 ±0.22	−4.13	−3.46	3.01 ±0.20	2.03	3.11
x_{13}	−14.61 ±0.22	−12.90	−14.08	−32.40 ±0.26	−30.29	−30.90
x_{22}	−2.44 ±0.17	−2.31	−2.46	−2.08 ±0.11	−1.91	−2.10
x_{23}	−18.98 ±0.21	−18.38	−18.91	−15.80 ±0.24	−14.91	−15.67
x_{33}	−51.71 ±0.21	−51.87	−51.88	−20.50 ±0.36	−20.74	−20.98
x_{ll}	5.35 ±0.09	5.24	5.40	3.29 ±0.64	3.13	3.33
$\alpha_1 \times 10^3$	10.068±0.068	9.741	9.655	6.542±0.051	6.420	6.290
$\alpha_2 \times 10^3$	−3.693±0.047	−3.295	−3.541	−4.391±0.038	−4.054	−4.236
$\alpha_3 \times 10^3$	10.418±0.043	9.648	10.020	10.264±0.037	9.648	9.883

a) Calculated standard error. See Footnote a of Table 4.

TABLE 7. CORIOLIS COUPLING CONSTANTS

	$H^{12}C^{14}N$	$H^{13}C^{14}N$	$H^{12}C^{15}N$	$D^{12}C^{14}N$	$D^{13}C^{14}N$	$D^{12}C^{15}N$
$\xi_{12}{}^x$	0.1529±0.0007[a]	0.1631	0.1536	−0.0871±0.0010[a]	−0.0645	−0.0719
$\xi_{23}{}^x$	0.9882±0.0001	0.9866	0.9881	0.9962±0.0001	0.9979	0.9974

a) Calculated standard error.

TABLE 8. BOND-STRETCHING ANHARMONICITIES FOR HCN IN COMPARISON WITH THOSE FOR CN AND CH (in $Å^{-1}$)

	Diatomic molec. CN or CH	HCN
CN bond a_3	2.268	2.229
a_4	2.294	2.228
CH bond a_3	1.981	1.802
a_4	2.087	1.872

than those of the *principal* terms.

The vibrational anharmonicity constants, x_{ij}, and the vibration-rotation interaction constants, α_i, were also calculated. They are tabulated in Table 6. The calculated values of the Coriolis coupling constants, $\zeta_{12}{}^x$ and $\zeta_{23}{}^x$, are listed in Table 7.

The *l*-type doubling constants and the centrifugal distortion constants were also calculated, together with their *v*- and *J*-dependent terms. The cal-

TABLE 9. RATIO OF THE FERMI RESONANCE TERM $|k_{stt}/(\omega_s-2\omega_t)|$

	$H^{12}C^{14}N$	$H^{1\text{-}}C^{14}N$	$H^{12}C^{15}N$	$D^{12}C^{14}N$	$D^{13}C^{14}N$	$D^{12}C^{15}N$
k_{122} (cm^{-1})	96.2	85.0	92.7	184.7	174.4	178.6
$\omega_1-2\omega_2$ (cm^{-1})	674.	653.	643.	792.	795.	769.
Ratio	0.143	0.130	0.144	0.233	0.219	0.232
k_{223} (cm^{-1})	608.9	613.7	612.7	269.7	278.3	277.1
$\omega_3-2\omega_2$ (cm^{-1})	1987.	1981.	1988.	1544.	1518.	1537.
Ratio	0.306	0.310	0.308	0.175	0.183	0.180

culated values of q_v and D_v are in good agreement with the observed values, as will be reported elsewhere.[11] This agreement offers positive support for the anharmonic potential constants obtained from ν and B_v in the present study.

Discussion

The two parameters a_3 and a_4 which are defined[12] by:

$$a_3 = -2f_{rrr}/f_r \tag{2}$$

and:

$$a_4 = [24f_{rrrr}/7f_r]^{1/2} \tag{3}$$

are convenient for expressing the bond-stretching anharmonicity. Their values for HCN are compared with those for CH and CN in Table 8. The table suggests that the potential function for a bond stretching in the HCN molecule is quite similar to that in the corresponding diatomic molecule, CH or CN.

As for the anharmonic resonance in HCN, an accidental perturbation of the $3\omega_1-2\omega_2$ type has been pointed out by Douglas and Sharma.[7] The perturbation of this type was disregarded in the present study without any serious effect on the potential constants determined above. This is because the perturbation mentioned above is significant only for highly-excited vibrational states, such as (00^04), (30^02), (10^04), and (40^02), and the weights of the observed values for these states were zero or small in the least-squares analysis.

Nevertheless, a problem was found in the present study concerning the Fermi resonance. In the present calculation the k_{122} and k_{223} terms were treated with a second-order perturbation theory without any special consideration of the Fermi resonances, $\omega_1-2\omega_2$ and $\omega_3-2\omega_3$. It was found, however, that the k_{122} and k_{223} constants thus obtained were not small enough compared with the energy differences, $\omega_1-2\omega_2$ and $\omega_3-2\omega_2$ respectively. Table 9 shows that the $|k_{stt}/(\omega_s-2\omega_t)|$ ratios for the $\omega_3-2\omega_2$ resonance of HCN and the $\omega_1-2\omega_2$ resonance of DCN are even larger than the ratio, 0.231, for the well-known case of the $\omega_1-2\omega_2$ resonance for OCS.[2] Rigorously speaking, these Fermi resonances must be treated separately from the usual perturbation calculation, as was done for OCS. According to such a treatment, some relations must be expected among the ν and B_v values; for instance:

$$B(02^00) - B_0 < 2[B(01^10)-B_0] \tag{4}$$

and:

$$B(02^20) > B(02^00). \tag{5}$$

The observed values, however, do not satisfy these relations. It seems likely that the discrepancies suggest the importance of such higher-order effects as the γ terms. In the present study no corrections for the third- and higher-order perturbation were taken into account; therefore, the exact diagonalization of the Fermi resonance terms remains to be done in the future.

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