JOURNAL OF MOLECULAR SPECTROSCOPY **174**, 151–171 (1995)

Pure Rotational Spectra of HNCO in the Far Infrared: Ground State Analysis

M. NIEDENHOFF, K. M. T. YAMADA,[1] S. P. BELOV,[2] AND G. WINNEWISSER

I. Physikalisches Institut, Universität zu Köln, D-50937 Cologne, Germany

Received May 18, 1995; in revised form August 3, 1995

The pure rotational spectrum of the quasilinear molecule HNCO and some of its isotopomers was measured with the Giessen high-resolution Fourier transform spectrometer in the far infrared. In addition to *a*-type transitions with high rotational quantum number, *b*-type transitions from $K_a = 1 \leftarrow 0$ to $K_a = 8 \leftarrow 7$ for HNCO and DNCO, and from $K_a = 1 \leftarrow 0$ to $K_a = 5 \leftarrow 4$ for $HN^{13}CO$ were identified. Several rotational transitions near 600 GHz were also measured using the Cologne submillimeter-wave spectrometer with a high-frequency backward wave oscillator as source. Rotational parameters were determined using both Watson's *S*-reduced asymmetric rotor Hamiltonian and for comparison a linear molecule Hamiltonian. The centrifugal distortion resonance between the ground state and the lowest excited bending vibration was clearly observed and analyzed by a second-order perturbation treatment. The observed *K* dependence of the rotational parameter *B*(*K*) is caused by the combined effects of centrifugal distortion resonance and quasilinearity.

I. INTRODUCTION

Isocyanic acid, HNCO, a near-prolate asymmetric top, exhibits several peculiarities in its rotational spectrum typical for a quasilinear molecule. Extraordinarily large centrifugal distortion effects were found in the millimeter-wave spectra measured by Kewley *et al.* (*1*) at the beginning of the 1960s, and later in low-resolution far-infrared (FIR) spectra obtained by Krakow and co-workers (*2*). The results of these works indicated clearly the quasilinear character of this molecule. Ashby and Werner (*3*) found strong *a*-type Coriolis interactions among the singly excited bending vibrations, ν_4, ν_5, and ν_6, in their spectra measured in the region from 450 to 1200 cm^{-1}.

Extensive microwave (MW) and millimeter-wave (mmW) measurements of HNCO, DNCO, $H^{15}NCO$, $HN^{13}CO$, and $HNC^{18}O$ were carried out by Hocking *et al.* (*4*), which supplied the basic information to determine the molecular structure of isocyanic acid. Using their data, a revised molecular structure (r_s) was reported by Yamada (*6*), who measured the pure rotational spectra of HNCO and DNCO in the FIR region from 80 to 350 cm^{-1} with a resolution of 0.1 cm^{-1}. For the main isotopomer, a new type of resonance interaction was found in the rotational spectra of high *K* states: the centrifu-

[1] Present address: National Institute for Advanced Interdisciplinary Research, Tsukuba, Japan.

[2] On leave of absence from the Microwave Spectroscopy Laboratory, Institute of Applied Physics, Nizhnii Novgorod, Russia.

0022-2852/95 $12.00

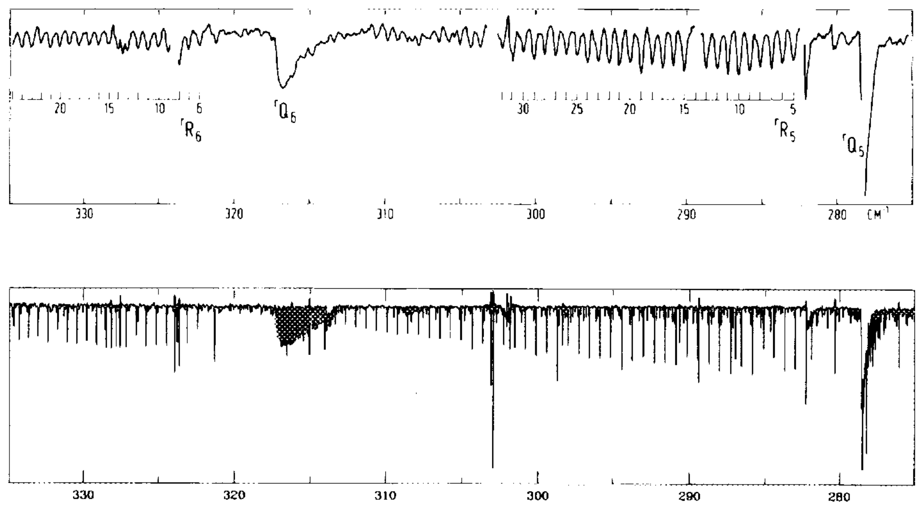

FIG. 1. A portion of the pure rotational spectrum of HNCO (cm^{-1}) measured by Yamada (*6*) (upper trace) is compared with that of the present measurements (lower trace), for which the resolution has been improved by a factor of ~50.

gal distortion resonance (*6*). Fusina and Carlotti extended the FIR measurements to the region between 8 and 80 cm^{-1} with a resolution of 0.004 cm^{-1} (*7*) with a Michelson-type interferometer.

In the present work we have remeasured the FIR spectra of HNCO in the wavenumber region between 20 and 350 cm^{-1}, using a Michelson-type Fourier transform infrared (FTIR) spectrometer with high resolution. We have identified *b*-type transitions up to $^rX_7$ of the main isotopomer in the ground state (where X denotes P, Q, and R following the standard notation for symmetric-top spectra), up to $^rX_6$ for the $v_5 = 1$ excited state, up to $^rX_5$ for the $v_6 = 1$ state, and up to $^rX_5$ for the $v_4 = 1$ state. Additionally, some *b*-type transitions for $HN^{13}CO$, in natural abundance, and DNCO, enriched by an accidental deuteration in the absorption cell, have been detected. In the lowest wavenumber region of the observed spectra, *a*-type transitions of all these isotopomers have been identified.

In addition we have measured some high-J transitions near 600 GHz with the Cologne submillimeter-wave (sub-mmW) spectrometer.

In our previous paper (*8*), the ground state transitions with a rotational quantum number J less than 10 were used to determine the quasilinear bending potential according to the semirigid-bender model. The potential hump at the linear configuration, measured from the potential minimum, was found to be about 2100 cm^{-1}.

II. EXPERIMENTAL PROCEDURES

The rotational spectra of HNCO were measured with the high-resolution Fourier transform spectrometer at Giessen (Bruker IFS-120) with a maximum resolution of 0.00185 cm^{-1} in the region between 20 and 350 cm^{-1}. At room temperature the 3-m sample cell was filled with a pressure of 25 Pa. The details of the experimental procedure concerning the operation of the spectrometer are very similar to those given

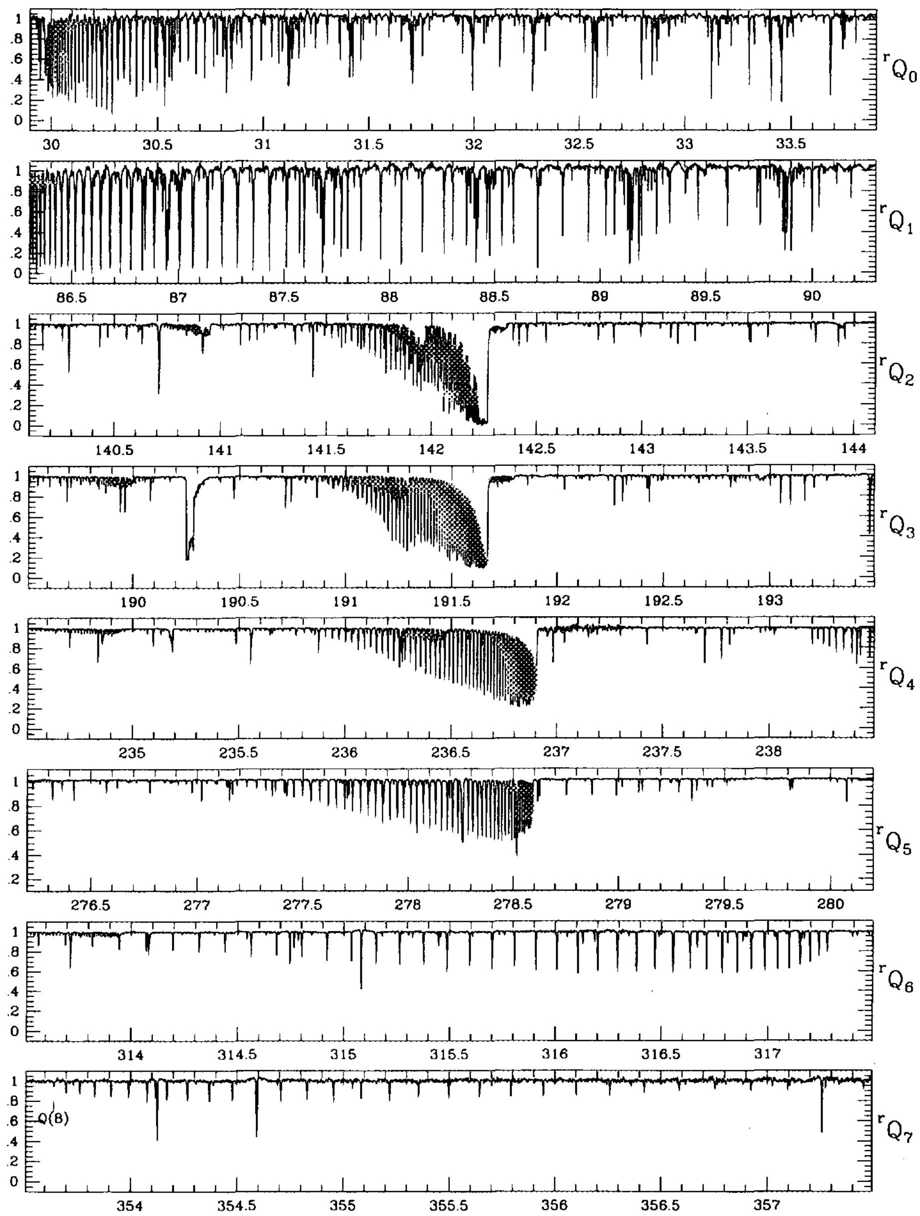

FIG. 2. The observed $^rQ_{K_a}$ ground state transitions of HNCO (cm^{-1}) are reproduced for $K_a'' = 0$ to 7. The $^rQ_0$ branch is overlapped by groups of a-type transitions occurring at constant wavenumber intervals. For the $^rQ_6$ branch a significant increase occurs in the wavenumber spacing between individual J transitions. For the $^rQ_7$ branch the degradation changes to the blue and again a large wavenumber spacing is displayed. Both effects are consequences of the centrifugal resonance between the ground state and the lowest excited bending state $v_5 = 1$.

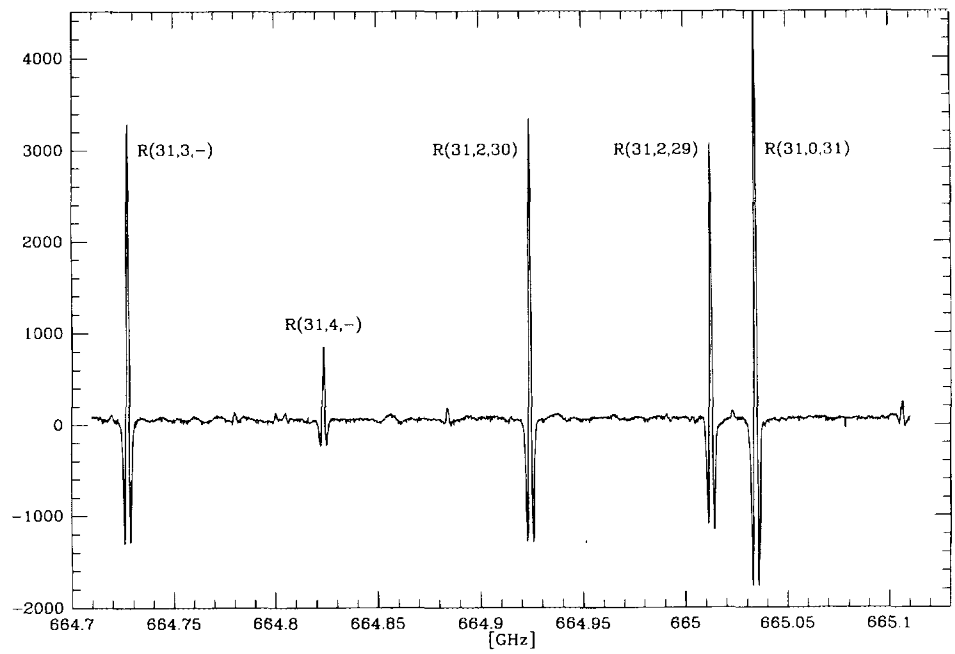

FIG. 3. A part of the observed sub-mmW spectra near 660 GHz is presented. The $J = 32 \leftarrow 31$ a-type transitions of $HNC^{18}O$ in natural abundance are displayed with the resolved K_a components. The $K_a = 1$ doublets are in frequency too far away to be shown here. The designation means $R(J, K_a, K_c)$.

in our previous paper on HNCS (*9*). The line positions were calibrated with precisely known water lines (*10*); H_2O was contained as an impurity in the HNCO sample. The precision of the line center determination in the present study is better than 0.05×10^{-3} cm^{-1} ($\sim$1.5 MHz). The accuracy of the line position is, in principle, limited by the accuracies of standards used for calibration. The uncertainties of the standard lines are claimed to be about 0.1×10^{-3} cm^{-1} or better. In our recent study on H_2S in the sub-mmW region (*11*), we were able to test the absolute accuracy of the FTIR measurements in the FIR region by a comparison of various line positions (Table V of Ref. *11*) measured with microwave accuracy ($\sim$20 kHz) using the Cologne terahertz spectrometer. The present HNCO data were calibrated with exactly the same method as H_2S. The proved accuracy of the FTIR measurements is about 1.5 MHz for the lines recorded with reasonable signal-to-noise ratio ($S/N > 20$) in the wavenumber range higher than 50 cm^{-1}.

In the recorded wavenumber region the b-type subbands range from $K_a = 1 \leftarrow 0$ to $K_a = 8 \leftarrow 7$. The a-type transitions cover $K_a = 0$ to $K_a = 5$ for the lowest wavenumber region of the present measurement. In comparison to the earlier measurements by Yamada (*6*), the spectral resolution and, consequently, the accuracy of the line positions were improved by a factor of larger than 50, which reveals the degradation and structure of the Q branches.

Figure 1 compares a part of the spectrum in the region of the ${}^rQ_6$ and the ${}^rQ_5$ branches of the present measurement with the older measurements. The effect of higher resolution can be seen in the recorded profiles of the ${}^rQ_6$ branch.

TABLE I

Spectroscopic Parameters of HNCO Determined in the Present Study Using a Watson-Type S-reduced Hamiltonian[a]

	HNCO	DNCO	$H^{15}NCO$	$HN^{13}CO$	$HNC^{18}O$	Unit
A	918.49365(11)	512.515983(51)	908.95360(22)	916.22692(27)	918.40335(19)	GHz
B	11071.01048(14)	10313.71447(14)	10737.8291(15)	11071.48037(79)	10470.89162(49)	MHz
C	10910.57803(15)	10079.67866(12)	10585.4635(14)	10910.73140(81)	10327.23824(52)	MHz
D_J	3.50114(13)	3.26612(21)	3.29630(69)	3.49729(54)	3.13544(23)	kHz
D_{JK}	934.858(59)	−242.155(36)	1015.45(46)	930.62(19)	819.54(40)	kHz
D_K	6052.18(12)	1573.824(67)	6052.18(*fix*)[b]	5994.50(21)	6052.18(*fix*)[b]	MHz
d_1	−72.828(19)	−203.522(19)	−63.70(41)	−73.022(47)	−61.384(43)	Hz
d_2	−30.542(19)	−52.608(23)	−71.28(21)	−30.634(35)	−25.82(56)	Hz
H_J	0.000730(51)	0.000967(97)	0.000730(*fix*)[b]	0.0(*fix*)[b]	0.000730(*fix*)[b]	Hz
H_{JK}	−2.997(23)	0.678(23)	−2.997(*fix*)[b]	−2.024(64)	−2.961(86)	Hz
H_{KJ}	33.931(24)	−6.8308(92)	36.00(48)	33.845(58)	28.66(28)	kHz
H_K	285.287(26)	30.685(18)	285.287(*fix*)[b]	281.965(36)	285.287(*fix*)[b]	MHz
h_1	0.0(*fix*)[b]	0.0001957(41)	0.0(*fix*)[b]	0.0(*fix*)[b]	0.0(*fix*)[b]	Hz
L_{44}	−0.1601(26)	0.0322(39)	−0.1601(*fix*)[b]	−0.0681(52)	−0.1601(*fix*)[b]	Hz
L_{26}	3.4074(44)	−0.05735(71)	3.389(48)	3.4107(82)	2.929(43)	kHz
L_K	14.7013(24)	0.9684(18)	14.7013(*fix*)[b]	14.5672(22)	14.7013(*fix*)[b]	MHz
S_{46}	−0.001869(75)	0.00340(21)	−0.001869(*fix*)[b]	0.0(*fix*)[b]	−0.001869(*fix*)[b]	Hz
S_{28}	158.03(28)	−0.202(20)	158.03(*fix*)[b]	158.46(46)	143.7(17)	Hz
S_K	0.48617(10)	0.025987(81)	0.48617(*fix*)[b]	0.483999(43)	0.48617(*fix*)[b]	MHz
T_{48}	0.0(*fix*)[b]	0.0000761(32)	0.0(*fix*)[b]	0.0(*fix*)[b]	0.0(*fix*)[b]	Hz
$T_{2,10}$	2.7453(58)	0.00163(19)	2.7453(*fix*)[b]	2.7738(86)	2.7453(*fix*)[b]	Hz
T_K	8.4257(20)	0.4102(17)	8.4257(*fix*)[b]	8.4257(*fix*)[b]	8.4257(*fix*)[b]	kHz
U_K	57.621(15)	2.675(13)	57.621(*fix*)[b]	57.621(*fix*)[b]	57.621(*fix*)[b]	Hz
σ	29.0	26.5	19.8	35.3	14.1	kHz

a) A, B and C correspond to B_z, B_x and B_y of Eq. (1).
The numbers in parentheses represent one standard deviation.

b) Fixed at the value of the main isotopomer HNCO.

Between the R-branch lines a large number of weak intensity transitions appear in the spectrum.

In addition to the main isotopomer, the b-type transitions of $HN^{13}CO$ from $K_a = 1 \leftarrow 0$ to $K_a = 5 \leftarrow 4$ and a-type transitions from $K_a = 0$ to $K_a = 5$ have been identified.

For the deuterated isotopomer, b-type transitions were assigned in the measured spectrum from $K_a = 1 \leftarrow 0$ to $K_a = 8 \leftarrow 7$ and a-type transitions from $K_a = 0$ to $K_a = 3$ in the low wavenumber region.

