

Inversion and Inversion–Rotation Spectrum of $^{14}\text{NH}_3$ in the ν_2 Excited State

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Using the vibration–inversion–rotation Hamiltonian for ammonia [V. Špirko, J. M. R. Stone, and D. Papoušek, *J. Mol. Spectrosc.* **60**, 159–178 (1976)], a modified theory is worked out for the $\Delta k = \pm 3n$ interactions between the inversion–rotation energy levels of NH_3 which takes into account the large amplitude inversion motion. Eighty frequencies of inversion and inversion–rotation transitions and two perturbation-allowed transitions in the ν_2 state of $^{14}\text{NH}_3$ are measured in the far-infrared region around 1 THz ($\approx 33\text{ cm}^{-1}$), mostly with the microwave accuracy, by the radiofrequency spectrometer with acoustic detector. By a least-squares fit of these data and the data of the infrared–microwave two-photon and infrared heterodyne measurements of the ν_2 band, a set of molecular constants for the ν_2 state of $^{14}\text{NH}_3$ is obtained which reproduces the submillimeterwave data with the accuracy of the experiment.

I. INTRODUCTION

The ground-state inversion and inversion–rotation spectrum of NH_3 has been extensively studied in the microwave region due to its importance for testing the results of theoretical description of the vibration–inversion–rotation interactions and hyperfine splittings (1) as well as for its astrophysical importance [see, e.g., Refs. (2, 3)].

At the present time, the most accurate ground-state inversion frequencies have been obtained in beam maser studies by Kukolich and co-workers (4–6) but they are limited to a few of the ammonia lines. Precision measurements (to accuracies of $\pm 0.003\text{ MHz}$) of 119 ground-state inversion lines by standard microwave techniques have been reported by Poynter and Kakar (8); Sinha and Smith (7) have recently measured 15 new inversion frequencies of $^{14}\text{NH}_3$ with the accuracy of $\pm 0.03\text{ MHz}$ by thermally populating higher rotational levels. Gordy *et al.* (9) and Krupnov *et al.* (10) measured accurately the frequency of the $J = 0 \rightarrow 1$, $\Delta K = 0$ inversion–rotation transition. The data of these authors should now be considered as the most accurate information on the inversion and inversion–rotation microwave transition frequencies in the ground state of $^{14}\text{NH}_3$.

Attempts at a quantitative description of the ground-state ammonia inversion spectrum have been so far based on two approaches. Either the standard power

TABLE I

Symmetry Species of the Inversion-Rotation Energy Levels in the Nondegenerate Vibrational States of NH_3 (in the D_{3h} Group)^a

$ J, k, m\rangle$ ^b	J even		J odd	
	s	a	s	a
$ J; 0, m\rangle$	A_1'	A_2''	A_2'	A_1''
$ J, +1, m\rangle, J, -1, m\rangle$	E''	E'	E''	E'
$ J, +2, m\rangle, J, -2, m\rangle$	E'	E''	E'	E''
$ J, +3, m\rangle + J, -3, m\rangle$	A_1''	A_2'	A_2''	A_1'
$ J, +3, m\rangle - J, -3, m\rangle$	A_2''	A_1'	A_1''	A_2'
$ J, +4, m\rangle, J, -4, m\rangle$	E'	E''	E'	E''
$ J, +5, m\rangle, J, -5, m\rangle$	E''	E'	E''	E'
$ J, +6, m\rangle + J, -6, m\rangle$	A_1'	A_2''	A_2'	A_1''
$ J, +6, m\rangle - J, -6, m\rangle$	A_2'	A_1''	A_1'	A_2''

^a Spin statistical weights: A_1 0, A_2' 4, A_2'' 4, A_1'' 0, E' 2, E'' 2.

^b Rotational quantum number k should be considered with modulo 6.

series expansion in the rotational quantum numbers J, K or semiempirical (and more flexible) expressions have been used to fit to measured frequencies. In the former approach [see, e.g., Ref. (8)], the expansion coefficients are related to the molecular parameters in the usual way but the experimental accuracy could not be approached without the major increase in the number of coefficients being fit. In the latter (and more frequently used) approach [see, e.g., Refs. (11, 12)], the physical meaning of the coefficients is somewhat less clear but the fit can more easily approach the accuracy of the most precise measurements. Using a Padé approximation with 19 terms, Young and Young (12) described the experimental inversion frequencies of Poynter and Kakar (8) with the accuracy of their experiment.

In both approaches, however, transitions involving rotational levels with $K = 3n$ require a special treatment. This is because higher order centrifugal distortion effects of the type $\langle J, k | H | J, k \pm 3n \rangle$ cause the K -type "splitting" (A_1, A_2 splitting, cf. Table I) of the $J, k = \pm 3n$ rotational levels, with the most pronounced effect for the $J, K = 3$ levels.

Nielsen and Dennison (13) first developed a perturbation theory of this effect and gave formula for the J -dependence of the K -type splitting. Their theory was later found to be incomplete [cf. Refs. (14, 15)]; a complete fourth-order theory of this effect was finally given by Aliev and Watson (16).