In Fig. 2 the observed Q branches of the main isotopomer HNCO are shown: starting with the ${}^rQ_0$ branch at the top and ending with the ${}^rQ_7$ branch (bottom line). Each portion of the spectrum spans a wavenumber range of 4 cm^{-1}. Between the lines of the ${}^rQ_0$ branch, groups of a-type transitions typical for near-prolate asymmetric rotors can be seen spaced by about $2B \sim 0.6$ cm^{-1}. The ${}^rQ_1$ branch is split into two components corresponding to the K-type doubling. The higher Q branches ($K_a \geqslant 2$), except for ${}^rQ_7$, degrade toward the lower wavenumber with increasing rotational quantum number J. This behavior reflects the centrifugal

TABLE II

Effective Parameters of HNCO for Each K_a State[a]

K	$E_0(K)$ in cm^{-1}	$B(K)$ in MHz	$D(K)$ in kHz	$H(K)$ in mHz	$L(K)$ in μHz
0		10990.79706(16)	4.40870(12)	3.565(32)	
1L	30.0782119(24)	10949.78330(13)	3.66267(11)	1.654(30)	
1U	30.0782106(25)	11029.99998(12)	3.809201(75)		
2L	118.353117(15)	10987.41821(17)	3.638091(94)		
2U	118.353088(15)	10987.41684(22)	2.79263(17)	−2.817(35)	
3L[b]	260.624483(21)	10983.51983(39)	3.40579(34)	−1.858(70)	
3U[b]	260.624493(21)	10983.51962(42)	3.40885(36)	1.156(70)	
4	452.301252(24)	10978.04536(27)	3.45694(20)	−0.677(47)	
5	689.217757(28)	10970.31239(22)	3.47011(12)		
6	967.829576(45)	10957.3173(15)	3.31250(43)		
7	1285.249406(93)	10884.923(15)	−9.826(26)	−2695(17)	−298.6(34)
8	1638.65072(21)	10983.557(31)	4.708(31)		

[a] The numbers in parentheses represent one standard deviation.

[b] With the parameters listed here, the upper–lower relation of K-type doublets are calculated to be reversed in low J with an insignificant amount of splitting; see text.

deformation of the molecule with increasing K_a quantum number. The greater distances between neighboring transitions of the $^rQ_6$ and $^rQ_7$ branches, as well as the change in the direction of degradation, are caused by a centrifugal resonance

TABLE III

Effective Parameters of DNCO for Each K_a State[a]

K	$E_0(K)$ in cm^{-1}	$B(K)$ in MHz	$D(K)$ in kHz	$H(K)$ in mHz	$L(K)$ in μHz
0		10196.70469(13)	6.71970(18)	30.523(99)	3.793(12)
1L	16.70406976(73)	10138.42931(13)	3.93886(21)	18.39(10)	
1U	16.70407621(74)	10255.44624(12)	4.34516(17)	−3.613(85)	
2L	66.240440(20)	10197.57205(19)	3.80905(34)	5.02(18)	
2U	66.240465(22)	10197.56551(26)	0.46966(76)	−1.760(66)	−5.52(17)
3L[b]	147.126465(28)	10198.37175(30)	2.84678(41)	−12.82(20)	
3U[b]	147.126399(28)	10198.37070(30)	2.84415(42)	9.01(21)	
4	257.428671(34)	10199.04842(23)	3.03670(12)		
5	395.122463(46)	10199.29256(23)	3.11235(12)		
6	558.285936(55)	10198.80704(26)	3.15194(16)		
7	745.178272(71)	10197.28149(47)	3.19363(80)		
8	954.25524(14)	10194.344(11)	3.4377(72)		

[a] The numbers in parentheses represent one standard deviation.

[b] With the parameters listed here, the upper–lower relation of K-type doublets are calculated to be reversed in low J with an insignificant amount of splitting; see text.

TABLE IV

Effective Parameters of $HN^{13}CO$ for Each K_a State[a]

	E_0 in cm^{-1}	$B(K)$ in MHz	$D(K)$ in kHz
0		10991.10037(56)	4.40187(38)
1L	30.0043485(31)	11030.39502(62)	3.80686(42)
1U	30.0043518(30)	10950.01948(61)	3.65794(42)
2L	118.075267(18)	10987.7526(10)	3.63856(69)
2U	118.075245(18)	10987.7496(10)	2.78930(69)
3	260.043918(23)	10983.86411(99)	3.40257(68)
4	451.347189(31)	10978.3829(21)	3.4517(14)
5	687.839658(42)	10970.5175(19)	3.4741(13)

[a] The numbers in parentheses represent one standard deviation.

between the ground state and the lowest excited bending state, which is discussed in detail in Section V.

Another remarkable phenomenon has been found in the shift of the transitions of $HN^{13}CO$. As can be seen in the spectra of the $^rQ_2$, $^rQ_3$, and $^rQ_4$ branches, the corresponding less intense Q branches of the ^{13}C-isotopomer are shifted to lower wavenumbers, indicating a reduction of the rotational constant A by the ^{13}C substitution. In contrast, the a-type transitions of $HN^{13}CO$ are shifted to higher frequencies, suggesting a larger rotational constant B. This means that the ^{13}C-isotopomer is more bent than the main isotopomer.

In addition to the FIR spectra measured by FTIR spectroscopy, we have recorded several sub-mmW transitions between 570 and 690 GHz of HNCO, DNCO, $H^{15}NCO$, $HN^{13}CO$, and $HNC^{18}O$ with the Cologne sub-mmW spectrometer using phase-locked backward wave oscillators. Details of the sub-mmW measurements have been presented in our previous paper on HNCS (*9*). These lines have been measured with an accuracy better than 30 kHz and in several cases better than 10 kHz. A section of the observed sub-mmW spectra is presented in Fig. 3, which shows the a-type $^qR_K(31)$ transitions of $HNC^{18}O$ in natural abundance. To measure DNCO spectra the sample cell was prepared with D_2O in advance in order to form DNCO in the cell from HNCO by substitution. The other isotopomers were measured in their natural abundance.

III. SPECTRA AND ASSIGNMENTS

HNCO is an asymmetric top molecule which is very close to the prolate symmetric limit. With an asymmetry parameter of $\kappa = -0.99965$, it is slightly more asymmetric than HNCS with $\kappa = -0.99994$. Due to the nonrigid configuration of the molecule, the HNCO spectra show peculiar properties summarized in the term *molecular quasilinearity* as in the case of HNCS (*11–13*). The quasilinearity of a molecule can be quantified with the quasilinearity parameter γ_0, which has the value $\gamma_0 = -1$ for a linear and $\gamma_0 = +1$ for a bent molecule. For HNCO the parameter is $\gamma_0 = +0.79$, indicating that HNCO is less quasilinear than HNCS with $\gamma_0 = +0.63$.

TABLE V

Observed Line Positions of HNCO (in cm^{-1}) Measured by FTIR Spectroscopy[a]

Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ
Rqr (27, 0, 27)	20.51760	14	Rqr (51, 1, 50)	38.19238	4	Rqr (71, 1, 71)	52.41353	-5	Rqr (47, 2, 46)	35.13024	-16
Rqr (28, 0, 28)	21.24912	-12	Rqr (52, 1, 51)	38.92401	3	Rqr (72, 1, 72)	53.13643	2	Rqr (48, 2, 47)	35.85948	-49
Rqr (30, 0, 30)	22.71232	-22	Rqr (53, 1, 52)	39.65554	8	Rqr (73, 1, 73)	53.85916	12	Rqr (50, 2, 49)	37.31869	0
Rqr (31, 0, 31)	23.44380	-21	Rqr (54, 1, 53)	40.38680	3				Rqr (51, 2, 50)	38.04782	-1
Rqr (32, 0, 32)	24.17559	21	Rqr (55, 1, 54)	41.11795	3	Rqr (27, 2, 25)	20.51602	17	Rqr (52, 2, 51)	38.77690	8
Rqr (34, 0, 34)	25.63773	-3	Rqr (56, 1, 55)	41.84892	3	Rqr (29, 2, 27)	21.98027	30	Rqr (53, 2, 52)	39.50561	-4
Rqr (35, 0, 35)	26.36891	14	Rqr (57, 1, 56)	42.57982	12	Rqr (30, 2, 28)	22.71232	39	Rqr (54, 2, 53)	40.23437	4
Rqr (36, 0, 36)	27.09976	11	Rqr (58, 1, 57)	43.31042	10	Rqr (31, 2, 29)	23.44380	-2	Rqr (55, 2, 54)	40.96295	10
Rqr (37, 0, 37)	27.83040	-1	Rqr (59, 1, 58)	44.04088	12	Rqr (32, 2, 30)	24.17559	-5	Rqr (56, 2, 55)	41.69121	1
Rqr (38, 0, 38)	28.56108	5	Rqr (60, 1, 59)	44.77108	6	Rqr (33, 2, 31)	24.90708	-30	Rqr (57, 2, 56)	42.41947	8
Rqr (39, 0, 39)	29.29152	1	Rqr (61, 1, 60)	45.50123	12	Rqr (34, 2, 32)	25.63892	-12	Rqr (58, 2, 57)	43.14746	6
Rqr (40, 0, 40)	30.02188	3	Rqr (62, 1, 61)	46.23108	9	Rqr (35, 2, 33)	26.37073	9	Rqr (59, 2, 58)	43.87531	6
Rqr (41, 0, 41)	30.75210	5	Rqr (63, 1, 62)	46.96077	9	Rqr (36, 2, 34)	27.10220	6	Rqr (60, 2, 59)	44.60314	22
Rqr (43, 0, 43)	32.21187	-12	Rqr (64, 1, 63)	47.69022	4	Rqr (37, 2, 35)	27.83360	3	Rqr (61, 2, 60)	45.33058	17
Rqr (44, 0, 44)	32.94138	-37	Rqr (65, 1, 64)	48.41960	12	Rqr (38, 2, 36)	28.56489	-2	Rqr (62, 2, 61)	46.05787	14
Rqr (45, 0, 45)	33.67119	-15	Rqr (66, 1, 65)	49.14867	9	Rqr (39, 2, 37)	29.29617	1	Rqr (63, 2, 62)	46.78499	12
Rqr (46, 0, 46)	34.40075	-1	Rqr (67, 1, 66)	49.87749	2	Rqr (40, 2, 38)	30.02738	6	Rqr (64, 2, 63)	47.51195	15
Rqr (47, 0, 47)	35.13024	21	Rqr (68, 1, 67)	50.60620	4	Rqr (41, 2, 39)	30.75846	7	Rqr (65, 2, 64)	48.23873	18
Rqr (49, 0, 49)	36.58810	5	Rqr (69, 1, 68)	51.33416	-48	Rqr (42, 2, 40)	31.48942	6	Rqr (66, 2, 65)	48.96535	23
Rqr (50, 0, 50)	37.31682	2	Rqr (70, 1, 69)	52.06281	-9	Rqr (43, 2, 41)	32.22025	1	Rqr (67, 2, 66)	49.69168	20
Rqr (51, 0, 51)	38.04548	11	Rqr (71, 1, 70)	52.79111	16	Rqr (44, 2, 42)	32.95109	8	Rqr (68, 2, 67)	50.41783	18
Rqr (52, 0, 52)	38.77386	10	Rqr (72, 1, 71)	53.51877	-1	Rqr (45, 2, 43)	33.68176	7	Rqr (69, 2, 68)	51.14365	3
Rqr (53, 0, 53)	39.50187	-9	Rqr (73, 1, 72)	54.24663	25	Rqr (46, 2, 44)	34.41236	10	Rqr (70, 2, 69)	51.86954	16
Rqr (54, 0, 54)	40.23010	12				Rqr (47, 2, 45)	35.14281	9	Rqr (71, 2, 70)	52.59523	29
Rqr (55, 0, 55)	40.95781	0	Rqr (27, 1, 27)	20.44308	6	Rqr (48, 2, 46)	35.87312	4	Rqr (72, 2, 71)	53.32035	6
Rqr (56, 0, 56)	41.68550	7	Rqr (28, 1, 28)	21.17220	-12	Rqr (49, 2, 47)	36.60390	57			
Rqr (57, 0, 57)	42.41289	2	Rqr (29, 1, 29)	21.90157	3	Rqr (50, 2, 48)	37.33353	7	Rq- (27, 3, -)	20.50684	6
Rqr (58, 0, 58)	43.14028	18	Rqr (30, 1, 30)	22.63064	-3	Rqr (51, 2, 49)	38.06352	5	Rq- (28, 3, -)	21.23839	-3
Rqr (59, 0, 59)	43.86685	-26	Rqr (31, 1, 31)	23.35960	-11	Rqr (52, 2, 50)	38.79331	-6	Rq- (29, 3, -)	21.97007	10
Rqr (60, 0, 60)	44.59407	12	Rqr (32, 1, 32)	24.08868	3	Rqr (53, 2, 51)	39.52328	12	Rq- (30, 3, -)	22.70151	7
Rqr (61, 0, 61)	45.32086	32	Rqr (33, 1, 33)	24.81753	3	Rqr (54, 2, 52)	40.25289	8	Rq- (31, 3, -)	23.43291	8
Rqr (62, 0, 62)	46.04702	9	Rqr (34, 1, 34)	25.54630	5	Rqr (55, 2, 53)	40.98241	7	Rq- (32, 3, -)	24.16420	7
Rqr (63, 0, 63)	46.77320	10	Rqr (35, 1, 35)	26.27490	1	Rqr (56, 2, 54)	41.71183	9	Rq- (33, 3, -)	24.89546	12
Rqr (64, 0, 64)	47.49930	25	Rqr (36, 1, 36)	27.00347	4	Rqr (57, 2, 55)	42.44108	6	Rq- (34, 3, -)	25.62654	9
Rqr (65, 0, 65)	48.22490	14	Rqr (37, 1, 37)	27.73185	-2	Rqr (58, 2, 56)	43.17021	5	Rq- (35, 3, -)	26.35753	6
Rqr (66, 0, 66)	48.95046	20	Rqr (38, 1, 38)	28.46017	-2	Rqr (59, 2, 57)	43.89924	7	Rq- (36, 3, -)	27.08845	6
Rqr (67, 0, 67)	49.67573	21	Rqr (39, 1, 39)	29.18843	4	Rqr (60, 2, 58)	44.62810	6	Rq- (37, 3, -)	27.81923	1
Rqr (68, 0, 68)	50.40080	25	Rqr (40, 1, 40)	29.91648	0	Rqr (61, 2, 59)	45.35690	12	Rq- (38, 3, -)	28.54999	6
Rqr (69, 0, 69)	51.12555	22	Rqr (41, 1, 41)	30.64447	1	Rqr (62, 2, 60)	46.08559	22	Rq- (39, 3, -)	29.28062	8
Rqr (70, 0, 70)	51.85011	24	Rqr (42, 1, 42)	31.37236	6	Rqr (63, 2, 61)	46.81384	2	Rq- (40, 3, -)	30.01117	12
Rqr (71, 0, 71)	52.57448	31	Rqr (43, 1, 43)	32.10008	5	Rqr (64, 2, 62)	47.54215	3	Rq- (41, 3, -)	30.74156	12
Rqr (73, 0, 73)	54.02236	34	Rqr (44, 1, 44)	32.82763	1	Rqr (65, 2, 63)	48.27036	9	Rq- (42, 3, -)	31.47178	8
Rqr (74, 0, 74)	54.74596	40	Rqr (45, 1, 45)	33.55515	7	Rqr (66, 2, 64)	48.99831	3	Rq- (43, 3, -)	32.20199	12
Rqr (75, 0, 75)	55.46937	51	Rqr (46, 1, 46)	34.28244	3	Rqr (67, 2, 65)	49.72620	7	Rq- (44, 3, -)	32.93199	10
			Rqr (47, 1, 47)	35.00962	2	Rqr (68, 2, 66)	50.45404	22	Rq- (45, 3, -)	33.66192	12
Rqr (27, 1, 26)	20.59251	8	Rqr (48, 1, 48)	35.73672	7	Rqr (69, 2, 67)	51.18147	11	Rq- (46, 3, -)	34.39167	8
Rqr (28, 1, 27)	21.32692	-11	Rqr (49, 1, 49)	36.46359	3	Rqr (70, 2, 68)	51.90897	24	Rq- (47, 3, -)	35.12137	12
Rqr (29, 1, 28)	22.06170	15	Rqr (50, 1, 50)	37.19040	7				Rq- (48, 3, -)	35.85088	11
Rqr (30, 1, 29)	22.79609	12	Rqr (51, 1, 51)	37.91697	3	Rqr (27, 2, 26)	20.51345	6	Rq- (49, 3, -)	36.58035	19
Rqr (31, 1, 30)	23.53035	5	Rqr (52, 1, 52)	38.64350	10	Rqr (28, 2, 27)	21.24527	6	Rq- (50, 3, -)	37.30954	12
Rqr (32, 1, 31)	24.26453	0	Rqr (53, 1, 53)	39.36977	6	Rqr (29, 2, 28)	21.97690	-4	Rq- (51, 3, -)	38.03862	9
Rqr (33, 1, 32)	24.99878	11	Rqr (54, 1, 54)	40.09596	10	Rqr (30, 2, 29)	22.70867	8	Rq- (52, 3, -)	38.76775	25
Rqr (34, 1, 33)	25.73277	8	Rqr (55, 1, 55)	40.82193	8	Rqr (31, 2, 30)	23.44009	-6	Rq- (53, 3, -)	39.49639	7
Rqr (35, 1, 34)	26.46671	10	Rqr (56, 1, 56)	41.54773	5	Rqr (32, 2, 31)	24.17168	7	Rq- (54, 3, -)	40.22522	22
Rqr (36, 1, 35)	27.20040	-2	Rqr (57, 1, 57)	42.27343	9	Rqr (33, 2, 32)	24.90303	5	Rq- (55, 3, -)	40.95373	21
Rqr (37, 1, 36)	27.93415	3	Rqr (58, 1, 58)	42.99895	12	Rqr (34, 2, 33)	25.63425	0	Rq- (56, 3, -)	41.68185	-4
Rqr (38, 1, 37)	28.66772	2	Rqr (59, 1, 59)	43.72426	11	Rqr (35, 2, 34)	26.36548	7	Rq- (57, 3, -)	42.41041	30
Rqr (39, 1, 38)	29.40123	6	Rqr (60, 1, 60)	44.44930	0	Rqr (36, 2, 35)	27.09656	9	Rq- (58, 3, -)	43.13836	20
Rqr (41, 1, 40)	30.86787	14	Rqr (61, 1, 61)	45.17436	9	Rqr (37, 2, 36)	27.82754	11	Rq- (60, 3, -)	44.59407	29
Rqr (42, 1, 41)	31.60084	3	Rqr (62, 1, 62)	45.89918	12	Rqr (38, 2, 37)	28.55837	10	Rq- (62, 3, -)	46.04916	43
Rqr (43, 1, 42)	32.33385	8	Rqr (63, 1, 63)	46.62377	10	Rqr (39, 2, 38)	29.28907	7	Rq- (63, 3, -)	46.77640	46
Rqr (44, 1, 43)	33.06663	4	Rqr (64, 1, 64)	47.34826	17	Rqr (40, 2, 39)	30.01970	9	Rq- (64, 3, -)	47.50338	40
Rqr (45, 1, 44)	33.79936	8	Rqr (65, 1, 65)	48.07239	7	Rqr (41, 2, 40)	30.75012	1	Rq- (65, 3, -)	48.23028	44
Rqr (46, 1, 45)	34.53182	-1	Rqr (66, 1, 66)	48.79646	10	Rqr (42, 2, 41)	31.48092	44	Rq- (67, 3, -)	49.68366	65
Rqr (47, 1, 46)	35.26427	4	Rqr (67, 1, 67)	49.52035	15	Rqr (43, 2, 42)	32.21116	44	Rq- (68, 3, -)	50.40979	48
Rqr (48, 1, 47)	35.99655	7	Rqr (68, 1, 68)	50.24403	18	Rqr (44, 2, 43)	32.94138	53	Rq- (69, 3, -)	51.13586	43
Rqr (49, 1, 48)	36.72868	9	Rqr (69, 1, 69)	50.96741	11	Rqr (45, 2, 44)	33.67119	36	Rq- (70, 3, -)	51.86194	59
Rqr (50, 1, 49)	37.46054	0	Rqr (70, 1, 70)	51.69070	16	Rqr (46, 2, 45)	34.40075	7			

[a] Transitions are indicated by ΔJ, ΔK_a, ΔK_c, followed by the lower state quantum numbers J'', K_a'', and K_c'' in parentheses. Capital P, Q, and R represent $\Delta J = -1$, 0, and $+1$, respectively. Lowercase p, q, and r are used to indicate ΔK_a and ΔK_c. Observed line positions are listed in the column of "Freq.". The observed − calculated values in the units of 10^{-5} cm^{-1} are in the column of Δ.

TABLE V—*Continued*

Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ
Rq- (27, 4, -)	20.49637	-4	Rq- (52, 4, -)	38.74727	5	Rq- (35, 5, -)	26.32546	9	Rq- (27, 6, -)	20.45799	-12
Rq- (28, 4, -)	21.22774	8	Rq- (53, 4, -)	39.47580	17	Rq- (36, 5, -)	27.05540	2	Rq- (28, 6, -)	21.18813	10
Rq- (29, 4, -)	21.95892	9	Rq- (54, 4, -)	40.20396	7	Rq- (37, 5, -)	27.78539	10	Rq- (29, 6, -)	21.91714	-73
Rq- (30, 4, -)	22.68996	4	Rq- (55, 4, -)	40.93207	7	Rq- (38, 5, -)	28.51511	2	Rq- (30, 6, -)	22.64756	-7
Rq- (31, 4, -)	23.42094	2	Rq- (56, 4, -)	41.66001	6	Rq- (39, 5, -)	29.24491	12	Rq- (31, 6, -)	23.37747	16
Rq- (32, 4, -)	24.15179	-5	Rq- (57, 4, -)	42.38778	3	Rq- (40, 5, -)	29.97431	-6	Rq- (32, 6, -)	24.10677	-12
Rq- (33, 4, -)	24.88276	10	Rq- (58, 4, -)	43.11548	10	Rq- (41, 5, -)	30.70388	4	Rq- (33, 6, -)	24.83589	-51
Rq- (34, 4, -)	25.61339	0	Rq- (59, 4, -)	43.84295	10	Rq- (42, 5, -)	31.43326	7	Rq- (34, 6, -)	25.56602	20
Rq- (35, 4, -)	26.34405	3	Rq- (60, 4, -)	44.57020	5	Rq- (43, 5, -)	32.16250	8	Rq- (35, 6, -)	26.29532	17
Rq- (36, 4, -)	27.07464	9	Rq- (61, 4, -)	45.29730	2	Rq- (44, 5, -)	32.89160	7	Rq- (36, 6, -)	27.02439	2
Rq- (37, 4, -)	27.80501	3	Rq- (62, 4, -)	46.02441	16	Rq- (45, 5, -)	33.62062	11	Rq- (37, 6, -)	27.75355	5
Rq- (38, 4, -)	28.53538	7	Rq- (63, 4, -)	46.75108	5	Rq- (46, 5, -)	34.34944	7	Rq- (38, 6, -)	28.48252	-1
Rq- (39, 4, -)	29.26560	8	Rq- (64, 4, -)	47.47782	18	Rq- (47, 5, -)	35.07807	-3	Rq- (39, 6, -)	29.21130	-15
Rq- (40, 4, -)	29.99574	11	Rq- (65, 4, -)	48.20439	32	Rq- (48, 5, -)	35.80676	7	Rq- (40, 6, -)	29.94038	11
Rq- (41, 4, -)	30.72573	11	Rq- (66, 4, -)	48.93057	25	Rq- (49, 5, -)	36.53527	12	Rq- (41, 6, -)	30.66893	-5
Rq- (42, 4, -)	31.45558	9	Rq- (67, 4, -)	49.65661	24	Rq- (50, 5, -)	37.26332	-15	Rq- (43, 6, -)	32.12627	20
Rq- (43, 4, -)	32.18529	4	Rq- (68, 4, -)	50.38264	40	Rq- (51, 5, -)	37.99175	11	Rq- (44, 6, -)	32.85458	15
Rq- (44, 4, -)	32.91488	0				Rq- (52, 5, -)	38.71983	16	Rq- (45, 6, -)	33.58225	-43
Rq- (45, 4, -)	33.64442	3	Rq- (27, 5, -)	20.48203	10	Rq- (53, 5, -)	39.44771	15	Rq- (46, 6, -)	34.31088	7
Rq- (46, 4, -)	34.37384	7	Rq- (28, 5, -)	21.21284	18	Rq- (54, 5, -)	40.17530	1	Rq- (47, 6, -)	35.03898	17
Rq- (47, 4, -)	35.10304	2	Rq- (29, 5, -)	21.94336	5	Rq- (55, 5, -)	40.90303	15	Rq- (48, 6, -)	35.76662	-7
Rq- (48, 4, -)	35.83221	7	Rq- (30, 5, -)	22.67396	8	Rq- (56, 5, -)	41.63033	3			
Rq- (49, 4, -)	36.56126	14	Rq- (31, 5, -)	23.40439	3	Rq- (57, 5, -)	42.35766	9			
Rq- (50, 4, -)	37.29000	4	Rq- (33, 5, -)	24.86508	2	Rq- (58, 5, -)	43.08459	-9			
Rq- (51, 4, -)	38.01872	6	Rq- (34, 5, -)	25.59530	3	Rq- (59, 5, -)	43.81258	96			

The special properties of the spectra require special care in the analysis of the spectral data. The application limit of the standard effective rotational Hamiltonian for asymmetric top molecules in polynomial expansion is easily noticed in the case of HNCO (see below). In the present study we used Watson's S-reduced Hamiltonian (I^r-representation) up to sextic centrifugal distortion terms (*14*)

$$\begin{aligned}\hat{H}^S_{\mathrm{rot}} = {} & \tfrac{1}{2}(\tilde{B}_x^{(S)} + \tilde{B}_y^{(S)})\hat{J}^2 + \{\tilde{B}_z^{(S)} - \tfrac{1}{2}(\tilde{B}_x^{(S)} + \tilde{B}_y^{(S)})\}\hat{J}_z^2 - D_J\hat{J}^4 - D_{JK}\hat{J}^2\hat{J}_z^2 - D_K\hat{J}_z^4 \\ & + H_J\hat{J}^6 + H_{JK}\hat{J}^4\hat{J}_z^2 + H_{KJ}\hat{J}^2\hat{J}_z^4 + H_K\hat{J}_z^6 + \{\tfrac{1}{4}(\tilde{B}_x^{(S)} - \tilde{B}_y^{(S)}) + d_1\hat{J}^2 + h_1\hat{J}^4\} \\ & \times (\hat{J}_+^2 + \hat{J}_-^2) + (d_2\hat{J}^2 + h_2\hat{J}^4)(\hat{J}_+^4 + \hat{J}_-^4) + h_3(\hat{J}_+^6 + \hat{J}_-^6) \qquad (1)\end{aligned}$$

with extension for higher-order terms up to J^{14} power as described by Yamada and Klee (*15*):

$$\begin{aligned}\hat{H}' = {} & -L_J\hat{J}^8 - L_{62}\hat{J}^6\hat{J}_z^2 - L_{44}\hat{J}^4\hat{J}_z^4 - L_{26}\hat{J}^2\hat{J}_z^6 - L_K\hat{J}_z^8 + S_J\hat{J}^{10} \\ & + S_{82}\hat{J}^8\hat{J}_z^2 + S_{64}\hat{J}^6\hat{J}_z^4 + S_{46}\hat{J}^4\hat{J}_z^6 + S_{28}\hat{J}^2\hat{J}_z^8 + S_K\hat{J}_z^{10} \\ & - T_{48}\hat{J}^4\hat{J}_z^8 - T_{2,10}\hat{J}^2\hat{J}_z^{10} - T_K\hat{J}_z^{12} + U_K\hat{J}_z^{14}. \qquad (2)\end{aligned}$$

The analysis has been performed with a least-squares fit to derive the molecular parameters by using the presently measured FTIR line positions and sub-mmW transition frequencies, together with the MW and mmW data available in literatures (*16*). The MW, mmW, and sub-mmW transitions were weighted in the fits reciprocally proportional to the squares of the estimated experimental uncertainties, while the FTIR data are weighted assuming the uncertainty in the line position to be 10^{-3} cm^{-1}, although we expect the experimental uncertainty to be better than this value. In the cases where the K-type splitting is not resolved, the weight is reduced by a factor of 2.

For the main isotopomer HNCO, the infrared transitions from $K_a = 1 \leftarrow 0$ to $K_a =$

TABLE VI

Observed Line Positions of HNCO (in cm^{-1}) Measured by FTIR Spectroscopy[a,b]

Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ
Qrp (1, 0, 1)	30.08098	15	Prp (13, 0, 13)	20.33487	12	Rrr (56, 0, 56)	67.51055	7	Qrp (55, 1, 54)	84.21908	17
Qrp (2, 0, 2)	30.08606	0	Prp (12, 0, 12)	21.10042	7	Rrr (57, 0, 57)	68.09846	7	Qrp (56, 1, 55)	84.08349	16
Qrp (3, 0, 3)	30.09401	10	Prp (11, 0, 11)	21.86341	10	Rrr (58, 0, 58)	68.68437	2	Qrp (57, 1, 56)	83.94635	17
Qrp (4, 0, 4)	30.10456	19	Prp (10, 0, 10)	22.62370	10	Rrr (59, 0, 59)	69.26843	2	Qrp (58, 1, 57)	83.80770	19
Qrp (5, 0, 5)	30.11756	10	Prp (9, 0, 9)	23.38131	8	Rrr (60, 0, 60)	69.85057	-2	Qrp (59, 1, 58)	83.66755	20
Qrp (6, 0, 6)	30.13333	16	Prp (8, 0, 8)	24.13626	10	Rrr (61, 0, 61)	70.43092	-1	Qrp (60, 1, 59)	83.52595	19
Qrp (7, 0, 7)	30.15160	10	Prp (7, 0, 7)	24.88853	12	Rrr (62, 0, 62)	71.00933	-12	Qrp (61, 1, 60)	83.38298	20
Qrp (8, 0, 8)	30.17245	-2	Prp (6, 0, 6)	25.63773	-23	Rrr (63, 0, 63)	71.58611	-8	Qrp (62, 1, 61)	83.23870	24
Qrp (9, 0, 9)	30.19587	-19	Prp (5, 0, 5)	26.38482	2	Rrr (64, 0, 64)	72.16097	-21	Qrp (63, 1, 62)	83.09305	21
Qrp (10, 0, 10)	30.22252	22	Prp (4, 0, 4)	27.12897	4	Rrr (65, 0, 65)	72.73425	-20	Qrp (64, 1, 63)	82.94616	18
Qrp (11, 0, 11)	30.25122	5	Prp (3, 0, 3)	27.87042	8	Rrr (66, 0, 66)	73.30568	-36	Qrp (65, 1, 64)	82.79811	19
Qrp (12, 0, 12)	30.28233	-36	Prp (2, 0, 2)	28.60930	26	Rrr (67, 0, 67)	73.87572	-26	Qrp (66, 1, 65)	82.64892	20
Qrp (13, 0, 13)	30.31668	-19				Rrr (68, 0, 68)	74.44382	-50	Qrp (68, 1, 67)	82.34715	9
Qrp (14, 0, 14)	30.35373	3	Rrr (0, 0, 0)	30.80867	-3	Rrr (69, 0, 69)	75.01054	-53	Qrp (69, 1, 68)	82.19479	7
Qrp (15, 0, 15)	30.39318	-2	Rrr (1, 0, 1)	31.53658	12	Rrr (70, 0, 70)	75.57555	-74	Qrp (70, 1, 69)	82.04140	-4
Qrp (16, 0, 16)	30.43520	-17	Rrr (2, 0, 2)	32.26151	5	Rrr (71, 0, 71)	76.13919	-81	Qrp (71, 1, 70)	81.88704	-23
Qrp (17, 0, 17)	30.48007	-16	Rrr (3, 0, 3)	32.98375	2				Qrp (72, 1, 71)	81.73212	-14
Qrp (18, 0, 18)	30.52773	-4	Rrr (4, 0, 4)	33.70332	7	Qrp (2, 1, 1)	88.26627	-9	Qrp (74, 1, 73)	81.41967	-30
Qrp (19, 0, 19)	30.57841	40	Rrr (5, 0, 5)	34.42003	0	Qrp (3, 1, 2)	88.25771	-12	Qrp (75, 1, 74)	81.26216	-63
Qrp (20, 0, 20)	30.63072	-23	Rrr (6, 0, 6)	35.13405	-2	Qrp (4, 1, 3)	88.24625	-23			
Qrp (21, 0, 21)	30.68684	23	Rrr (7, 0, 7)	35.84545	9	Qrp (5, 1, 4)	88.23218	-11	Qrp (2, 1, 2)	88.28241	-3
Qrp (22, 0, 22)	30.74502	2	Rrr (8, 0, 8)	36.55390	0	Qrp (6, 1, 5)	88.21489	-39	Qrp (3, 1, 3)	88.28995	-2
Qrp (23, 0, 23)	30.80654	42	Rrr (9, 0, 9)	37.25980	9	Qrp (7, 1, 6)	88.19521	-23	Qrp (4, 1, 4)	88.30005	4
Qrp (24, 0, 24)	30.86997	-2	Rrr (10, 0, 10)	37.96280	3	Qrp (8, 1, 7)	88.17240	-38	Qrp (5, 1, 5)	88.31270	12
Qrp (25, 0, 25)	30.93661	0	Rrr (11, 0, 11)	38.66311	0	Qrp (9, 1, 8)	88.14706	-25	Qrp (6, 1, 6)	88.32734	-29
Qrp (26, 0, 26)	31.00590	-11	Rrr (12, 0, 12)	39.36096	25	Qrp (10, 1, 9)	88.11844	-60	Qrp (7, 1, 7)	88.34547	25
Qrp (27, 0, 27)	31.07816	-3	Rrr (13, 0, 13)	40.05539	-19	Qrp (11, 1, 10)	88.08825	28	Qrp (8, 1, 8)	88.36486	-44
Qrp (28, 0, 28)	31.15321	5	Rrr (14, 0, 14)	40.74778	5	Qrp (12, 1, 11)	88.05385	-26	Qrp (9, 1, 9)	88.38739	-50
Qrp (29, 0, 29)	31.23092	-2	Rrr (15, 0, 15)	41.43729	12	Qrp (13, 1, 12)	88.01817	69	Qrp (10, 1, 10)	88.41266	-35
Qrp (30, 0, 30)	31.31159	5	Rrr (16, 0, 16)	42.12370	-18	Qrp (14, 1, 13)	87.97749	-59	Qrp (11, 1, 11)	88.43972	-91
Qrp (31, 0, 31)	31.39498	0	Rrr (17, 0, 17)	42.80767	-23	Qrp (15, 1, 14)	87.93556	-37	Qrp (12, 1, 12)	88.47078	2
Qrp (32, 0, 32)	31.48092	-35	Rrr (18, 0, 18)	43.48997	75	Qrp (16, 1, 15)	87.89087	-16	Qrp (13, 1, 13)	88.50291	-50
Qrp (33, 0, 33)	31.57050	8	Rrr (19, 0, 19)	44.16755	-29	Qrp (17, 1, 16)	87.84267	-73	Qrp (14, 1, 14)	88.53798	-59
Qrp (34, 0, 34)	31.66253	8	Rrr (20, 0, 20)	44.84362	-17	Qrp (18, 1, 17)	87.79346	40	Qrp (15, 1, 15)	88.57670	46
Qrp (35, 0, 35)	31.75743	5	Rrr (21, 0, 21)	45.51731	24	Qrp (19, 1, 18)	87.73964	-37	Qrp (16, 1, 16)	88.61566	-76
Qrp (36, 0, 36)	31.85528	6	Rrr (22, 0, 22)	46.18759	-9	Qrp (20, 1, 19)	87.68391	-36	Qrp (17, 1, 17)	88.65979	67
Qrp (37, 0, 37)	31.95606	7	Rrr (23, 0, 23)	46.85557	-7	Qrp (21, 1, 20)	87.62498	-89	Qrp (18, 1, 18)	88.70462	29
Qrp (38, 0, 38)	32.05977	6	Rrr (24, 0, 24)	47.52083	-12	Qrp (22, 1, 21)	87.56441	-40	Qrp (19, 1, 19)	88.75235	29
Qrp (39, 0, 39)	32.16651	12	Rrr (25, 0, 25)	48.18343	-21	Qrp (24, 1, 23)	87.43504	23	Qrp (20, 1, 20)	88.80300	70
Qrp (40, 0, 40)	32.27616	11	Rrr (26, 0, 26)	48.84365	-6	Qrp (25, 1, 24)	87.36539	-51	Qrp (21, 1, 21)	88.85511	6
Qrp (41, 0, 41)	32.38879	8	Rrr (27, 0, 27)	49.50127	10	Qrp (26, 1, 25)	87.29420	-22	Qrp (22, 1, 22)	88.91007	-25
Qrp (42, 0, 42)	32.50471	33	Rrr (28, 0, 28)	50.15594	-10	Qrp (27, 1, 26)	87.21989	-49	Qrp (23, 1, 23)	88.96738	-73
Qrp (43, 0, 43)	32.62318	8	Rrr (29, 0, 29)	50.80831	-1	Qrp (28, 1, 27)	87.14327	-52	Qrp (24, 1, 24)	89.02828	-12
Qrp (44, 0, 44)	32.74495	8	Rrr (30, 0, 30)	51.45807	2	Qrp (29, 1, 28)	87.06462	-9	Qrp (25, 1, 25)	89.09094	-28
Qrp (45, 0, 45)	32.86981	9	Rrr (31, 0, 31)	52.10534	12	Qrp (30, 1, 29)	86.98285	-29	Qrp (26, 1, 26)	89.15600	-56
Qrp (46, 0, 46)	32.99769	3	Rrr (32, 0, 32)	52.74990	5	Qrp (31, 1, 30)	86.89870	-40	Qrp (27, 1, 27)	89.22458	17
Qrp (47, 0, 47)	33.12887	15	Rrr (33, 0, 33)	53.39200	3	Qrp (32, 1, 31)	86.81238	-23	Qrp (28, 1, 28)	89.29519	42
Qrp (48, 0, 48)	33.26307	15	Rrr (34, 0, 34)	54.03150	-9	Qrp (33, 1, 32)	86.72341	-31	Qrp (29, 1, 29)	89.36718	-48
Qrp (49, 0, 49)	33.40039	11	Rrr (35, 0, 35)	54.66874	3	Qrp (34, 1, 33)	86.63239	-5	Qrp (30, 1, 30)	89.44277	-29
Qrp (50, 0, 50)	33.54094	11	Rrr (36, 0, 36)	55.30343	6	Qrp (35, 1, 34)	86.53877	-2	Qrp (31, 1, 31)	89.52064	-34
Qrp (51, 0, 51)	33.68466	9	Rrr (37, 0, 37)	55.93565	6	Qrp (36, 1, 35)	86.44278	-4	Qrp (32, 1, 32)	89.60102	-40
Qrp (52, 0, 52)	33.83171	16	Rrr (38, 0, 38)	56.56533	-3	Qrp (37, 1, 36)	86.34440	-14	Qrp (33, 1, 33)	89.68416	-22
Qrp (53, 0, 53)	33.98189	12	Rrr (39, 0, 39)	57.19281	8	Qrp (38, 1, 37)	86.24395	-3	Qrp (34, 1, 34)	89.77007	21
Qrp (54, 0, 54)	34.13538	11	Rrr (40, 0, 40)	57.81779	8	Qrp (39, 1, 38)	86.14130	12	Qrp (35, 1, 35)	89.85775	-11
Qrp (55, 0, 55)	34.29211	5	Rrr (41, 0, 41)	58.44040	9	Qrp (40, 1, 39)	86.03619	2	Qrp (36, 1, 36)	89.94841	3
Qrp (56, 0, 56)	34.45219	2	Rrr (42, 0, 42)	59.06059	2	Qrp (41, 1, 40)	85.92899	1	Qrp (37, 1, 37)	90.04139	-3
Qrp (57, 0, 57)	34.61562	-1	Rrr (43, 0, 43)	59.67859	10	Qrp (42, 1, 41)	85.81942	-22	Qrp (38, 1, 38)	90.13696	-2
Qrp (58, 0, 58)	34.78243	-3	Rrr (44, 0, 44)	60.29421	10	Qrp (43, 1, 42)	85.70828	9	Qrp (39, 1, 39)	90.23504	-2
Qrp (59, 0, 59)	34.95263	-5	Rrr (45, 0, 45)	60.90754	9	Qrp (44, 1, 43)	85.59462	-3	Qrp (40, 1, 40)	90.33563	-4
Qrp (60, 0, 60)	35.12644	12	Rrr (46, 0, 46)	61.51858	5	Qrp (45, 1, 44)	85.47913	6	Qrp (41, 1, 41)	90.43877	-2
Qrp (61, 0, 61)	35.30329	-12	Rrr (47, 0, 47)	62.12737	0	Qrp (46, 1, 45)	85.36157	9	Qrp (42, 1, 42)	90.54445	1
Qrp (62, 0, 62)	35.48388	-9	Rrr (48, 0, 48)	62.73407	8	Qrp (47, 1, 46)	85.24198	7	Qrp (43, 1, 43)	90.65260	-2
Qrp (63, 0, 63)	35.66777	-25	Rrr (49, 0, 49)	63.33861	18	Qrp (48, 1, 47)	85.12052	11	Qrp (44, 1, 44)	90.76331	-1
Qrp (64, 0, 64)	35.85532	-30	Rrr (50, 0, 50)	63.94081	10	Qrp (49, 1, 48)	84.99712	12	Qrp (45, 1, 45)	90.87654	0
Qrp (65, 0, 65)	36.04647	-28	Rrr (51, 0, 51)	64.54095	10	Qrp (50, 1, 49)	84.87187	12	Qrp (46, 1, 46)	90.99227	-1
Qrp (67, 0, 67)	36.43948	-31	Rrr (52, 0, 52)	65.13896	7	Qrp (51, 1, 50)	84.74476	11	Qrp (47, 1, 47)	91.11057	2
Qrp (68, 0, 68)	36.64129	-45	Rrr (53, 0, 53)	65.73495	11	Qrp (52, 1, 51)	84.61591	12	Qrp (48, 1, 48)	91.23139	5
Qrp (69, 0, 69)	36.84679	-57	Rrr (54, 0, 54)	66.32877	3	Qrp (53, 1, 52)	84.48534	16	Qrp (49, 1, 49)	91.35469	3
			Rrr (55, 0, 55)	66.92068	7	Qrp (54, 1, 53)	84.35300	12	Qrp (50, 1, 50)	91.48055	5