In our previous paper (17) we reported the first measurements of the 48 inversion transitions, 3 inversion-rotation transitions, and 2 perturbation-allowed transitions in the ν_2 excited state of $^{14}\text{NH}_3$, all carried out with the high-sensitivity Radiospectrometer with Acoustic Detector (RAD) at the Institute for Applied Physics of the Academy of Sciences of the USSR in Gorkii. In the present paper,

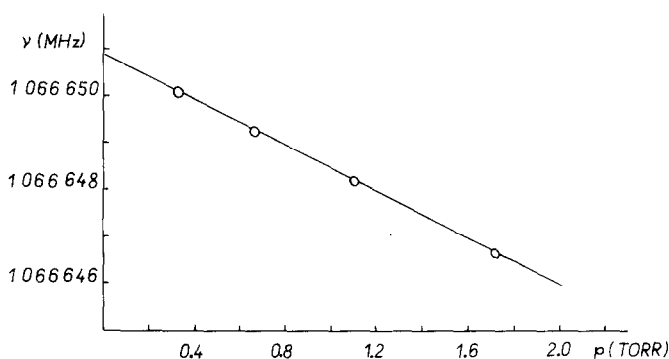


FIG. 1. Dependence of the frequency of the (1,1) inversion transition of $^{14}\text{NH}_3$ in the ν_2 state on the pressure of ammonia gas.

we have extended these measurements by 29 other lines of the inversion transitions in the ν_2 state.

The main purpose of the present paper, however, is a theoretical description of these spectra, with special consideration of the higher-order interactions between the J, k and $J, k \pm 3n$ rotational levels in the ν_2 state of NH_3 . In all the previous theoretical treatments of this effect (13, 15, 16), the inversion motion has been neglected. This seems to be a good approximation for the ground state of NH_3 because the ground-state inversion splitting in ammonia is small compared to the rotational spacings. However, in the ν_2 excited state, the inversion splitting ($\approx 30 \text{ cm}^{-1}$) is of the order of magnitude of the rotational spacings and the inversion motion has to be properly taken into account.

We have therefore modified the theory of the $\langle J, k | H | J, k \pm 3n \rangle$ interactions using the vibration-inversion-rotation Hamiltonian developed previously by us for ammonia (18, 19). Our submillimeterwave data on the inversion and inversion-rotation transitions in the ν_2 state were combined with the infrared-microwave two-photon (20, 21) and infrared heterodyne measurements (22) of the frequencies of transitions from the ground state to the ν_2 state to obtain a set of data with comparable experimental accuracy. A least-squares analysis of these data using the results of the modified theory was carried out to determine 29 parameters of the ν_2 state.

We have unequivocally shown that this approach lends itself to a quantitative description of the measured data with the accuracy of the experiment and provides a physically meaningful set of rotational and centrifugal distortion constants of the ν_2 excited state.

II. EXPERIMENTAL DETAILS

The measurement of the NH_3 submillimeterwave spectrum in the range 700–1100 GHz by the high-sensitivity spectrometer RAD (23) with the frequency stabilized backward wave oscillator (24) has been described previously (17). The accuracy of the measurements of frequencies by this spectrometer was $\pm 0.1 \text{ MHz}$. As we have already pointed out (17, 25), the line centers of ammonia for transi-

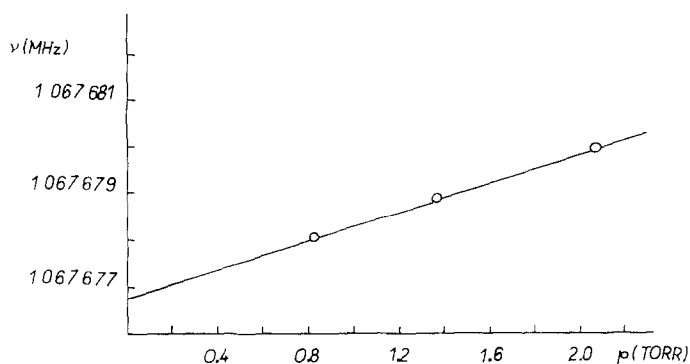


FIG. 2. Dependence of the frequency of the (2,2) inversion transition of $^{14}\text{NH}_3$ in the ν_2 state on the pressure of ammonia gas.

tions in the ν_2 state exhibit an anomalously large pressure dependence which can be described in the range of pressures 0–2 Torr by a linear equation (Figs. 1, 2)

$$\nu = \nu_0 + bp, \quad (1)$$

where ν_0 is the frequency at zero pressure, p is the pressure. The values of the constant b are given in Table II for some of the inversion and inversion-rotation transitions; the accuracy in the determination of b is approximately 10%. The observed pressure dependence of the line half-widths $(\Delta\nu)_{1/2}$ of the (1,1) and (2,2) inversion lines is illustrated by Fig. 3 [the peculiarity of the pressure dependence of $(\Delta\nu)_{1/2}$ at low pressures is related to the Doppler linewidth and the characteristics of our spectrometer]. An important characteristic of the type of collision interaction is the parameter $a = b/(\Delta\nu)_{1/2}$, where $(\Delta\nu)_{1/2}$ is the line half-width at 1 Torr. For the (1,1) line, $a = -0.16$, for the (2,2) line, $a = +0.14$.

Pressure-induced frequency shifts of the transitions in the ν_2 state of NH_3 are important for studying vibrational relaxation in collision processes [cf. Refs. (26–28) for a discussion of frequency shifts in the ground state] as well as for precise determination of microwave and infrared laser transition frequencies. A

TABLE II

Pressure Dependence of the Inversion and Inversion-Rotation Transitions in the ν_2 State of $^{14}\text{NH}_3$ [see Eq. (1)]

Inversion Transitions	b (MHz/Torr)	Inversion-Rotation Transitions	b (MHz/Torr)
(1,1)	- 2.4	s(3,0) - a(2,0)	+ 3.6
(2,2)	+ 1.5	s(3,1) - a(2,1)	+ 3.3
(2,1)	0	s(3,2) - a(2,2)	- 0.2
(7,5)	>0		
(8,5)	>0		
(9,6)	>0		