[a] For notation see Table V.

[b] Unresolved transition frequencies of partly resolved subbands are listed twice (with both quantum number sets) if greater differences of the observed − calculated values are calculated in the fit.

$5 \leftarrow 4$ could be included in the fit, with restriction to $J < 50$ in the case of ${}^{r}X_4$. One transition of each subband $K_a = 6 \leftarrow 5$ and of $K_a = 7 \leftarrow 6$ has been included in the fit. However, because of the centrifugal distortion resonance, we could not fit $K_a = 8 \leftarrow 7$ transitions at all with the Hamiltonian given above.

In the fits of $H^{15}NCO$, $HN^{13}CO$, and $HNC^{18}O$ some of the parameters were fixed

TABLE VI—*Continued*

Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ
Qrp (51, 1, 51)	91.60888	1	Prp (12, 1, 11)	79.25828	-1	Rrr (59, 1, 58)	127.19377	21	Rrp (11, 1, 11)	97.23650	4
Qrp (52, 1, 52)	91.73977	0	Prp (11, 1, 10)	80.02511	-3	Rrr (60, 1, 59)	127.75602	31	Rrp (12, 1, 12)	97.99962	1
Qrp (53, 1, 53)	91.87322	3	Prp (10, 1, 9)	80.78913	-7	Rrr (61, 1, 60)	128.31557	47	Rrp (13, 1, 13)	98.76536	6
Qrp (54, 1, 54)	92.00916	3	Prp (9, 1, 8)	81.55045	-1	Rrr (62, 1, 61)	128.87212	39	Rrp (14, 1, 14)	99.53355	1
Qrp (55, 1, 55)	92.14770	10	Prp (8, 1, 7)	82.30888	-2	Rrr (63, 1, 62)	129.42513	-47	Rrp (15, 1, 15)	100.30429	-3
Qrp (56, 1, 56)	92.28868	9	Prp (7, 1, 6)	83.06453	-1	Rrr (64, 1, 63)	129.97716	44	Rrp (16, 1, 16)	101.07765	-1
Qrp (57, 1, 57)	92.43227	16	Prp (6, 1, 5)	83.81734	-2	Rrr (65, 1, 64)	130.52575	65	Rrp (17, 1, 17)	101.85356	-1
Qrp (58, 1, 58)	92.57827	11	Prp (5, 1, 4)	84.56736	1				Rrp (18, 1, 18)	102.63208	2
Qrp (59, 1, 59)	92.72692	19	Prp (4, 1, 3)	85.31456	3	Prn (52, 1, 52)	53.88859	22	Rrp (19, 1, 19)	103.41314	1
Qrp (60, 1, 60)	92.87802	20	Prp (3, 1, 2)	86.05892	5	Prn (51, 1, 51)	54.47204	19	Rrp (20, 1, 20)	104.19684	4
Qrp (61, 1, 61)	93.03169	25				Prn (50, 1, 50)	55.05903	18	Rrp (21, 1, 21)	104.98311	3
Qrp (62, 1, 62)	93.18784	25	Rrr (1, 1, 0)	89.73804	-3	Prn (49, 1, 49)	55.64952	18	Rrp (22, 1, 22)	105.77198	0
Qrp (63, 1, 63)	93.34608	-17	Rrr (2, 1, 1)	90.46535	-3	Prn (48, 1, 48)	56.24345	18	Rrp (23, 1, 23)	106.56355	4
Qrp (64, 1, 64)	93.50773	28	Rrr (3, 1, 2)	91.18981	-3	Prn (47, 1, 47)	56.84071	10	Rrp (24, 1, 24)	107.35771	2
Qrp (65, 1, 65)	93.67160	44	Rrr (4, 1, 3)	91.91141	-4	Prn (46, 1, 46)	57.44143	9	Rrp (25, 1, 25)	108.15454	0
Qrp (66, 1, 66)	93.83756	16	Rrr (5, 1, 4)	92.63020	-1	Prn (45, 1, 45)	58.04553	12	Rrp (26, 1, 26)	108.95409	3
Qrp (67, 1, 67)	94.00571	-45	Rrr (6, 1, 5)	93.34608	-3	Prn (44, 1, 44)	58.65292	12	Rrp (27, 1, 27)	109.75630	3
Qrp (68, 1, 68)	94.17824	80	Rrr (7, 1, 6)	94.05912	-3	Prn (43, 1, 43)	59.26338	-8	Rrp (28, 1, 28)	110.56120	0
Qrp (70, 1, 70)	94.52685	-71	Rrr (8, 1, 7)	94.76928	-5	Prn (42, 1, 42)	59.87749	11	Rrp (29, 1, 29)	111.36886	2
			Rrr (9, 1, 8)	95.47664	-1	Prn (41, 1, 41)	60.49461	10	Rrp (30, 1, 30)	112.17925	2
Prp (62, 1, 61)	37.48397	38	Rrr (10, 1, 9)	96.18109	-2	Prn (40, 1, 40)	61.11496	12	Rrp (31, 1, 31)	112.99240	1
Prp (61, 1, 60)	38.38202	25	Rrr (11, 1, 10)	96.88270	0	Prn (39, 1, 39)	61.73842	9	Rrp (32, 1, 32)	113.80833	1
Prp (59, 1, 58)	40.17101	11	Rrr (12, 1, 11)	97.58144	2	Prn (38, 1, 38)	62.36502	7	Rrp (33, 1, 33)	114.62708	3
Prp (58, 1, 57)	41.06211	26	Rrr (13, 1, 12)	98.27726	-2	Prn (37, 1, 37)	62.99478	11	Rrp (34, 1, 34)	115.44863	3
Prp (57, 1, 56)	41.95044	11	Rrr (14, 1, 13)	98.97027	0	Prn (36, 1, 36)	63.62756	10	Rrp (35, 1, 35)	116.27292	-7
Prp (56, 1, 55)	42.83649	11	Rrr (15, 1, 14)	99.66036	-2	Prn (35, 1, 35)	64.26337	6	Rrp (36, 1, 36)	117.10020	-4
Prp (55, 1, 54)	43.72068	71	Rrr (16, 1, 15)	100.34763	0	Prn (34, 1, 34)	64.90222	5	Rrp (37, 1, 37)	117.93042	4
Prp (54, 1, 53)	44.60113	4	Rrr (17, 1, 16)	101.03201	1	Prn (33, 1, 33)	65.54409	6	Rrp (38, 1, 38)	118.76337	-5
Prp (53, 1, 52)	45.48007	35	Rrr (18, 1, 17)	101.71350	-1	Prn (32, 1, 32)	66.18892	6	Rrp (39, 1, 39)	119.59922	-17
Prp (52, 1, 51)	46.35590	3	Rrr (19, 1, 18)	102.39212	-2	Prn (31, 1, 31)	66.83669	6	Rrp (40, 1, 40)	120.43835	3
Prp (51, 1, 50)	47.22960	8	Rrr (20, 1, 19)	103.06788	-1	Prn (30, 1, 30)	67.48736	3	Rrp (41, 1, 41)	121.28026	4
Prp (50, 1, 49)	48.10066	0	Rrr (21, 1, 20)	103.74077	-1	Prn (29, 1, 29)	68.14094	1	Rrp (42, 1, 42)	122.12512	0
Prp (49, 1, 48)	48.96930	2	Rrr (22, 1, 21)	104.41078	-1	Prn (28, 1, 28)	68.79747	7	Rrp (43, 1, 43)	122.97309	4
Prp (48, 1, 47)	49.83540	4	Rrr (23, 1, 22)	105.07792	-1	Prn (27, 1, 27)	69.45667	-5	Rrp (44, 1, 44)	123.82407	3
Prp (47, 1, 46)	50.69893	2	Rrr (24, 1, 23)	105.74219	0	Prn (26, 1, 26)	70.11896	8	Rrp (45, 1, 45)	124.67816	5
Prp (46, 1, 45)	51.56007	16	Rrr (25, 1, 24)	106.40355	-4	Prn (25, 1, 25)	70.78385	1	Rrp (46, 1, 46)	125.53536	8
Prp (45, 1, 44)	52.41835	0	Rrr (26, 1, 25)	107.06212	1	Prn (24, 1, 24)	71.45151	-9	Rrp (47, 1, 47)	126.39565	6
Prp (44, 1, 43)	53.27424	2	Rrr (27, 1, 26)	107.71776	0	Prn (23, 1, 23)	72.12200	-12	Rrp (48, 1, 48)	127.25912	5
Prp (43, 1, 42)	54.12752	1	Rrr (28, 1, 27)	108.37050	-3	Prn (22, 1, 22)	72.79536	-5	Rrp (49, 1, 49)	128.12584	10
Prp (42, 1, 41)	54.97825	3	Rrr (29, 1, 28)	109.02043	-1	Prn (21, 1, 21)	73.47157	14	Rrp (50, 1, 50)	128.99572	8
Prp (41, 1, 40)	55.82640	7	Rrr (30, 1, 29)	109.66747	-1	Prn (20, 1, 20)	74.14995	-22	Rrp (51, 1, 51)	129.86889	10
Prp (40, 1, 39)	56.67186	2	Rrr (31, 1, 30)	110.31160	-6	Prn (19, 1, 19)	74.83172	11	Rrp (52, 1, 52)	130.74533	11
Prp (39, 1, 38)	57.51475	1	Rrr (32, 1, 31)	110.95297	0	Prn (18, 1, 18)	75.51562	-11	Rrp (53, 1, 53)	131.62510	12
Prp (38, 1, 37)	58.35505	3	Rrr (33, 1, 32)	111.59139	-2	Prn (17, 1, 17)	76.20242	-10	Rrp (54, 1, 54)	132.50824	17
Prp (37, 1, 36)	59.19268	1	Rrr (34, 1, 33)	112.22694	-5	Prn (16, 1, 16)	76.89183	-14	Rrp (55, 1, 55)	133.39470	15
Prp (36, 1, 35)	60.02775	7	Rrr (35, 1, 34)	112.85970	-1	Prn (15, 1, 15)	77.58401	-5	Rrp (56, 1, 56)	134.28457	12
Prp (35, 1, 34)	60.86006	1	Rrr (36, 1, 35)	113.48956	-1	Prn (14, 1, 14)	78.27870	-7	Rrp (57, 1, 57)	135.17796	17
Prp (34, 1, 33)	61.68984	7	Rrr (37, 1, 36)	114.11662	5	Prn (13, 1, 13)	78.97612	2	Rrp (58, 1, 58)	136.07478	17
Prp (33, 1, 32)	62.51689	7	Rrr (38, 1, 37)	114.74071	-1	Prn (12, 1, 12)	79.67588	-16	Rrp (59, 1, 59)	136.97513	18
Prp (32, 1, 31)	63.34119	-2	Rrr (39, 1, 38)	115.36202	1	Prn (11, 1, 11)	80.37848	-8	Rrp (60, 1, 60)	137.87903	19
Prp (31, 1, 30)	64.16297	5	Rrr (40, 1, 39)	115.98046	1	Prn (10, 1, 10)	81.08364	-3	Rrp (61, 1, 61)	138.78639	8
Prp (30, 1, 29)	64.98196	1	Rrr (41, 1, 40)	116.59598	-7	Prn (9, 1, 9)	81.79141	6	Rrp (62, 1, 62)	139.69757	16
Prp (29, 1, 28)	65.79838	9	Rrr (42, 1, 41)	117.20896	16	Prn (8, 1, 8)	82.50161	2	Rrp (63, 1, 63)	140.61234	17
Prp (28, 1, 27)	66.61191	-2	Rrr (43, 1, 42)	117.81872	1	Prn (7, 1, 7)	83.21444	6	Rrp (64, 1, 64)	141.53042	-20
Prp (27, 1, 26)	67.42284	-4	Rrr (44, 1, 43)	118.42576	-2	Prn (6, 1, 6)	83.92972	0	Rrp (65, 1, 65)	142.45289	8
Prp (26, 1, 25)	68.23103	-7	Rrr (45, 1, 44)	119.03006	5	Prn (5, 1, 5)	84.64763	3	Rrp (66, 1, 66)	143.37889	12
Prp (25, 1, 24)	69.03656	-6	Rrr (46, 1, 45)	119.63136	-5	Prn (4, 1, 4)	85.36811	10			
Prp (24, 1, 23)	69.83926	-15	Rrr (47, 1, 46)	120.22998	-1	Prn (3, 1, 3)	86.09103	8	Qr- (4, 2, -)	142.26891	11
Prp (23, 1, 22)	70.63946	-1	Rrr (48, 1, 47)	120.82574	1				Qr- (5, 2, -)	142.26708	-41
Prp (22, 1, 21)	71.43676	-3	Rrr (49, 1, 48)	121.41873	8	Rrp (1, 1, 1)	89.74330	-9	Qr- (7, 2, -)	142.26482	76
Prp (21, 1, 20)	72.23115	-22	Rrr (50, 1, 49)	122.00873	-3	Rrp (2, 1, 2)	90.48142	2	Qr- (8, 2, -)	142.26234	40
Prp (20, 1, 19)	73.02314	-7	Rrr (51, 1, 50)	122.59608	3	Rrp (3, 1, 3)	91.22192	-1	Qr- (9, 2, -)	142.25980	25
Prp (19, 1, 18)	73.81216	-12	Rrr (52, 1, 51)	123.18058	5	Rrp (4, 1, 4)	91.96496	1	Qr- (10, 2, -)	142.25707	21
Prp (18, 1, 17)	74.59836	-25	Rrr (53, 1, 52)	123.76227	7	Rrp (5, 1, 5)	92.71050	1	Qr- (11, 2, -)	142.25417	28
Prp (17, 1, 16)	75.38213	-3	Rrr (54, 1, 53)	124.34115	8	Rrp (6, 1, 6)	93.45853	0	Qr- (12, 2, -)	142.25096	33
Prp (16, 1, 15)	76.16292	-3	Rrr (55, 1, 54)	124.91730	16	Rrp (7, 1, 7)	94.20909	0	Qr- (13, 2, -)	142.24749	42
Prp (15, 1, 14)	76.94081	-15	Rrr (56, 1, 55)	125.49055	12	Rrp (8, 1, 8)	94.96216	1	Qr- (14, 2, -)	142.24388	68
Prp (14, 1, 13)	77.71602	-17	Rrr (57, 1, 56)	126.06111	19	Rrp (9, 1, 9)	95.71775	2	Qrp (15, 2, 13)	142.23971	69
Prp (13, 1, 12)	78.48864	1	Rrr (58, 1, 57)	126.62889	26	Rrp (10, 1, 10)	96.47585	2	Qrp (16, 2, 14)	142.23482	29

to the values obtained for the main isotopomer, if they could not be adjusted in fitting the isotopomer data. For the deuterated isotopomer, as well as the *a*-type transitions, all the *b*-type transitions up to $K_a = 7 \leftarrow 6$ could be fitted with the effective Hamiltonian.

Table I gives a summary of the rotational and centrifugal distortion constants revised in the present study. In comparison with the previous work of Yamada (*6*), the accuracies of all parameters have been improved, and some parameters are even determined for the first time.

As mentioned above, it was impossible to include all *b*-type transitions in the fit

TABLE VI—*Continued*

Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ
Qrp (17, 2, 15)	142.22938	-33	Qrp (42, 2, 41)	142.06182	39	Rr- (2, 2, -)	144.46880	-2	Prn (60, 2, 59)	98.03388	57
Qrp (19, 2, 17)	142.21848	-57	Qrp (43, 2, 42)	142.05258	-7	Rr- (3, 2, -)	145.20074	-3	Prn (59, 2, 58)	98.76983	-23
Qrp (20, 2, 18)	142.21299	-20	Qrp (44, 2, 43)	142.04368	-11	Rr- (4, 2, -)	145.93239	-5	Prn (58, 2, 57)	99.50701	-3
Qrp (21, 2, 19)	142.20722	25	Qrp (45, 2, 44)	142.03429	-55	Rr- (5, 2, -)	146.66381	-2	Prn (57, 2, 56)	100.24408	-17
Qrp (22, 2, 20)	142.20092	53	Qrp (46, 2, 45)	142.02574	-8	Rr- (6, 2, -)	147.39492	-1	Prn (56, 2, 55)	100.98169	3
Qrp (23, 2, 21)	142.19340	-1	Qrp (47, 2, 46)	142.01656	-17	Rr- (7, 2, -)	148.12574	-1	Prn (55, 2, 54)	101.71931	3
Qrp (24, 2, 22)	142.18589	-15	Qrp (48, 2, 47)	142.00744	-14	Rr- (8, 2, -)	148.85630	3	Prn (54, 2, 53)	102.45715	7
Qrp (25, 2, 23)	142.17785	-41	Qrp (49, 2, 48)	141.99830	-8	Rr- (9, 2, -)	149.58655	6	Prn (53, 2, 52)	103.19514	9
Qrp (26, 2, 24)	142.17039	33				Rr- (10, 2, -)	150.31654	14	Prn (52, 2, 51)	103.93370	52
Qrp (27, 2, 25)	142.16145	1	Prp (63, 2, 61)	95.36830	14	Rr- (11, 2, -)	151.04617	18	Prn (51, 2, 50)	104.67151	8
Qrp (28, 2, 26)	142.15231	-6	Prp (62, 2, 60)	96.13220	1	Rr- (12, 2, -)	151.77553	26	Prn (50, 2, 49)	105.40996	12
Qrp (29, 2, 27)	142.14268	-16	Prp (61, 2, 59)	96.89512	-7	Rr- (13, 2, -)	152.50450	31	Prn (49, 2, 48)	106.14833	-1
Qrp (30, 2, 28)	142.13285	1	Prp (60, 2, 58)	97.65709	-9	Rr- (14, 2, -)	153.23333	55	Prn (48, 2, 47)	106.88724	28
Qrp (31, 2, 29)	142.12237	2	Prp (59, 2, 57)	98.41817	-2	Rr- (15, 2, -)	153.96158	56	Prn (47, 2, 46)	107.62581	14
Qrp (32, 2, 30)	142.11151	15	Prp (58, 2, 56)	99.17805	-20	Rrr (16, 2, 14)	154.68913	23	Prn (46, 2, 45)	108.36460	12
Qrp (33, 2, 31)	142.09992	6	Prp (57, 2, 55)	99.93716	-22	Rrr (17, 2, 15)	155.41644	4	Prn (45, 2, 44)	109.10341	8
Qrp (34, 2, 32)	142.08749	-33	Prp (56, 2, 54)	100.69545	-15	Rrr (18, 2, 16)	156.14352	0	Prn (44, 2, 43)	109.84232	7
Qrp (35, 2, 33)	142.07514	-10	Prp (54, 2, 52)	102.20927	-16	Rrr (19, 2, 17)	156.87025	1	Prn (43, 2, 42)	110.58128	7
Qrp (36, 2, 34)	142.06182	-26	Prp (53, 2, 51)	102.96490	-19	Rrr (20, 2, 18)	157.59649	-7	Prn (42, 2, 41)	111.32029	8
Qrp (37, 2, 35)	142.04848	12	Prp (52, 2, 50)	103.71986	-8	Rrr (21, 2, 19)	158.32243	-2	Prn (41, 2, 40)	112.05929	6
Qrp (38, 2, 36)	142.03429	25	Prp (51, 2, 49)	104.47382	-18	Rrr (22, 2, 20)	159.04787	-4	Prn (40, 2, 39)	112.79832	6
Qrp (39, 2, 37)	142.01920	11	Prp (50, 2, 48)	105.22694	-36	Rrr (23, 2, 21)	159.77289	-4	Prn (39, 2, 38)	113.53737	7
Qrp (40, 2, 38)	142.00355	4	Prp (49, 2, 47)	105.97965	-20	Rrr (24, 2, 22)	160.49744	-4	Prn (38, 2, 37)	114.27639	6
Qrp (41, 2, 39)	141.98745	17	Prp (48, 2, 46)	106.73151	-17	Rrr (25, 2, 23)	161.22151	-5	Prn (37, 2, 36)	115.01540	6
Qrp (42, 2, 40)	141.97043	6	Prp (47, 2, 45)	107.48264	-18	Rrr (26, 2, 24)	161.94509	-6	Prn (36, 2, 35)	115.75437	4
Qrp (43, 2, 41)	141.95220	-57	Prp (46, 2, 44)	108.23312	-15	Rrr (27, 2, 25)	162.66817	-6	Prn (35, 2, 34)	116.49332	5
Qrp (44, 2, 42)	141.93419	-26	Prp (45, 2, 43)	108.98293	-14	Rrr (28, 2, 26)	163.39073	-6	Prn (34, 2, 33)	117.23196	-21
Qrp (45, 2, 43)	141.91544	3	Prp (44, 2, 42)	109.73206	-16	Rrr (29, 2, 27)	164.11275	-6	Prn (33, 2, 32)	117.97067	-34
Qrp (46, 2, 44)	141.89584	23	Prp (43, 2, 41)	110.48060	-15	Rrr (30, 2, 28)	164.83423	-5	Prn (32, 2, 31)	118.70964	-15
Qrp (47, 2, 45)	141.87523	19	Prp (42, 2, 40)	111.22853	-15	Rrr (31, 2, 29)	165.55512	-6	Prn (31, 2, 30)	119.44849	0
Qrp (48, 2, 46)	141.85392	25	Prp (41, 2, 39)	111.97590	-12	Rrr (32, 2, 30)	166.27544	-4	Prn (30, 2, 29)	120.18710	-1
Qrp (49, 2, 47)	141.83147	-1	Prp (40, 2, 38)	112.72267	-12	Rrr (33, 2, 31)	166.99510	-8	Prn (29, 2, 28)	120.92564	1
Qrp (50, 2, 48)	141.80871	25	Prp (39, 2, 37)	113.46890	-12	Rrr (34, 2, 32)	167.71422	-3	Prn (28, 2, 27)	121.66408	2
			Prp (38, 2, 36)	114.21460	-12	Rrr (35, 2, 33)	168.43261	-6	Prn (27, 2, 26)	122.40236	-2
Qr- (4, 2, -)	142.26891	14	Prp (37, 2, 35)	114.95979	-10	Rrr (36, 2, 34)	169.15036	-7	Prn (26, 2, 25)	123.14058	0
Qr- (5, 2, -)	142.26708	-39	Prp (36, 2, 34)	115.70447	-9	Rrr (37, 2, 35)	169.86740	-10	Prn (25, 2, 24)	123.87865	0
Qr- (7, 2, -)	142.26482	71	Prp (35, 2, 33)	116.44864	-11	Rrr (38, 2, 36)	170.58376	-10	Prn (24, 2, 23)	124.61657	-3
Qr- (8, 2, -)	142.26234	30	Prp (34, 2, 32)	117.19225	-21	Rrr (39, 2, 37)	171.29942	-8	Prn (23, 2, 22)	125.35438	-3
Qr- (9, 2, -)	142.25980	8	Prp (33, 2, 31)	117.93564	-8	Rrr (40, 2, 38)	172.01430	-8	Prn (22, 2, 21)	126.09206	0
Qr- (10, 2, -)	142.25707	-8	Prp (32, 2, 30)	118.67844	-9	Rrr (41, 2, 39)	172.72841	-9	Prn (21, 2, 20)	126.82934	-23
Qr- (11, 2, -)	142.25417	-16	Prp (31, 2, 29)	119.42084	-7	Rrr (42, 2, 40)	173.44171	-10	Prn (20, 2, 19)	127.56692	0
Qr- (12, 2, -)	142.25096	-31	Prp (30, 2, 28)	120.16277	-10	Rrr (43, 2, 41)	174.15423	-8	Prn (19, 2, 18)	128.30403	-7
Qr- (13, 2, -)	142.24749	-46	Prp (29, 2, 27)	120.90435	-8	Rrr (44, 2, 42)	174.86587	-10	Prn (18, 2, 17)	129.04104	-6
Qr- (14, 2, -)	142.24388	-51	Prp (28, 2, 26)	121.64552	-7	Rrr (45, 2, 43)	175.57667	-9	Prn (17, 2, 16)	129.77792	-1
Qrp (16, 2, 15)	142.23655	-2	Prp (27, 2, 25)	122.38630	-7	Rrr (46, 2, 44)	176.28656	-11	Prn (16, 2, 15)	130.51451	-6
Qrp (17, 2, 16)	142.23260	30	Prp (26, 2, 24)	123.12674	-4	Rrr (47, 2, 45)	176.99551	-14	Pr- (15, 2, -)	131.25005	-97
Qrp (18, 2, 17)	142.22809	29	Prp (25, 2, 23)	123.86678	-5	Rrr (48, 2, 46)	177.70357	-12	Pr- (14, 2, -)	131.98657	-70
Qrp (19, 2, 18)	142.22348	41	Prp (24, 2, 22)	124.60649	-4	Rrr (49, 2, 47)	178.41068	-10	Pr- (13, 2, -)	132.72280	-51
Qrp (20, 2, 19)	142.21848	37	Prp (23, 2, 21)	125.34584	-5	Rrr (50, 2, 48)	179.11676	-11	Pr- (12, 2, -)	133.45880	-36
Qrp (21, 2, 20)	142.21299	5	Prp (22, 2, 20)	126.08485	-6	Rrr (51, 2, 49)	179.82183	-11	Pr- (11, 2, -)	134.19438	-41
Qrp (22, 2, 21)	142.20722	-32	Prp (21, 2, 19)	126.82358	-3	Rrr (52, 2, 50)	180.52588	-8	Pr- (10, 2, -)	134.93000	-20
Qrp (24, 2, 23)	142.19611	-1	Prp (20, 2, 18)	127.56192	-8	Rrr (53, 2, 51)	181.22882	-9	Pr- (9, 2, -)	135.66527	-12
Qrp (25, 2, 24)	142.19008	-2	Prp (19, 2, 17)	128.30003	-4	Rrr (54, 2, 52)	181.93079	4	Pr- (8, 2, -)	136.40026	-9
Qrp (26, 2, 25)	142.18405	17	Prp (18, 2, 16)	129.03787	2	Rrr (55, 2, 53)	182.63141	-5	Pr- (7, 2, -)	137.13502	-6
Qrp (27, 2, 26)	142.17785	39	Prp (17, 2, 15)	129.77530	-3	Rrr (56, 2, 54)	183.33098	-3	Pr- (6, 2, -)	137.86956	-2
Qrp (28, 2, 27)	142.17039	-46	Prp (16, 2, 14)	130.51254	2	Rrr (57, 2, 55)	184.02936	-1	Pr- (5, 2, -)	138.60381	-2
Qrp (29, 2, 28)	142.16402	-4	Pr- (15, 2, -)	131.25005	62	Rrr (58, 2, 56)	184.72654	2	Pr- (4, 2, -)	139.33781	-3
Qrp (30, 2, 29)	142.15705	-3	Pr- (14, 2, -)	131.98657	51	Rrr (59, 2, 57)	185.42250	9			
Qrp (31, 2, 30)	142.14994	1	Pr- (13, 2, -)	132.72280	38	Rrr (60, 2, 58)	186.11703	2	Rr- (2, 2, -)	144.46880	-1
Qrp (32, 2, 31)	142.14268	7	Pr- (12, 2, -)	133.45880	30	Rrr (61, 2, 59)	186.81033	2	Rr- (3, 2, -)	145.20074	-1
Qrp (33, 2, 32)	142.13499	-14	Pr- (11, 2, -)	134.19438	5	Rrr (62, 2, 60)	187.50244	18	Rr- (4, 2, -)	145.93239	-4
Qrp (34, 2, 33)	142.12746	-3	Pr- (10, 2, -)	134.93000	11	Rrr (63, 2, 61)	188.19273	-10	Rr- (5, 2, -)	146.66381	-2
Qrp (35, 2, 34)	142.11968	-2	Pr- (9, 2, -)	135.66527	8	Rrr (64, 2, 62)	188.88237	38	Rr- (6, 2, -)	147.39492	-4
Qrp (36, 2, 35)	142.11151	-25	Pr- (8, 2, -)	136.40026	3	Rrr (65, 2, 63)	189.57034	63	Rr- (7, 2, -)	148.12574	-8
Qrp (37, 2, 36)	142.10355	-12	Pr- (7, 2, -)	137.13502	1				Rr- (8, 2, -)	148.85630	-9
Qrp (38, 2, 37)	142.09539	-8	Pr- (6, 2, -)	137.86956	1	Prn (64, 2, 63)	95.08877	-25	Rr- (9, 2, -)	149.58655	-14
Qrp (39, 2, 38)	142.08749	36	Pr- (5, 2, -)	138.60381	-1	Prn (63, 2, 62)	95.82457	-10	Rr- (10, 2, -)	150.31654	-18
Qrp (40, 2, 39)	142.07855	-12	Pr- (4, 2, -)	139.33781	-4	Prn (62, 2, 61)	96.56072	12	Rr- (11, 2, -)	151.04617	-29
Qrp (41, 2, 40)	142.07001	-9				Prn (61, 2, 60)	97.29701	19	Rr- (12, 2, -)	151.77553	-39

because of the centrifugal distortion resonance between the ground state and the lowest excited bending vibration ν_5. Thus we tentatively used a linear molecule expression to fit the data. We determined rotational and centrifugal parameters for each K_a substate individually, taking observed K-type splitting (for $K_a = 1$, 2, and 3) into consideration. Using K in the place of K_a the modified linear molecule Hamiltonian reads:

$$E(J, K, \gamma) = E_0(K) + B(K, \gamma)J(J+1) - D(K, \gamma)J^2(J+1)^2 + H(K, \gamma)J^3(J+1)^3 - L(K, \gamma)J^4(J+1)^4. \quad (3)$$