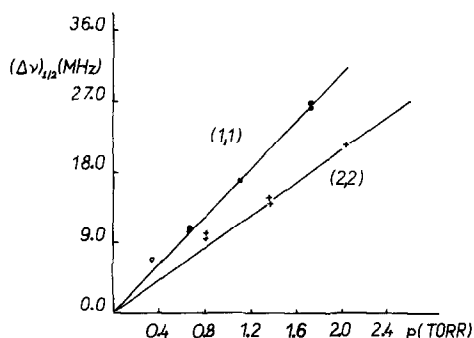


FIG. 3. Dependence of the line half-width $(\Delta\nu)_{1/2}$ of the (1,1) and (2,2) inversion line of $^{14}\text{NH}_3$ in the ν_2 state on the pressure of ammonia gas.

preliminary discussion of the relation of the pressure-induced frequency shifts in the ν_2 state of NH_3 to the shifts of the line centers by the Stark effect (due to dipole-dipole interactions) has been published elsewhere (29, 30). For the purpose of the present paper these shifts are important because they influence the accuracy of our measurements. Most of our submillimeterwave measurements (with a frequency stabilized backward wave scillator) were done for a single value of pressure (in the range 0.3–0.6 Torr); the accuracy of those frequencies is therefore about ± 1 MHz. A better accuracy of ± 0.2 MHz was obtained by extrapolating to zero pressure from at least three measurements at different pressures (Tables III and IV).

Besides these measurements carried out with the microwave accuracy, we measured 29 inversion transitions in the ν_2 state of $^{14}\text{NH}_3$ with the accuracy of the standard high-resolution infrared spectroscopy. In those measurements, the NH_3 spectrum was recorded simultaneously with the SO_2 spectrum, and the NH_3 frequencies have been determined by interpolating between the SO_2 frequencies (31). The experimental uncertainty of those 29 lines can be estimated by comparing the precise transition frequencies [determined by us by using a frequency stabilized backward wave oscillator or from the combination of the two-photon measurements of the ν_2 infrared band (20) with the ground-state inversion frequencies] with the frequencies of the same transitions determined by using SO_2 as the calibration standard. The r.m.s. error in the SO_2 calibration technique was found to be approximately 0.024 GHz.

The high sensitivity of the RAD spectrometer has made it possible to detect also lines of the inversion transitions in the ν_2 state of $^{15}\text{NH}_3$ occurring in the natural isotopic abundance. A part of the spectrum of NH_3 in the ν_2 state around 1 THz which contains also lines of $^{15}\text{NH}_3$ in the ν_2 state and illustrates the sensitivity of our spectrometer is shown in Fig. 4. A detailed analysis of the $^{15}\text{NH}_3$ spectrum in the ν_2 state will be carried out later in our laboratories after measuring frequencies in the sample enriched by $^{15}\text{NH}_3$.

III. THEORY

In developing the fourth-order theory of the $\langle J, k | H | J, k \pm 3n \rangle$ interactions in the ν_2 excited state of ammonia, it is convenient to follow the theory of the

TABLE III

Submillimeterwave Inversion Transition Frequencies of $^{14}\text{NH}_3$ in the ν_2 State (in MHz)

J	K	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}^a$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}^b$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}^c$
1	1	1 066 650.82 ^c	1 066 650.70	0.12	0.42	1.00	0.12
2	1	1 045 318.70	1 045 319.07	- 0.37	11.32	12.77	- 0.37
2	2	1 067 676.77 ^c	1 067 676.97	- 0.20	- 8.38	- 8.03	- 0.20
3	1	1 014 084.00	1 014 084.69	- 0.69	19.72	19.46	- 0.04
3	2	1 035 816.20	1 035 816.21	- 0.01	10.90	12.40	0.04
3	3	1 073 050.70	1 073 050.26	0.44	47.78	47.02	71.01
4	1	973 826.50	973 826.53	- 0.03	18.22	12.33	- 0.59
4	2	994 747.80	994 747.64	0.16	21.76	19.73	0.41
4	3	1 030 531.20	1 030 530.29	0.91	6.05	12.20	2.13
4	4	1 082 600. ^d	1 082 593.49	7.	- 40.	- 41.18	6.
5	1	925 657.40	925 657.39	0.01	5.13	- 9.08	- 2.47
5	2	945 604.80	945 604.38	0.42	20.79	10.79	- 0.01
5	3	979 650.00	979 650.82	- 0.82	- 31.25	- 49.25	- 72.35
5	4	1 029 374.50	1 029 375.56	- 1.06	- 1.99	2.03	- 5.41
5	5	1 096 600. ^d	1 096 591.63	8.	- 53.	- 59.	7.
6	1	-	870 877.05	-	-	-	-
6	2	889 710.90	889 710.26	0.64	12.91	- 5.26	- 3.52
6	3	921 940.30	921 940.41	- 0.11	3.30	35.55	14.36
6	4	968 810.00	968 809.59	0.41	19.21	17.64	- 13.98
6	5	1 032 323.00	1 032 322.21	0.79	- 7.63	- 1.10	- 6.19
6	6	-	1 115 083.22	-	-	-	-
7	1	810 918.65	810 918.05	0.60	- 16.46	- 32.77	- 27.51
7	2	828 521.90	828 524.75	- 2.85	11.21	- 7.23	- 16.85
7	3	858 394.20	858 395.29	- 1.09	- 99.53	- 224.44	- 252.78
7	4	902 459.20	902 459.00	0.20	15.86	3.95	- 39.06
7	5	961 885.20	961 884.92	0.28	19.94	21.24	- 20.96
7	6	1 039 360.80	1 039 360.66	0.14	- 15.33	- 7.15	- 11.04
7	7	-	1 138 215.24	-	-	-	-
8	1	747 286.80	747 287.19	- 0.39	22.18	27.59	- 56.57
8	2	763 583.33	763 583.29	0.04	54.69	52.74	- 33.06
8	3	791 531.42	791 531.54	- 0.12	- 69.21	143.52	58.31
8	4	831 969.25	831 969.15	0.10	4.04	- 11.15	- 91.10
8	5	887 018.80	887 018.67	0.13	22.99	13.28	- 56.55
8	6	958 827.90	958 828.19	- 0.29	13.92	18.72	- 32.51
8	7	1 050 521.50	1 050 521.25	0.25	- 15.79	- 10.01	- 16.98
8	8	-	1 166 172.70	-	-	-	-
9	1	681 490. ^d	681 505.98	- 16.	128.	172.	- 112.
9	2	691 430. ^d	696 438.81	- 7.	164.	198.	- 70.
9	3	721 283.71	721 283.44	0.27	- 102.76	- 506.71	- 743.91
9	4	759 001.20	759 001.48	- 0.28	6.11	6.80	- 185.80
9	5	809 481.89	809 481.92	- 0.03	22.50	12.40	- 128.57
9	6	875 388.80	875 388.95	- 0.15	16.09	10.75	- 83.51