TABLE VI—*Continued*

Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ
Rr- (13, 2, -)	152.50450	-60	Qr- (17, 3, -)	191.62069	-4	Qrp (58, 3, 56)	191.03365	17	Pr- (7, 3, -)	186.54009	4
Rr- (14, 2, -)	153.23333	-66	Qr- (18, 3, -)	191.61408	-4	Qrp (59, 3, 57)	191.01078	8	Pr- (6, 3, -)	187.27495	2
Rrp (16, 2, 15)	154.69057	-37	Qr- (19, 3, -)	191.60710	-3	Qrp (60, 3, 58)	190.98754	4	Pr- (5, 3, -)	188.00946	1
Rrp (17, 2, 16)	155.41896	-4	Qr- (20, 3, -)	191.59972	-6	Qrp (61, 3, 59)	190.96394	7			
Rrp (18, 2, 17)	156.14672	-5	Qr- (21, 3, -)	191.59200	-5	Qrp (63, 3, 61)	190.91543	10	Rr- (3, 3, -)	194.60403	-1
Rrp (19, 2, 18)	156.87422	-4	Qr- (22, 3, -)	191.58388	-6	Qrp (64, 3, 62)	190.89059	17	Rr- (4, 3, -)	195.33489	-4
Rrp (20, 2, 19)	157.60146	-1	Qr- (23, 3, -)	191.57541	-5	Qrp (65, 3, 63)	190.86479	-29	Rr- (5, 3, -)	196.06540	-4
Rrp (21, 2, 20)	158.32837	-3	Qr- (24, 3, -)	191.56658	-3	Qrp (66, 3, 64)	190.83941	10	Rr- (6, 3, -)	196.79554	-2
Rrp (22, 2, 21)	159.05507	1	Qr- (25, 3, -)	191.55734	-3	Qrp (67, 3, 65)	190.81327	17	Rr- (7, 3, -)	197.52527	-3
Rrp (23, 2, 22)	159.78144	0	Qr- (26, 3, -)	191.54773	-3	Qrp (68, 3, 66)	190.78650	4	Rr- (8, 3, -)	198.25462	-3
Rrp (24, 2, 23)	160.50756	1	Qr- (27, 3, -)	191.53773	-4	Qrp (69, 3, 67)	190.75915	-24	Rr- (9, 3, -)	198.98356	-5
Rrp (25, 2, 24)	161.23338	0	Qr- (28, 3, -)	191.52739	0	Qrp (70, 3, 68)	190.73167	-21	Rr- (10, 3, -)	199.71214	-4
Rrp (26, 2, 25)	161.95896	2	Qr- (29, 3, -)	191.51662	-2				Rr- (11, 3, -)	200.44027	-8
Rrp (27, 2, 26)	162.68425	2	Qr- (30, 3, -)	191.50548	-2	Prp (63, 3, 60)	144.88625	7	Rr- (12, 3, -)	201.16806	-5
Rrp (28, 2, 27)	163.40929	3	Qr- (31, 3, -)	191.49368	-30	Prp (62, 3, 59)	145.63791	-21	Rr- (13, 3, -)	201.89544	-3
Rrp (29, 2, 28)	164.13405	3	Qr- (32, 3, -)	191.48205	-2	Prp (61, 3, 58)	146.38971	-5	Rr- (14, 3, -)	202.62246	3
Rrp (30, 2, 29)	164.85857	4	Qr- (33, 3, -)	191.46975	-2	Prp (60, 3, 57)	147.14104	-7	Rr- (15, 3, -)	203.34894	-3
Rrp (31, 2, 30)	165.58283	6	Qr- (34, 3, -)	191.45708	-1	Prp (59, 3, 56)	147.89204	-12	Rr- (16, 3, -)	204.07506	-4
Rrp (32, 2, 31)	166.30681	5	Qr- (35, 3, -)	191.44401	0	Prp (58, 3, 55)	148.64275	-17	Rr- (17, 3, -)	204.80077	-4
Rrp (33, 2, 32)	167.03054	4	Qr- (36, 3, -)	191.43057	3	Prp (57, 3, 54)	149.39330	-9	Rr- (18, 3, -)	205.52609	-1
Rrp (34, 2, 33)	167.75404	6	Qr- (37, 3, -)	191.41669	1	Prp (56, 3, 53)	150.14328	-28	Rr- (19, 3, -)	206.25093	-4
Rrp (35, 2, 34)	168.47731	8	Qr- (38, 3, -)	191.40248	6	Prp (55, 3, 52)	150.89316	-29	Rr- (20, 3, -)	206.97538	-3
Rrp (36, 2, 35)	169.20036	12	Qr- (39, 3, -)	191.38780	4	Prp (54, 3, 51)	151.64272	-33	Rr- (21, 3, -)	207.69939	-2
Rrp (37, 2, 36)	169.92309	9	Qr- (40, 3, -)	191.37277	6	Pr- (53, 3, -)	152.39244	8	Rr- (22, 3, -)	208.42304	5
Rrp (38, 2, 37)	170.64554	1	Qr- (41, 3, -)	191.35734	9	Pr- (52, 3, -)	153.14207	69	Rr- (23, 3, -)	209.14607	-5
Rrp (39, 2, 38)	171.36810	25	Qr- (42, 3, -)	191.34150	11	Pr- (51, 3, -)	153.89055	44	Rr- (24, 3, -)	209.86878	-3
Rrp (40, 2, 39)	172.09004	11	Qr- (43, 3, -)	191.32525	12	Pr- (50, 3, -)	154.63894	38	Rr- (25, 3, -)	210.59103	-2
Rrp (41, 2, 40)	172.81192	12	Qr- (44, 3, -)	191.30862	18	Pr- (49, 3, -)	155.38706	34	Rr- (26, 3, -)	211.31281	-3
Rrp (42, 2, 41)	173.53358	14	Qr- (45, 3, -)	191.29150	14	Pr- (48, 3, -)	156.13489	30	Rr- (27, 3, -)	212.03417	-1
Rrp (43, 2, 42)	174.25505	16	Qr- (46, 3, -)	191.27415	29	Pr- (47, 3, -)	156.88239	22	Rr- (28, 3, -)	212.75533	26
Rrp (44, 2, 43)	174.97631	18	Qr- (47, 3, -)	191.25627	33	Pr- (46, 3, -)	157.62965	18	Rr- (29, 3, -)	213.47526	-21
Rrp (45, 2, 44)	175.69734	16	Qr- (48, 3, -)	191.23795	34	Pr- (45, 3, -)	158.37666	18	Rr- (30, 3, -)	214.19543	1
Rrp (46, 2, 45)	176.41824	20	Qr- (49, 3, -)	191.21913	26	Pr- (44, 3, -)	159.12336	16	Rr- (31, 3, -)	214.91490	0
Rrp (47, 2, 46)	177.13909	38	Qr- (50, 3, -)	191.20033	65	Pr- (43, 3, -)	159.86974	11	Rr- (32, 3, -)	215.63392	1
Rrp (48, 2, 47)	177.85939	18	Qr- (51, 3, -)	191.18062	53	Pr- (42, 3, -)	160.61584	7	Rr- (33, 3, -)	216.35245	2
Rrp (49, 2, 48)	178.57980	26	Qr- (52, 3, -)	191.16057	51	Pr- (41, 3, -)	161.36169	7	Rr- (34, 3, -)	217.07052	4
Rrp (50, 2, 49)	179.29993	24	Qr- (53, 3, -)	191.13999	41	Pr- (40, 3, -)	162.10723	4	Rr- (35, 3, -)	217.78807	4
Rrp (51, 2, 50)	180.01994	24	Qrp (54, 3, 51)	191.11893	25	Pr- (39, 3, -)	162.85247	1	Rr- (36, 3, -)	218.50514	5
Rrp (52, 2, 51)	180.73980	25	Qrp (55, 3, 52)	191.09688	-46	Pr- (38, 3, -)	163.59746	2	Rr- (37, 3, -)	219.22171	5
Rrp (53, 2, 52)	181.45947	21	Qrp (56, 3, 53)	191.07546	-10	Pr- (37, 3, -)	164.34212	-1	Rr- (38, 3, -)	219.93780	7
Rrp (54, 2, 53)	182.17904	20	Qrp (57, 3, 54)	191.05293	-41	Pr- (36, 3, -)	165.08653	1	Rr- (39, 3, -)	220.65338	10
Rrp (55, 2, 54)	182.89846	17	Qrp (58, 3, 55)	191.03055	-12	Pr- (35, 3, -)	165.83061	-1	Rr- (40, 3, -)	221.36831	-2
Rrp (56, 2, 55)	183.61782	20	Qrp (59, 3, 56)	191.00752	-2	Pr- (34, 3, -)	166.57441	-2	Rr- (41, 3, -)	222.08300	12
Rrp (57, 2, 56)	184.33697	12	Qrp (60, 3, 57)	190.98382	-14	Pr- (33, 3, -)	167.31791	-2	Rr- (42, 3, -)	222.79704	16
Rrp (58, 2, 57)	185.05611	14	Qrp (61, 3, 58)	190.95992	1	Pr- (32, 3, -)	168.06114	0	Rr- (43, 3, -)	223.51047	10
Rrp (59, 2, 58)	185.77511	12	Qrp (62, 3, 59)	190.93523	-18	Pr- (31, 3, -)	168.80403	-3	Rr- (44, 3, -)	224.22356	24
Rrp (60, 2, 59)	186.49420	25	Qrp (63, 3, 60)	190.91052	9	Pr- (30, 3, -)	169.54666	-1	Rr- (45, 3, -)	224.93600	25
Rrp (61, 2, 60)	187.21295	14	Qrp (64, 3, 61)	190.88512	14	Pr- (29, 3, -)	170.28900	2	Rr- (46, 3, -)	225.64796	33
Rrp (62, 2, 61)	187.93167	5				Pr- (28, 3, -)	171.03094	-4	Rr- (47, 3, -)	226.35932	36
Rrp (63, 2, 62)	188.65031	-6	Qr- (36, 3, -)	191.43057	-3	Pr- (27, 3, -)	171.77264	-5	Rr- (48, 3, -)	227.07015	40
Rrp (64, 2, 63)	189.36913	6	Qr- (37, 3, -)	191.41669	-7	Pr- (26, 3, -)	172.51406	-2	Rr- (49, 3, -)	227.78052	53
Rrp (65, 2, 64)	190.08771	-4	Qr- (38, 3, -)	191.40248	-5	Pr- (25, 3, -)	173.25515	-2	Rr- (50, 3, -)	228.49014	50
Rrp (66, 2, 65)	190.80626	-14	Qr- (39, 3, -)	191.38780	-10	Pr- (24, 3, -)	173.99592	-3	Rr- (51, 3, -)	229.19929	55
Rrp (67, 2, 66)	191.52461	-42	Qr- (40, 3, -)	191.37277	-11	Pr- (23, 3, -)	174.73640	-2	Rr- (52, 3, -)	229.90782	55
Rrp (68, 2, 67)	192.24418	51	Qr- (41, 3, -)	191.35734	-12	Pr- (22, 3, -)	175.47656	-1	Rr- (53, 3, -)	230.61583	62
Rrp (69, 2, 68)	192.96188	-43	Qr- (42, 3, -)	191.34150	-15	Pr- (21, 3, -)	176.21639	-3	Rr- (54, 3, -)	231.32291	33
			Qr- (43, 3, -)	191.32525	-18	Pr- (20, 3, -)	176.95601	7	Rrr (55, 3, 52)	232.02960	25
Qr- (5, 3, -)	191.67156	28	Qr- (44, 3, -)	191.30862	-20	Pr- (19, 3, -)	177.69510	-5	Rrr (56, 3, 53)	232.73569	17
Qr- (6, 3, -)	191.66919	10	Qr- (45, 3, -)	191.29150	-31	Pr- (18, 3, -)	178.43392	-11	Rrr (57, 3, 54)	233.44124	15
Qr- (7, 3, -)	191.66655	2	Qr- (46, 3, -)	191.27415	-24	Pr- (17, 3, -)	179.17257	-3	Rrr (58, 3, 55)	234.14619	15
Qr- (8, 3, -)	191.66362	2	Qr- (47, 3, -)	191.25627	-30	Pr- (16, 3, -)	179.91083	-1	Rrr (59, 3, 56)	234.85080	41
Qr- (9, 3, -)	191.66030	-1	Qr- (48, 3, -)	191.23795	-40	Pr- (15, 3, -)	180.64874	-1	Rrr (60, 3, 57)	235.55404	-7
Qr- (10, 3, -)	191.65666	1	Qr- (49, 3, -)	191.21913	-59	Pr- (14, 3, -)	181.38618	-16	Rrr (61, 3, 58)	236.25638	-82
Qr- (11, 3, -)	191.65257	-6	Qr- (50, 3, -)	191.20033	-35	Pr- (13, 3, -)	182.12358	-1	Rrr (62, 3, 59)	236.96004	39
Qr- (12, 3, -)	191.64820	-3	Qr- (51, 3, -)	191.18062	-61	Pr- (12, 3, -)	182.86049	-2	Rrr (63, 3, 60)	237.66171	25
Qr- (13, 3, -)	191.64349	2	Qr- (52, 3, -)	191.16057	-80	Pr- (11, 3, -)	183.59708	-2	Rrr (64, 3, 61)	238.36297	35
Qr- (14, 3, -)	191.63833	-1	Qrp (55, 3, 53)	191.09944	14	Pr- (10, 3, -)	184.33335	0			
Qr- (15, 3, -)	191.63280	-4	Qrp (56, 3, 54)	191.07801	23	Pr- (9, 3, -)	185.06924	-2	Prn (62, 3, 60)	145.64251	-2
Qr- (16, 3, -)	191.62699	2	Qrp (57, 3, 55)	191.05622	38	Pr- (8, 3, -)	185.80482	-1	Prn (61, 3, 59)	146.39403	31

The first term $E_0(K)$ represents the energy contribution of the K rotation. $B(K)$ is the effective rotational constant, $D(K)$, $H(K)$, and $L(K)$ are effective centrifugal distortion parameters. γ indicates upper (U) and lower (L) components, if K-type splitting is observed. The results of the analysis are collected in Tables II to IV for HNCO, DNCO, and $HN^{13}CO$, respectively.

The measured frequencies for the main isotopomer are listed in Table V for the a-type transitions with FTIR, in Table VI for b-type transitions with FTIR, and in Table VII for the sub-mmW data. In each case, the observed − calculated values listed are those obtained by the fits based on the linear molecule Hamiltonian given above. For

TABLE VI—*Continued*

Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ
Prn (60, 3, 58)	147.14462	-3	Qr- (20, 4, -)	236.80803	-6	Pr- (41, 4, -)	206.49671	-6	Rr- (36, 4, -)	263.62763	5
Prn (59, 3, 57)	147.89522	-10	Qr- (21, 4, -)	236.79719	-5	Pr- (40, 4, -)	207.24757	-4	Rr- (37, 4, -)	264.33837	5
Prn (58, 3, 56)	148.64566	-7	Qr- (22, 4, -)	236.78584	-4	Pr- (39, 4, -)	207.99800	-4	Rr- (38, 4, -)	265.04849	6
Prn (57, 3, 55)	149.39602	12	Qr- (23, 4, -)	236.77396	-3	Pr- (38, 4, -)	208.74799	-6	Rr- (39, 4, -)	265.75798	6
Prn (56, 3, 54)	150.14590	12	Qr- (24, 4, -)	236.76155	-4	Pr- (37, 4, -)	209.49748	-17	Rr- (40, 4, -)	266.46684	8
Prn (55, 3, 53)	150.89560	19	Qr- (25, 4, -)	236.74861	-5	Pr- (36, 4, -)	210.24678	-4	Rr- (41, 4, -)	267.17505	7
Prn (54, 3, 52)	151.64491	14	Qr- (26, 4, -)	236.73518	-4	Pr- (35, 4, -)	210.99555	-3	Rr- (42, 4, -)	267.88265	10
Pr- (52, 3, -)	153.14207	-63	Qr- (27, 4, -)	236.72124	-2	Pr- (34, 4, -)	211.74388	-3	Rr- (43, 4, -)	268.58956	8
Pr- (51, 3, -)	153.89055	-71	Qr- (28, 4, -)	236.70675	-3	Pr- (33, 4, -)	212.49180	-2	Rr- (44, 4, -)	269.29585	9
Pr- (50, 3, -)	154.63894	-62	Qr- (29, 4, -)	236.69175	-3	Pr- (32, 4, -)	213.23927	-2	Rr- (45, 4, -)	270.00151	12
Pr- (49, 3, -)	155.38706	-51	Qr- (30, 4, -)	236.67625	-1	Pr- (31, 4, -)	213.98630	-3	Rr- (46, 4, -)	270.70648	10
Pr- (48, 3, -)	156.13489	-44	Qr- (31, 4, -)	236.66022	0	Pr- (30, 4, -)	214.73293	-1	Rr- (47, 4, -)	271.41084	14
Pr- (47, 3, -)	156.88239	-41	Qr- (32, 4, -)	236.64364	-1	Pr- (29, 4, -)	215.47907	-5	Rr- (48, 4, -)	272.11449	12
Pr- (46, 3, -)	157.62965	-36	Qr- (33, 4, -)	236.62657	0	Pr- (28, 4, -)	216.22481	-4	Rr- (49, 4, -)	272.81753	15
Pr- (45, 3, -)	158.37666	-26	Qr- (34, 4, -)	236.60896	-1	Pr- (27, 4, -)	216.97011	-3	Rr- (50, 4, -)	273.51997	24
Pr- (44, 3, -)	159.12336	-22	Qr- (35, 4, -)	236.59083	-1	Pr- (26, 4, -)	217.71495	-4	Rr- (51, 4, -)	274.22154	12
Pr- (43, 3, -)	159.86974	-20	Qr- (36, 4, -)	236.57219	-1	Pr- (25, 4, -)	218.45935	-4	Rr- (52, 4, -)	274.92255	12
Pr- (42, 3, -)	160.61584	-19	Qr- (37, 4, -)	236.55302	-1	Pr- (24, 4, -)	219.20329	-5	Rr- (53, 4, -)	275.62289	12
Pr- (41, 3, -)	161.36169	-14	Qr- (38, 4, -)	236.53335	1	Pr- (23, 4, -)	219.94680	-3	Rr- (54, 4, -)	276.32256	14
Pr- (40, 3, -)	162.10723	-12	Qr- (39, 4, -)	236.51313	0	Pr- (22, 4, -)	220.68985	-3	Rr- (55, 4, -)	277.02178	38
Pr- (39, 3, -)	162.85247	-12	Qr- (40, 4, -)	236.49239	-1	Pr- (21, 4, -)	221.43230	-16	Rr- (56, 4, -)	277.71983	12
Pr- (38, 3, -)	163.59746	-8	Qr- (41, 4, -)	236.47119	5	Pr- (20, 4, -)	222.17463	4	Rr- (57, 4, -)	278.41745	12
Pr- (37, 3, -)	164.34212	-9	Qr- (42, 4, -)	236.44944	8	Pr- (19, 4, -)	222.91622	-3	Rr- (58, 4, -)	279.11436	11
Pr- (36, 3, -)	165.08653	-5	Qr- (43, 4, -)	236.42709	3	Pr- (18, 4, -)	223.65742	-3	Rr- (59, 4, -)	279.81066	17
			Qr- (44, 4, -)	236.40408	-15	Pr- (17, 4, -)	224.39816	-2	Rr- (60, 4, -)	280.50633	29
Rr- (36, 3, -)	218.50514	-1	Qr- (45, 4, -)	236.38104	16	Pr- (16, 4, -)	225.13828	-16	Rr- (61, 4, -)	281.20109	20
Rr- (37, 3, -)	219.22171	-3	Qr- (46, 4, -)	236.35708	8	Pr- (15, 4, -)	225.87788	-35	Rr- (62, 4, -)	281.89569	65
Rr- (38, 3, -)	219.93780	-3	Qr- (47, 4, -)	236.33269	8	Pr- (14, 4, -)	226.61752	-2	Rr- (63, 4, -)	282.58863	12
Rr- (39, 3, -)	220.65338	-4	Qr- (48, 4, -)	236.30770	2	Pr- (13, 4, -)	227.35636	-2	Rr- (64, 4, -)	283.28159	34
Rr- (40, 3, -)	221.36831	-19	Qr- (49, 4, -)	236.28221	-3	Pr- (12, 4, -)	228.09472	-1	Rr- (66, 4, -)	284.66477	15
Rr- (41, 3, -)	222.08300	-8	Qr- (50, 4, -)	236.25638	12	Pr- (11, 4, -)	228.83259	-1	Rr- (67, 4, -)	285.35567	43
Rr- (42, 3, -)	222.79704	-10	Qr- (51, 4, -)	236.22987	10	Pr- (10, 4, -)	229.56996	-3			
Rr- (43, 3, -)	223.51047	-21	Qr- (52, 4, -)	236.20276	1	Pr- (9, 4, -)	230.30686	-2	Qr- (6, 5, -)	278.59384	22
Rr- (44, 3, -)	224.22356	-14	Qr- (53, 4, -)	236.17519	-1	Pr- (8, 4, -)	231.04327	-2	Qr- (7, 5, -)	278.58780	24
Rr- (45, 3, -)	224.93600	-20	Qr- (54, 4, -)	236.14714	2	Pr- (7, 4, -)	231.77921	1	Qr- (8, 5, -)	278.58085	21
Rr- (46, 3, -)	225.64796	-20	Qr- (55, 4, -)	236.11853	0	Pr- (6, 4, -)	232.51463	2	Qr- (9, 5, -)	278.57301	16
Rr- (47, 3, -)	226.35932	-28	Qr- (56, 4, -)	236.08933	-7				Qr- (10, 5, -)	278.56432	12
Rr- (48, 3, -)	227.07015	-34	Qr- (57, 4, -)	236.05979	4	Rr- (4, 4, -)	240.57054	-5	Qr- (11, 5, -)	278.55481	12
Rr- (49, 3, -)	227.78052	-32	Qr- (58, 4, -)	236.02957	0	Rr- (5, 4, -)	241.29978	-5	Qr- (12, 5, -)	278.54439	6
Rr- (50, 3, -)	228.49014	-50	Qr- (59, 4, -)	235.99889	2	Rr- (6, 4, -)	242.02850	-4	Qr- (13, 5, -)	278.53313	3
Rr- (51, 3, -)	229.19929	-60	Qr- (60, 4, -)	235.96764	0	Rr- (7, 4, -)	242.75664	-7	Qr- (15, 5, -)	278.50818	9
Rr- (52, 3, -)	229.90782	-77	Qr- (61, 4, -)	235.93587	-2	Rr- (8, 4, -)	243.48428	-6	Qr- (16, 5, -)	278.49432	2
Rr- (53, 3, -)	230.61583	-90	Qr- (62, 4, -)	235.90362	1	Rr- (9, 4, -)	244.21132	-11	Qr- (17, 5, -)	278.47965	-2
Rrp (55, 3, 53)	232.03144	14	Qr- (63, 4, -)	235.87063	-17	Rr- (10, 4, -)	244.93794	-4	Qr- (18, 5, -)	278.46416	-3
Rrp (56, 3, 54)	232.73808	35	Qr- (64, 4, -)	235.83739	-8	Rr- (11, 4, -)	245.66391	-7	Qr- (19, 5, -)	278.44778	-8
Rrp (57, 3, 55)	233.44397	38	Qr- (65, 4, -)	235.80370	9	Rr- (12, 4, -)	246.38938	-5	Qr- (20, 5, -)	278.43058	-11
Rrp (58, 3, 56)	234.14921	35	Qr- (66, 4, -)	235.76927	5	Rr- (13, 4, -)	247.11427	-5	Qr- (21, 5, -)	278.41262	-6
Rrp (59, 3, 57)	234.85389	34				Rr- (14, 4, -)	247.83863	-3	Qr- (22, 5, -)	278.39370	-12
Rrp (60, 3, 58)	235.55789	24	Pr- (63, 4, -)	189.87958	22	Rr- (15, 4, -)	248.56239	-6	Qr- (23, 5, -)	278.37397	-18
Rrp (61, 3, 59)	236.26094	-21	Pr- (62, 4, -)	190.63844	-16	Rr- (16, 4, -)	249.28562	-5	Qr- (24, 5, -)	278.35351	-12
Rrp (62, 3, 60)	236.96433	26	Pr- (61, 4, -)	191.39746	-3	Rr- (17, 4, -)	250.00827	-5	Qr- (25, 5, -)	278.33210	-18
Rrp (63, 3, 61)	237.66670	34	Pr- (60, 4, -)	192.15580	-22	Rr- (18, 4, -)	250.73037	-4	Qr- (26, 5, -)	278.30992	-19
Rrp (64, 3, 62)	238.36831	25	Pr- (59, 4, -)	192.91404	-16	Rr- (19, 4, -)	251.45189	-4	Qr- (27, 5, -)	278.28689	-23
			Pr- (57, 4, -)	194.42918	-26	Rr- (20, 4, -)	252.17278	-10	Qr- (28, 5, -)	278.26267	-64
Qr- (5, 4, -)	236.90877	0	Pr- (56, 4, -)	195.18646	-7	Rr- (21, 4, -)	252.89322	-3	Qr- (29, 5, -)	278.23860	-8
Qr- (6, 4, -)	236.90566	-1	Pr- (55, 4, -)	195.94312	-11	Rr- (22, 4, -)	253.61303	0	Qr- (30, 5, -)	278.21309	-15
Qr- (7, 4, -)	236.90199	-7	Pr- (54, 4, -)	196.69951	-6	Rr- (23, 4, -)	254.33239	15	Qr- (31, 5, -)	278.18684	-15
Qr- (8, 4, -)	236.89788	-5	Pr- (53, 4, -)	197.45543	-9	Rr- (24, 4, -)	255.05085	-1	Qr- (32, 5, -)	278.15980	-14
Qr- (9, 4, -)	236.89324	-5	Pr- (52, 4, -)	198.21095	-15	Rr- (25, 4, -)	255.76888	-2	Qr- (33, 5, -)	278.13197	-11
Qr- (10, 4, -)	236.88810	-3	Pr- (51, 4, -)	198.96620	-10	Rr- (26, 4, -)	256.48634	0	Qr- (34, 5, -)	278.10331	-12
Qr- (11, 4, -)	236.88236	-9	Pr- (50, 4, -)	199.72101	-11	Rr- (27, 4, -)	257.20319	0	Qr- (35, 5, -)	278.07389	-10
Qr- (12, 4, -)	236.87620	-6	Pr- (49, 4, -)	200.47534	-21	Rr- (28, 4, -)	257.91944	0	Qr- (36, 5, -)	278.04338	-39
Qr- (13, 4, -)	236.86950	-5	Pr- (48, 4, -)	201.22948	-11	Rr- (29, 4, -)	258.63511	2	Qr- (37, 5, -)	278.01268	-7
Qr- (14, 4, -)	236.86228	-4	Pr- (47, 4, -)	201.98317	-6	Rr- (30, 4, -)	259.35009	-5	Qr- (38, 5, -)	277.98091	-5
Qr- (15, 4, -)	236.85452	-6	Pr- (46, 4, -)	202.73636	-12	Rr- (31, 4, -)	260.06447	-11	Qr- (39, 5, -)	277.94836	-4
Qr- (16, 4, -)	236.84625	-6	Pr- (45, 4, -)	203.48929	-6	Rr- (32, 4, -)	260.77844	3	Qr- (40, 5, -)	277.91504	-3
Qr- (17, 4, -)	236.83750	-4	Pr- (44, 4, -)	204.24176	-5	Rr- (33, 4, -)	261.49168	5	Qr- (41, 5, -)	277.88078	-19
Qr- (18, 4, -)	236.82821	-3	Pr- (43, 4, -)	204.99384	-3	Rr- (34, 4, -)	262.20431	8	Qr- (42, 5, -)	277.84616	4
Qr- (19, 4, -)	236.81837	-6	Pr- (42, 4, -)	205.74546	-6	Rr- (35, 4, -)	262.91630	8	Qr- (43, 5, -)	277.81053	2

the other isotopomers, a corresponding list may be obtained from the authors upon request.

V. CENTRIFUGAL DISTORTION RESONANCE

The difficulties in fitting the higher *b*-type transitions ${}^{r}X_6$ and ${}^{r}X_7$ with the Watson-type Hamiltonian can be understood by the extremely large and anomalous centrifugal distortion parameters of the $K_a = 7$ level obtained by the linear

TABLE VI—*Continued*

Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ	Transition	Freq.	Δ
Qr- {44, 5, -}	277.77424	8	Rr- {5, 5, -}	282.98491	22	Qr- {17, 6, -}	316.71908	-36	Pr- {13, 6, -}	307.55141	-9
Qr- {45, 5, -}	277.73717	11	Rr- {6, 5, -}	283.71065	22	Qr- {18, 6, -}	316.64148	-28	Pr- {12, 6, -}	308.33729	-6
Qr- {46, 5, -}	277.69938	15	Rr- {7, 5, -}	284.43544	16	Qr- {19, 6, -}	316.56054	-22	Pr- {11, 6, -}	309.11916	12
Qr- {47, 5, -}	277.66083	16	Rr- {8, 5, -}	285.15944	18	Qr- {20, 6, -}	316.47641	-15	Pr- {10, 6, -}	309.89669	20
Qr- {48, 5, -}	277.62160	22	Rr- {9, 5, -}	285.88250	16	Qr- {21, 6, -}	316.38921	-10	Pr- {9, 6, -}	310.66984	25
Qr- {49, 5, -}	277.58158	20	Rr- {10, 5, -}	286.60460	6	Qr- {22, 6, -}	316.29912	-3			
Qr- {50, 5, -}	277.54082	16	Rr- {11, 5, -}	287.32594	9	Qr- {23, 6, -}	316.20633	14	Rr- {6, 6, -}	322.40334	58
Qr- {51, 5, -}	277.49943	20	Rr- {12, 5, -}	288.04634	7	Qr- {24, 6, -}	316.11081	23	Rr- {7, 6, -}	323.09631	39
Qr- {52, 5, -}	277.45736	25	Rr- {13, 5, -}	288.76588	8	Qr- {25, 6, -}	316.01265	20	Rr- {8, 6, -}	323.78487	26
Qr- {53, 5, -}	277.41447	18	Rr- {14, 5, -}	289.48448	5	Qr- {26, 6, -}	315.91216	24	Rr- {9, 6, -}	324.46895	7
Qr- {54, 5, -}	277.37096	17	Rr- {15, 5, -}	290.20220	2	Qr- {27, 6, -}	315.80941	29	Rr- {10, 6, -}	325.14880	-5
Qr- {55, 5, -}	277.32675	14	Rr- {16, 5, -}	290.91900	-2	Qr- {28, 6, -}	315.70449	33	Rr- {11, 6, -}	325.82445	-16
Qr- {56, 5, -}	277.28182	7	Rr- {17, 5, -}	291.63496	-2	Qr- {29, 6, -}	315.59747	31	Rr- {12, 6, -}	326.49604	-22
Qr- {57, 5, -}	277.23623	0	Rr- {18, 5, -}	292.35001	-2	Qr- {30, 6, -}	315.48838	14	Rr- {13, 6, -}	327.16366	-26
Qr- {58, 5, -}	277.19001	-4	Rr- {19, 5, -}	293.06416	-3	Qr- {31, 6, -}	315.37771	22	Rr- {14, 6, -}	327.82738	-34
Qr- {59, 5, -}	277.14311	-11	Rr- {20, 5, -}	293.77741	-5	Qr- {32, 6, -}	315.26511	9	Rr- {15, 6, -}	328.48740	-35
Qr- {60, 5, -}	277.09542	-32	Rr- {21, 5, -}	294.48978	-5	Qr- {33, 6, -}	315.15099	7	Rr- {16, 6, -}	329.14380	-36
Qr- {61, 5, -}	277.04718	-45	Rr- {22, 5, -}	295.20122	-8	Qr- {34, 6, -}	315.03524	-5	Rr- {17, 6, -}	329.79676	-31
Qr- {62, 5, -}	276.99837	-52	Rr- {23, 5, -}	295.91180	-8	Qr- {35, 6, -}	314.91806	-15	Rr- {18, 6, -}	330.44646	-14
Qr- {63, 5, -}	276.94887	-67	Rr- {24, 5, -}	296.62145	-11	Qr- {36, 6, -}	314.79948	-28	Rr- {19, 6, -}	331.09278	-12
			Rr- {25, 5, -}	297.33023	-12	Qr- {37, 6, -}	314.67976	-25	Rr- {20, 6, -}	331.73603	-5
Pr- {53, 5, -}	238.73727	-16	Rr- {26, 5, -}	298.03815	-9	Qr- {38, 6, -}	314.55872	-34	Rr- {21, 6, -}	332.37626	-4
Pr- {52, 5, -}	239.50767	8	Rr- {27, 5, -}	298.74509	-15	Qr- {39, 6, -}	314.43667	-28	Rr- {22, 6, -}	333.01373	7
Pr- {51, 5, -}	240.27725	6	Rr- {28, 5, -}	299.45125	-9	Qr- {40, 6, -}	314.31353	-25	Rr- {23, 6, -}	333.64848	16
Pr- {50, 5, -}	241.04630	7	Rr- {29, 5, -}	300.15649	-6	Qr- {41, 6, -}	314.18942	-19	Rr- {24, 6, -}	334.28065	26
Pr- {49, 5, -}	241.81463	-6	Rr- {30, 5, -}	300.86080	-7	Qr- {42, 6, -}	314.06449	-3	Rr- {25, 6, -}	334.91030	32
Pr- {48, 5, -}	242.58268	11	Rr- {31, 5, -}	301.56422	-8	Qr- {43, 6, -}	313.93879	21	Rr- {26, 6, -}	335.53756	32
Pr- {47, 5, -}	243.34988	2	Rr- {32, 5, -}	302.26683	-1	Qr- {44, 6, -}	313.81217	28	Rr- {27, 6, -}	336.16268	41
Pr- {46, 5, -}	244.11645	-10	Rr- {33, 5, -}	302.96855	6	Qr- {45, 6, -}	313.68500	46	Rr- {28, 6, -}	336.78559	40
Pr- {45, 5, -}	244.88262	-1	Rr- {34, 5, -}	303.66919	-7	Qr- {46, 6, -}	313.55704	40	Rr- {29, 6, -}	337.40645	34
Pr- {44, 5, -}	245.64805	-4	Rr- {35, 5, -}	304.36898	-16	Qr- {47, 6, -}	313.42866	35	Rr- {30, 6, -}	338.02542	30
Pr- {43, 5, -}	246.41286	-7	Rr- {36, 5, -}	305.06814	0	Qr- {48, 6, -}	313.29967	-3	Rr- {31, 6, -}	338.64253	20
Pr- {42, 5, -}	247.17717	3	Rr- {37, 5, -}	305.76629	3	Qr- {49, 6, -}	313.17024	-73	Rr- {32, 6, -}	339.25801	18
Pr- {41, 5, -}	247.94052	-18	Rr- {38, 5, -}	306.46360	11				Rr- {34, 6, -}	340.48387	-16
Pr- {40, 5, -}	248.70349	-12	Rr- {39, 5, -}	307.15995	9	Pr- {49, 6, -}	277.53248	-53	Rr- {35, 6, -}	341.09478	-12
Pr- {39, 5, -}	249.46572	-15	Rr- {40, 5, -}	307.85546	12	Pr- {47, 6, -}	279.24602	19	Rr- {36, 6, -}	341.70421	-18
Pr- {38, 5, -}	250.22733	-12	Rr- {41, 5, -}	308.55015	19	Pr- {46, 6, -}	280.10166	-20	Rr- {37, 6, -}	342.31233	-23
Pr- {37, 5, -}	250.98823	-15	Rr- {42, 5, -}	309.24385	15	Pr- {45, 6, -}	280.95752	6	Rr- {38, 6, -}	342.91932	-16
Pr- {36, 5, -}	251.74816	-46	Rr- {43, 5, -}	309.93681	23	Pr- {44, 6, -}	281.81247	-4	Rr- {39, 6, -}	343.52504	-19
Pr- {35, 5, -}	252.50795	-22	Rr- {44, 5, -}	310.62883	24	Pr- {43, 6, -}	282.66672	-21	Rr- {40, 6, -}	344.12989	1
Pr- {34, 5, -}	253.26681	-22	Rr- {45, 5, -}	311.32006	31	Pr- {42, 6, -}	283.52022	-41	Rr- {41, 6, -}	344.73367	17
Pr- {33, 5, -}	254.02493	-25	Rr- {46, 5, -}	312.01030	25	Pr- {41, 6, -}	284.37318	-33	Rr- {42, 6, -}	345.33633	17
Pr- {32, 5, -}	254.78247	-16	Rr- {47, 5, -}	312.69983	35	Pr- {40, 6, -}	285.22513	-37	Rr- {43, 6, -}	345.93839	43
Pr- {31, 5, -}	255.53915	-21	Rr- {48, 5, -}	313.38844	37	Pr- {39, 6, -}	286.07602	-51	Rr- {44, 6, -}	346.53944	46
Pr- {30, 5, -}	256.29518	-19	Rr- {49, 5, -}	314.07510	-71	Pr- {38, 6, -}	286.92605	-46	Rr- {45, 6, -}	347.13992	60
Pr- {29, 5, -}	257.05045	-20	Rr- {50, 5, -}	314.76315	45	Pr- {37, 6, -}	287.77503	-35	Rr- {46, 6, -}	347.73976	64
Pr- {28, 5, -}	257.80502	-17	Rr- {51, 5, -}	315.44913	38	Pr- {36, 6, -}	288.62278	-28	Rr- {47, 6, -}	348.33877	25
Pr- {27, 5, -}	258.55880	-19	Rr- {52, 5, -}	316.13439	42	Pr- {35, 6, -}	289.46932	-15	Rr- {48, 6, -}	348.93711	-53
Pr- {26, 5, -}	259.31190	-15	Rr- {53, 5, -}	316.81875	40	Pr- {34, 6, -}	290.31444	-8			
Pr- {25, 5, -}	260.06447	12	Rr- {54, 5, -}	317.50220	30	Pr- {33, 6, -}	291.15830	18	Qr- {10, 7, -}	353.75707	-40
Pr- {24, 5, -}	260.81575	-15	Rr- {55, 5, -}	318.18494	31	Pr- {32, 6, -}	292.00034	16	Qr- {11, 7, -}	353.82727	-9
Pr- {23, 5, -}	261.56656	-11	Rr- {56, 5, -}	318.86691	38	Pr- {31, 6, -}	292.84081	21	Qr- {12, 7, -}	353.90296	-14
Pr- {22, 5, -}	262.31659	-9	Rr- {57, 5, -}	319.54768	6	Pr- {30, 6, -}	293.67956	26	Qr- {13, 7, -}	353.98466	8
Pr- {21, 5, -}	263.06584	-7	Rr- {58, 5, -}	320.22794	4	Pr- {29, 6, -}	294.51629	17	Qr- {14, 7, -}	354.07194	28
Pr- {20, 5, -}	263.81431	-4	Rr- {59, 5, -}	320.90751	15	Pr- {28, 6, -}	295.35126	25	Qr- {15, 7, -}	354.16444	22
Pr- {19, 5, -}	264.56199	-2	Rr- {60, 5, -}	321.58603	0	Pr- {27, 6, -}	296.18399	20	Qr- {16, 7, -}	354.26216	6
Pr- {18, 5, -}	265.30888	0	Rr- {61, 5, -}	322.26361	-29	Pr- {26, 6, -}	297.01455	16	Qr- {17, 7, -}	354.36534	17
Pr- {17, 5, -}	266.05498	3	Rr- {62, 5, -}	322.94074	-24	Pr- {25, 6, -}	297.84271	6	Qr- {18, 7, -}	354.47348	20
Pr- {16, 5, -}	266.80025	3				Pr- {24, 6, -}	298.66855	9	Qr- {20, 7, -}	354.70414	16
Pr- {15, 5, -}	267.54475	7	Qr- {7, 6, -}	317.28664	68	Pr- {23, 6, -}	299.49168	1	Qr- {21, 7, -}	354.82624	-3
Pr- {14, 5, -}	268.28843	10	Qr- {8, 6, -}	317.24866	46	Pr- {22, 6, -}	300.31205	-11	Qr- {22, 7, -}	354.95286	-10
Pr- {13, 5, -}	269.03128	12	Qr- {9, 6, -}	317.20625	26	Pr- {21, 6, -}	301.12960	-19	Qr- {23, 7, -}	355.08377	-14
Pr- {12, 5, -}	269.77332	15	Qr- {10, 6, -}	317.15952	14	Pr- {20, 6, -}	301.94420	-22	Qr- {24, 7, -}	355.21888	-8
Pr- {11, 5, -}	270.51454	19	Qr- {11, 6, -}	317.10845	-6	Pr- {19, 6, -}	302.75556	-36	Qr- {25, 7, -}	355.35770	-25
Pr- {10, 5, -}	271.25511	40	Qr- {12, 6, -}	317.05333	-12	Pr- {18, 6, -}	303.56382	-32	Qr- {26, 7, -}	355.50055	-17
Pr- {9, 5, -}	271.99444	21	Qr- {13, 6, -}	316.99406	-25	Pr- {17, 6, -}	304.36898	3	Qr- {27, 7, -}	355.64701	-12
Pr- {8, 5, -}	272.73310	19	Qr- {14, 6, -}	316.93092	-31	Pr- {16, 6, -}	305.16993	-29	Qr- {28, 7, -}	355.79699	-2
Pr- {7, 5, -}	273.47102	25	Qr- {15, 6, -}	316.86399	-32	Pr- {15, 6, -}	305.96756	-25	Qr- {29, 7, -}	355.95061	38
			Qr- {16, 6, -}	316.79328	-39	Pr- {14, 6, -}	306.76144	-18			

molecule Hamiltonian; see Table II. This anomaly is caused by a centrifugal distortion resonance between the ground state and the lowest excited bending state. As can be seen from Fig. 4, the energy of the $K_a = 7$ level of the ground state is lower than that of the $K_a = 6$ level of the ν_5 bending excited state by less than 20 cm^{-1}. For the next higher pair of K_a levels, the situation is interchanged. The $K_a = 8$ ground state level is located higher in energy than the $K_a = 7$ level in the excited state by more than 60 cm^{-1}.