s sextic centrifugal distortion constants of Aliev and Watson (16). We use the notation H_{mn} for the various terms in the expansion of the vibration-inversion-rotation Hamiltonian for ammonia (18, 19). Here the first subscript is the degree in the vibrational operators (Q and P) and the second subscript is the degree in the components of the total angular momentum J [cf. Ref. (32)].

TABLE III—Continued

J	K	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}^a$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}^b$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}^c$
9	7	959 569.00	959 566.44	2.56	6.45	14.48	- 46.12
9	8	1 065 868.20	1 065 868.57	- 0.37	- 3.00	- 8.31	- 25.80
9	9	-	1 199 179.16	-	-	-	-
10	1	-	615 055.02	-	-	-	-
10	2	628 590. d	628 594.90	- 5.	394.	464.	- 103.
10	3	651 990. d	651 991.46	- 1.	- 97.	692.	184.
10	4	685 170. d	685 169.28	1.	45.	82.	- 338.
10	5	730 990. d	730 985.03	5.	47.	59.	- 250.
10	6	790 818.23	790 818.06	0.17	25.56	15.59	- 183.18
10	7	867 343.50	867 343.57	- 0.07	- 0.68	- 4.71	- 119.64
10	8	984 080.30	984 059.95	0.35	- 3.98	4.13	- 69.35
10	9	1 085 505. d	1 085 501.15	4.	32.	0.	- 32.
10	10	-	1 237 497.36	-	-	-	-
11	1	-	549 329.51	-	-	-	-
11	2	561 483. d	561 480.24	3.	758.	808.	- 118.
11	3	580 475. d	580 479.16	- 4.	130.	- 987.	- 1 846.
11	4	611 960. d	611 979.37	- 19.	95.	161	- 586.
11	5	653 120. d	653 128.19	8.	79.	129.	- 449.
11	6	706 896.96	706 899.12	- 0.16	24.62	63.57	- 352.89
11	7	775 717.64 ^M	775 727.42	- 9.78	- 11.04	- 12.47	- 264.42
11	8	862 810. 70	862 811.45	- 0.75	- 21.03	- 24.14	- 167.02
11	9	972 301.60	972 301.83	0.27	- 0.63	3.09	- 96.50
11	10	-	1 109 551.07	-	-	-	-
11	11	-	1 281 429.87	-	-	-	-
12	1	-	485 621.55	-	-	-	-
12	2	-	496 409.56	-	-	-	-
12	3	515 387. d	515 386.76	0.	- 64.	1 648.	532.
12	4	540 810. d	540 784.43	26.	187.	186.	- 860.
12	5	-	577 349.65	-	-	-	-
12	6	625 160. d	625 156.06	4.	112.	112.	- 615.
12	7	686 430. d	686 411.79	18.	24.	50.	- 461.
12	8	763 996.18	763 996.19	- 0.01	- 22.62	- 23.07	- 345.13
12	9	861 672.90	861 674.21	- 1.31	16.36	- 19.54	- 226.51
12	10	984 300. d	984 314.10	14.	5.	1.	- 116.
12	11	-	1 138 183.66	-	-	-	-
12	12	-	1 331 319.64	-	-	-	-
13	1	-	425 186.71	-	-	-	-
13	2	-	434 658.83	-	-	-	-
13	3	446 588. d	446 589.47	- 1.	71.	- 3 066.	- 3 940.
13	4	472 755. d	472 750.84	4.	22.	- 322.	- 1 301.
13	5	504 864. d	504 889.20	- 25.	- 21.	- 161.	- 1 174.
13	6	546 936. d	546 945.91	- 10.	- 167.	- 35.	- 991.
13	7	600 866. d	600 861.05	5.	- 36.	1.	- 810.
13	8	669 244. d	669 239.71	4.	- 27.	- 2.	- 635.
13	9	755 447.62	755 447.42	0.20	9.40	9.	- 456.90
13	10	863 860. d	863 864.34	- 4.	52.	53.	- 298.
13	11	1 000 151.60	1 000 151.56	0.04	38.3	28.36	- 173.40
13	12	-	1 171 597.15	-	-	-	-
13	13	-	1 387 550.49	-	-	-	-

Using the harmonic vibrational energy H_{20} ,

$$H_{20} = \frac{1}{2} \sum_{k=1,3a,3b,4a,4b} [\lambda_k(\rho) Q_k^2 + P_k^2] \quad (2)$$

as the unperturbed Hamiltonian, we find the perturbation terms required in the

TABLE III—Continued

J	K	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}^a$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}^b$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}^c$
14	1	-	369 829.28	-	-	-	-
14	2	-	378 046.93	-	-	-	-
14	3	-	391 650.09	-	-	-	-
14	4	-	408 847.88	-	-	-	-
14	5	-	436 772.47	-	-	-	-
14	6	473 296. d	473 319.91	- 24.	- 152.	- 873.	- 1 523.
14	7	-	520 281.39	-	-	-	-
14	8	579 880. d	579 883.21	- 3.	- 173.	- 163.	- 1 059.
14	9	655 120. d	655 135.71	- 16.	1.	23.	- 839.
14	10	749 930. d	749 936.40	- 6.	181.	188.	- 596.
14	11	-	869 343.00	-	-	-	-
14	12	1 019 895.50	1 019 895.53	- 0.03	- 12.69	- 9.92	- 225.55
14	13	-	1 210 022.25	-	-	-	-
14	14	-	1 450 547.30	-	-	-	-

^a Calculated in the approximation used by Nielsen and Dennison (13). ^b Calculated using only the polynomial expression for the inversion-rotation energy levels of the ν_2 state [Eq. (12)].

^c Value obtained by extrapolating to zero pressure. ^d Value obtained by interpolating between the SO₂ lines (cf. Part II). ^e $\nu_{\text{calc.}}$ are transition frequencies between the unperturbed inversion-rotation energy levels in the ν_2 state.

fourth-order theory of the $\langle J, k | H | J, k \pm 3n \rangle$ interactions to be

$$H_{02} = \frac{1}{2} \sum_{\alpha=x,y,z,\rho} \mu_{\alpha\alpha}^0 J_{\alpha}^2, \quad (3)$$

$$H_{12} = \frac{1}{2} \sum_k \sum_{\alpha,\beta} X_k^{\alpha\beta} Q_k J_{\alpha} J_{\beta} + \frac{1}{2} \sum_k \sum_{\alpha} (J_{\rho} X_k^{\rho\alpha}) Q_k J_{\alpha}, \quad (4)$$

$$H_{22} = \frac{1}{2} \sum_{k,l} \sum_{\alpha,\beta} Y_{kl}^{\alpha\beta} Q_k Q_l J_{\alpha} J_{\beta} + \frac{1}{2} \sum_{k,l} \sum_{\alpha} (J_{\rho} Y_{kl}^{\rho\alpha}) Q_k Q_l J_{\alpha}, \quad (5)$$

$$H_{21} = -\frac{1}{2} \sum_{\alpha} \mu_{\alpha\alpha}^0 (J_{\alpha} p_{\alpha} + p_{\alpha} J_{\alpha}) - \frac{1}{2} (J_{\rho} \mu_{\rho\rho}^0) p_{\rho}, \quad (6)$$

$$H_{30} = \frac{1}{6} \sum_{lmn} k_{lmn} Q_l Q_m Q_n. \quad (7)$$

In Eqs. (3)–(6), the sum is over x, y, z and the inversion coordinate ρ (18, 19), $J_{\rho} = -i\hbar \partial/\partial\rho$, and

$$X_k^{\alpha\beta} [\equiv (\partial\mu_{\alpha\beta}/\partial Q_k)_0] = -a_k^{\alpha\beta} \mu_{\alpha\alpha}^0 \mu_{\beta\beta}^0, \quad (8a)$$

$$Y_{kl}^{\alpha\beta} \left[\equiv \frac{1}{2} (\partial^2 \mu_{\alpha\beta} / \partial Q_k \partial Q_l)_0 \right] = \frac{3}{8} \sum_{\epsilon=x,y,z,\rho} (a_k^{\alpha\epsilon} a_l^{\beta\epsilon} + a_l^{\alpha\epsilon} a_k^{\beta\epsilon}) \mu_{\alpha\alpha}^0 \mu_{\beta\beta}^0 \mu_{\epsilon\epsilon}^0, \quad (8b)$$

where

$$a_k^{\alpha\beta} = (\partial I_{\alpha\beta} / \partial Q_k)_0 \quad (8c)$$

are the derivatives of the instantaneous inertia tensor $I_{\alpha\beta}$ evaluated at the reference configuration (18). We have included certain terms in H_{12} , H_{22} , H_{21} although their contribution is below the order of our approximation to preserve the Her-

TABLE IV

Submillimeterwave Inversion-Rotation Transition Frequencies of $^{14}\text{NH}_3$ in the ν_2 State (MHz)

Inversion-rotation transitions					
$\begin{pmatrix} J \\ K \end{pmatrix}$	$\begin{pmatrix} J' \\ K' \end{pmatrix}$	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	$\nu_{\text{calc.}}$
1,0	0,0 ^a	466 245.1 ^{b,d}	466 245.1	0.0	-
2,0	1,0	-	-	-	2 244 466.2
2,1	1,1	140 143.5 ^c	140 142.5	1.0	2 252 112.3
3,0	2,0	769 710.2 ^d	769 710.1	0.1	-
3,1	2,1	762 852.3 ^d	762 852.4	- 0.1	2 822 256.2
3,2	2,2	741 788.1 ^d	741 788.1	0.0	2 845 281.2
4,0	3,0	-	-	-	3 373 611.2
4,1	3,1	1 393 104. ^e	1 393 077.2	27.	3 380 988.5
4,2	3,2	1 373 090. ^e	1 373 047.3	42.	3 403 611.2
4,3	3,3	1 338 675. ^e	1 338 678.1	- 3.	3 442 258.7
5,0	4,0	-	2 035 450.8	-	-
5,1	4,1	-	2 029 198.6	-	3 928 682.5
5,2	4,2	-	2 010 367.8	-	3 950 719.8
5,3	4,3	-	1 978 108.9	-	3 988 290.0
5,4	4,4	-	1 931 048.3	-	4 043 017.3