TABLE VII

Observed Submillimeter-Wave Transitions of HNCO in MHz[a,b]

Transition	Frequency	O–C	Transition	Frequency	O–C
Rqr(26,0,26)	593156.225	-17	Rqr(30,2,29)	680786.396	-4
Rqr(30,0,30)	680904.669	-2	Rqr(26,3,23)	592841.770	-4
Rqr(25,1,24)	573292.195	-2	Rqr(30,3,27)	680572.138	c
Rqr(26,1,25)	595320.089	-4	Rqr(26,3,24)	592841.770	4
Rqr(30,1,29)	683406.097	17	Rqr(30,3,28)	680572.138	c
Rqr(26,1,26)	591000.074	3	Rqr(26,4,–)	592542.209	-11
Rqr(30,1,30)	678450.395	5	Rqr(29,4,–)	658309.304	30
Rqr(26,2,24)	593100.383	-14	Rqr(30,4,–)	680226.749	-5
Rqr(30,2,28)	680886.583	4	Rqr(26,5,–)	592123.655	-5
Rqr(26,2,25)	593034.143	-6	Rqr(30,5,–)	679745.856	-1

a) For Notation see Table V.
b) See Table VI.
c) Not used in the fit.

The positions of the vibrational energy levels have been determined by analyzing the spectra measured in the present work, in which we have assigned the b-type rotational transitions arising from molecules in the bending excited states and several forbidden transitions between these vibrational states as well. The analysis of these data will be presented in a forthcoming paper.

As in the case of HNCS (*9*), the centrifugal–distortion resonance couples the ground state and the lowest excited bending state $v_5 = 1$ by the selection rule $\Delta K_a = \pm 1$. Following Urban and Yamada (*17*), the operator which represents the interaction is

$$\hat{H}_{12}^{(5)} = -\omega_5 q_5 C_5^{ab}[J_a, J_b]_+ = -\tfrac{1}{2}\omega_5 q_5 C_5^{ab}[\hat{J}_+ + \hat{J}_-, \hat{J}_a]_+, \tag{4}$$

where C_5^{ab} is a dimensionless parameter

$$C_5^{ab} = [4\pi^2 h/(\omega_5 c)]^{3/2} a_5^{ab}/(2I_a I_b), \tag{5}$$

and ω_5 is the wavenumber of the harmonic oscillation of the ν_5 mode. The standard second-order perturbation treatment of the $\hat{H}_{12}$ of Eq. (4) for deducing the effective rotational Hamiltonian, which assumes a good separation of the rotational and vibrational motion of a molecule, is not adequate for the present case. Because of the huge rotational constant A, the energy difference between the levels coupled by the interaction depends strongly on the quantum number K_a.

In the symmetric top approximation, the correction energy, $\Delta E_{cd}(J, K)$, due to the $H_{12}^{(5)}$ term in Eq. (4) for the rotational levels of the ground state, is thus calculated on the basis of harmonic-oscillator-symmetric-rotor wavefunctions (*16*) as

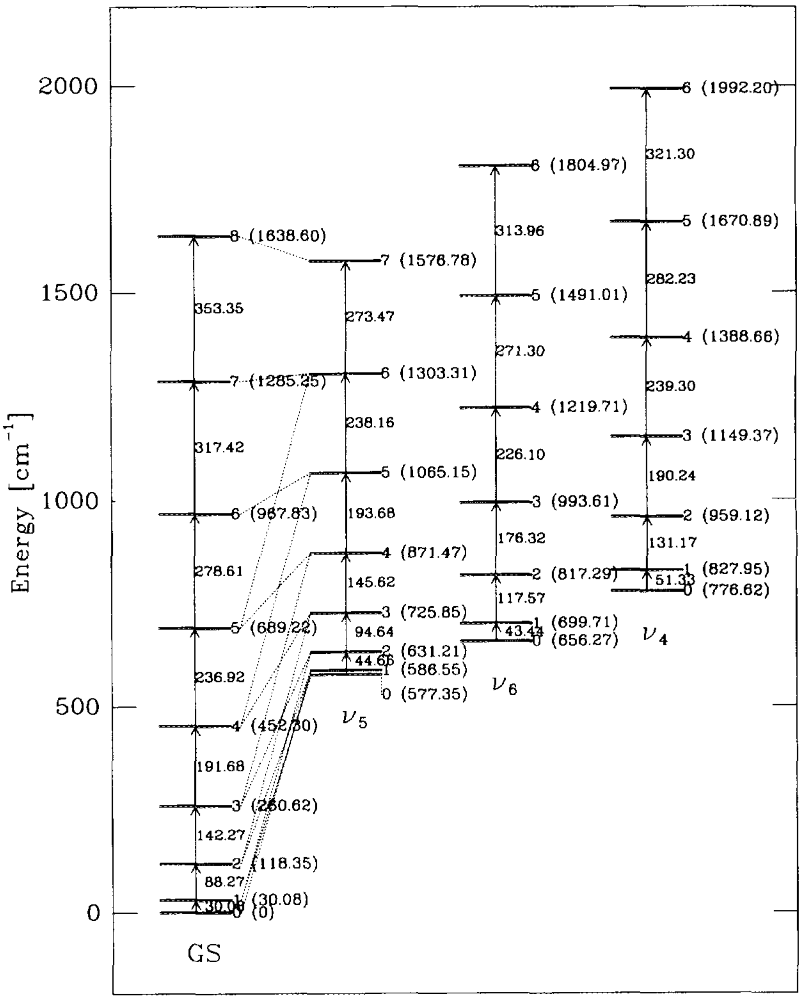

FIG. 4. The K_a rotational levels are plotted for the ground and the three lowest bending states. The near resonance condition can be seen for the ground state $K_a = 7$ level and the $v_5 = 1$ state $K_a = 6$ level. The dashed lines between the ground and the $v_5 = 1$ excited state indicate the resonances.

$$\Delta E_{cd}(J, K) = \langle v = 0; J, K|\hat{H}_{12}^{(5)}|v = 0; J, K\rangle$$
$$= \tfrac{1}{8}(\omega_5 C_5^{ab})^2\left\{\frac{(2K + 1)^2[J(J + 1) - K(K + 1)]}{E_0(J, K) - E_5(J, K + 1)} + \frac{(2K - 1)^2[J(J + 1) - K(K - 1)]}{E_0(J, K) - E_5(J, K - 1)}\right\}, \quad (6)$$

where $E_0(J, K) - E_5(J, K \pm 1)$ in the denominators are the energy differences between the interacting levels. In the equation above K represents K_a. With the second-order perturbation expression given above, we were able to explain the observed anomalies

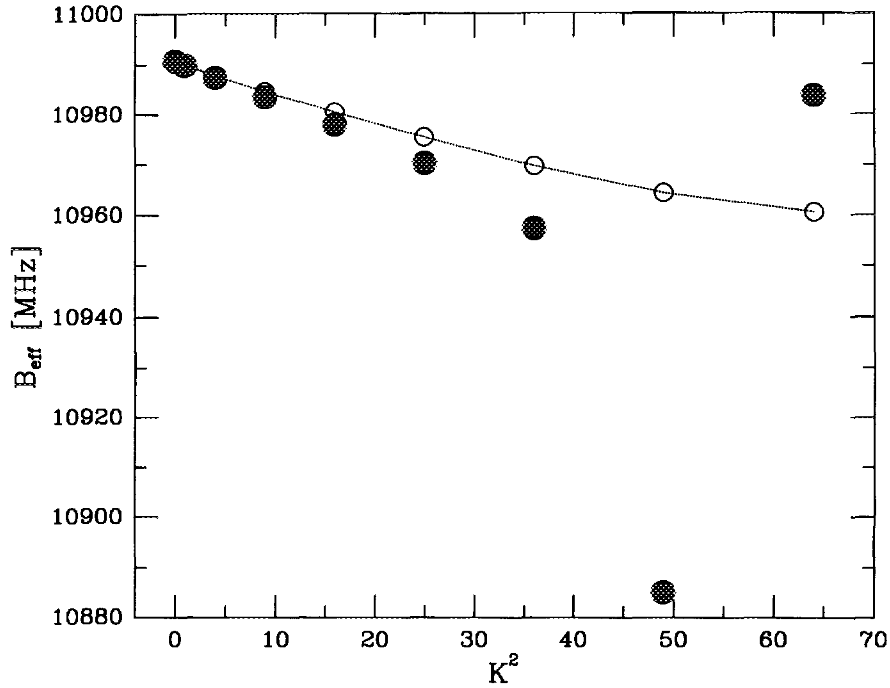

FIG. 5. The K_a dependence of the effective rotational constant $B(K)$ of HNCO is shown. The solid circles indicate the experimental values. For those substates, where the K-doubling has been observed, the average values for the two components are used in the plot. By removing the contribution from the centrifugal distortion resonance, the deperturbed $B(K)$ values were obtained, which depend smoothly on K_a as indicated by the open circles.

in the effective B values; the interaction matrix elements are sufficiently small compared to the denominators in Eq. (6) and thus the correction energy can be calculated by the perturbation treatment. The resonance effect, as well as the avoided level crossing effect, is interpreted by the strong K-dependence of the denominators. The J-dependence of the denominators in Eq. (6) was ignored because it is much smaller than the K-dependence.

The denominators were evaluated from the observed K_a-rotational term values of the ground and the excited states given in Fig. 4. For the $v_5 = 1$ excited state the energy of the $K_a = 8$ level was roughly estimated by extrapolation to be 1930 cm^{-1}. By an iterative procedure, with an assumption of $\omega_5 = 577.35$ cm^{-1}, the dimensionless interaction coefficient C_5^{ab} has been determined to be $8.09(5) \times 10^{-5}$, by requiring the dependence of the deperturbed $B(K)$ values on K to be as smooth as possible. The estimated deperturbed $B(K)$ values are also indicated in Fig. 5 by open circles.

VI. DISCUSSION

The deperturbed values of the rotational constant $B(K)$ of HNCO decrease monotonically with increasing K as shown in Fig. 5. For semirigid molecules, the deperturbed rotational constants are expected to depend on K^2 linearly. The deviation from the linear dependence observed here indicates the contribution of the molecular quasilin-

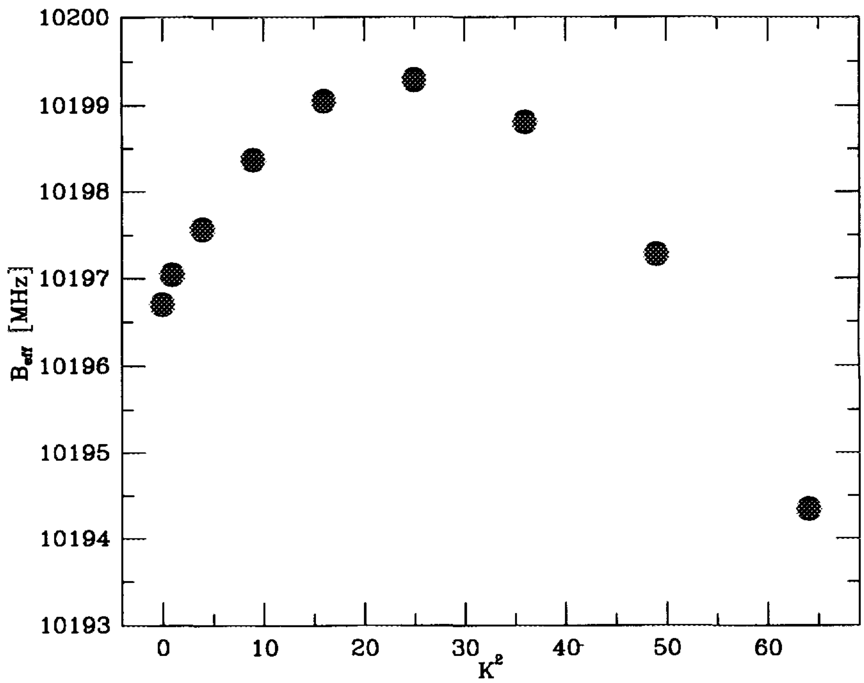

FIG. 6. The K_a dependence of the $B(K)$ values of DNCO is shown. The $B(K)$ values increase with K_a in the low K_a range, indicating the quasilinear behavior of this molecule. The effect of the centrifugal distortion resonance effect is not as obvious as in HNCO, although the presence of the resonance in DNCO is suggested by the decrease of $B(K)$ in the high K_a range.

earity. In comparison to HNCS, the quasilinear effects exposed in this nonlinearity are clearly weaker in HNCO, in consequence of its relatively high potential barrier of 2100 cm^{-1}. The K_a-rotational levels of the ground state up to $K_a = 8$ (at 1640 cm^{-1} above the zero-point energy) are below this barrier.

A more detailed analysis should include the Coriolis coupling between the three bending states $v_4 = 1$, $v_5 = 1$, and $v_6 = 1$. The analysis of the Coriolis resonance will be presented in a forthcoming paper.

Figure 6 shows the K-dependence of the effective rotational constants $B(K)$ of the deuterated species DNCO in the ground state. It should be noted that the $B(K)$ value of DNCO varies in a very small region of 10 MHz for the observed K_a states, whereas the variation of the $B(K)$ in HNCO is one order of magnitude larger: 110 MHz.

The $B(K)$ values of DNCO increase with K in the low K range. This behavior is very similar to that observed in HNCS (*9*). The effect of the centrifugal distortion resonance is not as obvious as in HNCO, although the presence of this resonance in DNCO is suggested by the decrease of $B(K)$ for high K states. Thus, the observed K dependence is caused by the combined effects of centrifugal distortion resonance and quasilinearity. Because the energies of the excited bending vibrational states of DNCO are known only very poorly (*18*), we could not analyze the centrifugal distortion resonance for this isotopomer. However, from the observed values of $B(K)$, the deperturbed $B(K)$ of DNCO is estimated to increase with K, at least for the low K range, as we have observed in HNCS. This behavior may be explained by the floppiness of the HNC bond angle. By increasing angular velocity along the a-principal axis, the hydrogen atom is pushed away from the rotation axis by the centrifugal force and consequently the HNC bond bends more, resulting in the increase of $B(K)$. The opposite behavior in the K-dependence of $B(K)$ observed for HNCO suggests that the contributions from the other two low vibrational states (NCO bending) to the deperturbed $B(K)$ values through the centrifugal effect are so significant, because of the enormous rotational constant A of HNCO, that the increase of $B(K)$ due to the HNC angle change seems to be cancelled.

The K-type splitting for $K_a = 3$ is observed for HNCO and DNCO. The $K_a = 3$ splitting in DNCO is relatively large; the K-type doubling of the a-type transition ${}^{q}R_3(29)$ has been observed to be about 3.5 MHz in the sub-mmW region. These splittings are essentially represented by the different $H(K)$ values for the doublet pair, whereas the $K_a = 2$ splittings are represented by the $D(K)$ values. The calculation of the energy levels of $K_a = 3$ of DNCO, based on the parameters listed in Table III, results in the reversing of the upper–lower relation in the K doublet for some low J values. However, the amounts of splitting in such cases are very small, less than the observed linewidth, and the apparent reversal of the energy levels originates just in the fitting error. In the J range, where the splittings are observed, the $J_{3,J-3}$ level, which we denoted by U in Table II following the usual order of the K doublet, is indeed higher in energy than the $J_{3,J-2}$ denoted by L.

In comparison, the observed $K_a = 3$ splittings of HNCO are very small; the K-type doubling of the a-type transition ${}^{q}R_3(30)$ has not been resolved even by the sub-mmW spectrometer. However, we have observed the $K_a = 3$ splittings of HNCO directly as the splitting in the high-J b-type transitions of ${}^{r}P_3$, ${}^{r}Q_3$, and ${}^{r}R_3$ in the FIR–FTIR spectra. The anomalous K-doubling reported for H_2S_2 (see for example Ref. (*19*)), where the energy ordering of the K-doublets for $K_a \geqslant 2$ are reversed by the centrifugal distortion effect, has not been observed for HNCO; the inertial asymmetry contributes significantly to the K-type doubling effect in this molecule.

ACKNOWLEDGMENTS

The authors express their thanks to Dr. M. Liedtke and Th. Klaus for their assistance with the measurements in Cologne and to the spectroscopy group of Professor Manfred Winnewisser for their support during the measurements in Giessen. The assistance of Dr. S. Klee and Mr. G. Mellau with the measurements is deeply appreciated. The work was supported in part by the Deutsche Forschungsgemeinschaft (DFG) through a special grant (SFB-301). The work of S.P.B. at Cologne was made possible by DFG through grants for the support of Eastern and Central European countries and the Republics of the former Soviet Union; this support is gratefully acknowledged.

REFERENCES

1. R. Kewley, K. V. L. N. Sastry, and M. Winnewisser, *J. Mol. Spectrosc.* **10**, 418–441 (1963).
2. B. Krakow, R. C. Lord, and G. O. Neely, *J. Mol. Spectrosc.* **27**, 148–176 (1968).
3. R. A. Ashby and R. L. Werner, *J. Mol. Spectrosc.* **18**, 184–201 (1965).
4. W. H. Hocking, M. C. L. Gerry, and G. Winnewisser, *Can. J. Phys.* **53**, 1869–1901 (1975).
5. K. Yamada, M. Winnewisser, G. Winnewisser, L. B. Szalanski, and M. C. Gerry, *J. Mol. Spectrosc.* **79**, 295–313 (1980).
6. K. Yamada, *J. Mol. Spectrosc.* **79**, 323–344 (1980).
7. L. Fusina and M. Carlotti, *Can. J. Phys.* **62**, 1452–1466 (1984).
8. M. Niedenhoff, K. M. T. Yamada, G. Winnewisser, and C. Ross, *J. Mol. Struct.* **352/353**, 423–433 (1995).

9. M. Niedenhoff, G. Winnewisser, K. M. T. Yamada, and S. P. Belov, *J. Mol. Spectrosc.* **169,** 224–242 (1995).
10. G. Guelachvili and K. Narahari Rao, "Handbook of Infrared Standards," Academic Press, Orlando, FL, 1986.
11. S. P. Belov, K. M. T. Yamada, G. Winnewisser, L. Poteau, R. Bocquet, J. Demaison, M. Yu. Trtyakov, and O. L. Polyansky, *J. Mol. Spectrosc.*, to appear.
12. K. Yamada and M. Winnewisser, *Z. Naturforsch. A* **31,** 139–144 (1976).
13. B. P. Winnewisser, *in* "Molecular Spectroscopy: Modern Research," (K. Narahari Rao, Ed.), Vol. 3, Academic Press, New York, 1985.
14. J. K. G. Watson, *in* "Vibrational Spectra and Structure" (J. R. Durig, Ed.), Vol. 6, Elsevier, Amsterdam, 1977.
15. K. M. T. Yamada and S. Klee, *J. Mol. Spectrosc.* **166,** 395–405 (1994).
16. G. Winnewisser, W. H. Hocking, and M. C. L. Gerry, *J. Phys. Chem. Ref. Data* **5**(1), 79–101 (1976).
17. S. Urban and K. M. T. Yamada, *J. Mol. Spectrosc.* **160,** 279–288 (1993).
18. R. A. Ashby and R. L. Werner, *Spectrochim. Acta* **22,** 1345–1353 (1966).
19. G. Winnewisser and K. M. T. Yamada, *Vib. Spectrosc.* **1,** 263–272 (1991).