Perturbation-allowed transitions					
$\begin{pmatrix} J \\ K \end{pmatrix}$	$\begin{pmatrix} J' \\ K' \end{pmatrix}$	$\nu_{\text{obs.}}$	$\nu_{\text{calc.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	I^g
a(3,3)	a(2,0)	772 594.9	772 594.3	0.6	2.63
s(3,0)	s(3,3)	1 070 166.6	1 070 166.1	0.5	2.63
s(5,0)	s(5,3)	-	1 058 860.6	-	0.09
s(7,0)	s(7,3)	-	1 043 127.2	-	0.12
s(9,0)	s(9,3)	1 023 797. ^f	1 023 790.5	7	0.20
s(11,0)	s(11,3)	-	1 001 749.6	-	0.33

^a The a(0,0) energy level of the ν_2 state is higher than the s(1,0) level.^b Ref. (25).^c Ref. (35).^d Value obtained by extrapolating to zero pressure. ^e Obtained by combining the infrared (20-21) and ground state microwave data (2).^f Value obtained by interpolating between the SO₂ lines (cf. Part II). ^g Intensity of the line of the $\Delta J = \pm 1, 0$; $\Delta k = \pm 3$ "forbidden" transition (in percents) related to the intensity of the line of the corresponding inversion-rotation or inversion transition $\Delta J = \pm 1, 0$; $\Delta k = 0$ from the lower level. Calculated from the coefficients of the mixing of wavefunctions.

mitian properties of these operators. It should be emphasized that in our treatment λ_k , $\mu_{\alpha\beta}$, and the Q -independent $\mu_{\alpha\beta}^0$, $X_k^{\alpha\beta}$, $Y_{kl}^{\alpha\beta}$, ζ_{kl}^{α} (in p_α), and k_{lmn} are functions of the inversion coordinate ρ (18, 19).

Following the derivation of Aliev and Watson (16), we find that the following combinations of the above perturbation terms contribute in the fourth order to the interaction between the rotational levels J , k and J , $k \pm 3n$:

- (i) Harmonic: $H_{12}H_{12}H_{22}$,
- (ii) Coriolis: $H_{12}H_{12}H_{02}H_{02}$, $H_{12}H_{12}H_{21}H_{21}$, $H_{12}H_{12}H_{21}H_{02}$,
- (iii) Anharmonic: $H_{30}H_{12}H_{12}H_{12}$.

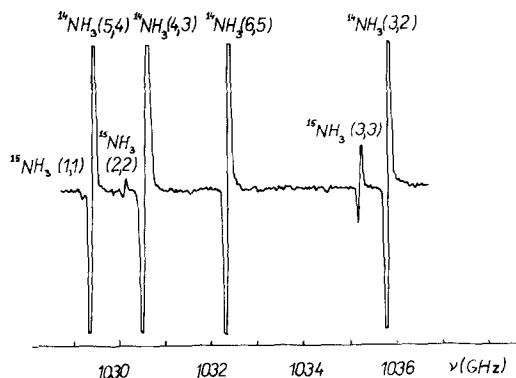


FIG. 4. Part of the submillimeterwave spectrum of NH_3 in the 1 THz region.

After a perturbation diagonalization of the vibrational operators (Q, P) we find the following inversion-rotational operators:

$$H^{(v)}(\text{harmonic}) = \frac{1}{64} \sum_{t,t'} (Y_{tat'a}^{xx} - Y_{tat'a}^{yy})(X_{ta}^{xx} X_{t'a}^{xx}) \lambda_t^{-1} \lambda_{t'}^{-1} \times (J_+^6 + J_-^6) = H_1(\rho)(J_+^6 + J_-^6), \quad (9a)$$

$$H^{(v)}(\text{Coriolis}) = -\frac{1}{8} \sum_t (X_{ta}^{xx} X_{ta}^{xz} \lambda_t^{-1}) [(J_+^3 + J_-^3) J_z + J_z (J_+^3 + J_-^3)] + \frac{i}{4} \sum_t \left[X_{ta}^{xx} X_{ta}^{y\rho} \lambda_t^{-1} J_\rho + \frac{1}{2} (J_\rho X_{ta}^{xx} X_{ta}^{y\rho} \lambda_t^{-1}) \right] \times (J_+^3 - J_-^3) + \frac{1}{16} \sum_{t \leq t'} (\mu_{xx}^0)^2 \times (\zeta_{itb}^x \zeta_{t'b}^x) \cdot (X_{ta}^{xx} X_{t'a}^{xx}) \cdot \lambda_t^{-1} \lambda_{t'}^{-1} \cdot (2 - \delta_{tt'}) (J_+^6 + J_-^6) = H_2(\rho) [(J_+^3 + J_-^3) J_z + J_z (J_+^3 + J_-^3)] + H_3(\rho) (J_+^3 - J_-^3) + H_4(\rho) (J_+^6 + J_-^6), \quad (9b)$$

$$H^{(v)}(\text{anharmonic}) = -\frac{1}{12} \sum_{t \leq t' \leq t''} \frac{1}{8} k_{tt't''} X_{ta}^{xx} X_{t'a}^{xx} X_{t''a}^{xx} (\lambda_t \lambda_{t'} \lambda_{t''})^{-1} \times (J_+^6 + J_-^6) = H_5(\rho) (J_+^6 + J_-^6). \quad (9c)$$

The symmetry relations between the nonvanishing coefficients $X_k^{\alpha\beta}$, $Y_{kl}^{\alpha\beta}$, and k_{lmn} were used in the derivation of Eqs. (9); $J_\pm = J_x \pm iJ_y$; the sum is over $t = 3, 4$ in these equations.

Consider now the matrix elements of the operator

$$H = H_0 + H^{(v)}(\text{harmonic}) + H^{(v)}(\text{Coriolis}) + H^{(v)}(\text{anharmonic}) \quad (10)$$

in the basis of the inversion-rotation wavefunctions

$$|(\pm)\varphi_{i,j,k}\rangle = \frac{1}{\sqrt{2}} |\psi_{i,j,k}\rangle [|J,k\rangle \pm |J,-k\rangle], \quad (11)$$

TABLE V

Matrix of the Interactions between the Para-States of NH_3 in the ν_2 State^a

	$ ^{(\pm)}\varphi_{(\beta)}; J, 1\rangle$	$ ^{(\mp)}\varphi_{(\beta)}; J, 2\rangle$	$ ^{(\pm)}\varphi_{(\beta)}; J, 4\rangle$	$ ^{(\pm)}\varphi_{(\beta)}; J, 5\rangle$	$ ^{(\pm)}\varphi_{(\beta)}; J, 7\rangle$...
$ ^{(\pm)}\varphi_{(\beta)}; J, 1\rangle$	$(\frac{1}{2})E^0(J, 1)/h$	$\pm f(J, 2)(\alpha \mp \beta)$	$f(J, 4)(5\alpha \mp \beta)$	0	0	
$ ^{(\mp)}\varphi_{(\beta)}; J, 2\rangle$		$(\frac{1}{2})E^0(J, 2)/h$	0	$f(J, 5)(7\alpha \pm \beta)$	0	
$ ^{(\mp)}\varphi_{(\beta)}; J, 4\rangle$			$(\frac{1}{2})E^0(J, 4)/h$	0	$f(J, 7)(11\alpha \pm \beta)$	
$ ^{(\pm)}\varphi_{(\beta)}; J, 5\rangle$	Hermitian			$(\frac{1}{2})E^0(J, 5)/h$	0	
$ ^{(\pm)}\varphi_{(\beta)}; J, 7\rangle$					$(\frac{1}{2})E^0(J, 7)/h$	

^a The upper and lower signs of $f(J, 2)$ correlate with the upper and lower signs in the term $^{(\pm)}\varphi$; the upper and lower signs of β correlate with the upper and lower symbol α and α in $\varphi_{(\beta)}$.

where the inversion wavefunctions $|\psi_{i;J,k}\rangle$ depend on the inversion coordinate ρ (as the dynamic variable) and on the rotational quantum numbers J and k (as parameters) [cf. Ref. (33)]. The unperturbed Hamiltonian H'_0 in Eq. (10) was defined by Eqs. (9) and (10) (as $H'_0 = H_0 + H'$) in our previous paper (17).

In the following we specify the matrix elements which were used in the numerical treatment of our problem (cf. Tables V and VI and Section IV). In some cases we included into the expressions for these elements certain terms which correspond to higher-order approximation compared to the fourth-order theory of the $\Delta k = \pm 3, 6$ interactions discussed above (e.g., we have included the octic centrifugal distortion constants). This is consistent with the fact that in our approach higher-order formulae can be obtained from the lower-order terms of the expansion of

TABLE VI

Matrix of the Interactions between the Ortho-States of NH_3 in the ν_2 State^a

	$ \varphi_{(\beta)}; J, 0\rangle$	$ ^{(\mp)}\varphi_{(\beta)}; J, 3\rangle$	$ ^{(\pm)}\varphi_{(\beta)}; J, 6\rangle$	$ ^{(\mp)}\varphi_{(\beta)}; J, 9\rangle$	$ ^{(\pm)}\varphi_{(\beta)}; J, 12\rangle$...
$\varphi_{(\beta)}; J, 0\rangle$	$(\frac{1}{2})E^0(J, 0)/h$	$\mp f(J, 3)(3\alpha \mp \beta)$	0	0	0	
$ ^{(\mp)}\varphi_{(\beta)}; J, 3\rangle$		$(\frac{1}{2})E^0(J, 3)/h \mp \frac{1}{3}f(J, 3)$	$f(J, 6)(9\alpha \pm \beta)$	0	0	
$ ^{(\pm)}\varphi_{(\beta)}; J, 6\rangle$			$(\frac{1}{2})E^0(J, 6)/h \mp \frac{1}{6}f(J, 6)$	$f(J, 9)(15\alpha \mp \beta)$	0	
$ ^{(\mp)}\varphi_{(\beta)}; J, 9\rangle$	Hermitian			$(\frac{1}{2})E^0(J, 9)/h$	$f(J, 12)(21\alpha \pm \beta)$	
$ ^{(\pm)}\varphi_{(\beta)}; J, 12\rangle$					$(\frac{1}{2})E^0(J, 12)/h$	

^a The upper and lower signs of η_{3n} correlate with the upper and lower signs in the term $^{(\pm)}\varphi$;

the upper and lower signs of β correlate with the upper and lower symbol α and α in $\varphi_{(\beta)}$.

Only the states with nonzero spin statistical weights should be considered in this table (cf. Table I).

the vibration-inversion-rotation Hamiltonian in terms of Q after a subsequent expansion of the ρ -dependent terms with respect to the inversion coordinate ρ [for more details, see Ref. (17)]. Such terms have been found important in the numerical analysis of the data which is described in Section IV of this paper. For the diagonal matrix elements of H'_0 [cf. Eq. (10) and Tables V and VI] we used the following expression:

$$\begin{aligned} {}^{(i)}E^0(J, K)/h = & E_i^0/h + B_i J(J+1) + (C_i - B_i)K^2 - D_J^{(i)}J^2(J+1)^2 \\ & - D_{JK}^{(i)}J(J+1)K^2 - D_K^{(i)}K^4 + H_{JJJ}^{(i)}J^3(J+1)^3 \\ & + H_{JJK}^{(i)}J^2(J+1)^2K^2 + H_{JKK}^{(i)}J(J+1)K^4 + H_{KKK}^{(i)}K^6 \\ & + G_{JJJ}^{(i)}J^4(J+1)^4 + G_{JJK}^{(i)}J^3(J+1)^3K^2 + G_{JJK}^{(i)}J^2(J+1)^2K^4 \\ & + G_{JKK}^{(i)}J(J+1)K^6 + G_{KKK}^{(i)}K^8, \quad (12) \end{aligned}$$

where i indicates the parity of the ν_2 inversion state [lower (denoted by s) or upper (denoted by a) component of the inversion doublet].

From the matrix elements of the operators containing the sixth power of J_{\pm} [Eq. (9)], we consider only those which are diagonal in $K = |k|$ in the basis defined by Eq. (11).

Let us define

$$\eta_3^{(i)} = \langle \psi_{i,J,3} | H_1(\rho) + H_4(\rho) + H_5(\rho) | \psi_{i,J,3} \rangle / h \quad (13a)$$

and

$$g(J, K) = \prod_{r=1}^K [J(J+1) - r(r-1)] = (J+K)!/(J-K)! \quad (13b)$$

We found (cf. Section IV) that the experimental data used in this paper do not allow for a separate determination of $\eta_3^{(s)}$ and $\eta_3^{(a)}$ but that $\eta_3 = (\eta_3^{(s)} + \eta_3^{(a)})/2$ can be determined. On the other hand, we found that the dependence of η_3 on the rotational quantum numbers (due to the parametric dependence of the inversion wavefunction $\psi_{i,J,K}$ on J, K) should be taken into account. It can be shown by a simple perturbation treatment of the J, K dependence of $\psi_{i,J,K}$, that the J, K dependence of η_3 must have the following form:

$$\eta_3 = \eta_3^0 + \eta_3^J J(J+1) + \eta_3^K K^2 + \text{higher-order terms}. \quad (14)$$

We also found by the numerical analysis of the data that the matrix element of the operator of the type $H'(\rho)(J_{\pm}^{12} + J^{12})$ diagonal in K in the basis defined by Eq. (11), should be introduced. Thus we have introduced the parameter $\eta_6^{(i)}$ defined as

$$\eta_6^{(i)} = \langle \psi_{i,J,6} | H'(\rho) | \psi_{i,J,6} \rangle / h. \quad (15)$$

Similarly as in the case of $\eta_3^{(i)}$, only $\eta_6 = (\eta_6^{(s)} + \eta_6^{(a)})/2$ can be determined. We found that the J, K -dependent parts of η_6 cannot be determined and thus only η_6^0 was used in the fit.

Let us further define

$$\alpha = \langle \psi_{s,J,k}^a | H_2(\rho) | \psi_{s,J,k\pm 3}^s \rangle / h = \langle \psi_{a,J,k\pm 3}^s | H_2(\rho) | \psi_{s,J,k}^a \rangle / h, \quad (16a)$$

$$\beta = -\langle \psi_{a,J,k}^s | H_3(\rho) | \psi_{s,J,k\pm 3}^a \rangle / h = \langle \psi_{s,J,k\pm 3}^a | H_3(\rho) | \psi_{a,J,k}^s \rangle / h, \quad (16b)$$

and

$$f(J, K) = \{[J(J+1) - K(K-1)][J(J+1) - (K-1)(K-2)] \\ \times [J(J+1) - (K-2)(K-3)]\}^{1/2}. \quad (17)$$

The off-diagonal matrix elements α and β in Eq. (16) depend slightly on J, K [cf. Eq. (14)]. However, we were not able to determine the J, K -dependent parts of α and β by the numerical analysis of experimental data.

It is easy to see from the overall symmetry species of the inversion-rotation states (Table I) that the problem factorizes into eight submatrices, four for the para-states of ammonia ($K \neq 3$ modulo 3) (Table V) and four for the ortho-states ($K = 3$ modulo 3) (Table VI).

From the four matrices for para-NH₃ (Table V), two pairs of matrices have identical eigenvalues because no higher-order perturbations can remove the K -degeneracy of the rotational levels of the overall symmetry species E . For ortho-NH₃, depending on the parity of the rotational quantum number J , only one of the A_1 or A_2 states has nonzero spin statistical weight (Table I). In NH₃ there is therefore no real splitting into A_1 and A_2 sublevels but only a shift of that level which corresponds to the state with nonzero weight.

IV. RESULTS AND DISCUSSION

By diagonalizing the above-discussed interaction matrices by a second-order perturbation treatment, formulae (which are rather involved) can be obtained for the individual inversion-rotation energy levels $E_{ir}(J, K)$ in the ν_2 state of NH₃ corrected for the higher-order vibrational-inversion-rotational interactions discussed in Section III. The appropriate differences $[E_{ir}(J', K') - E_{ir}(J'', K'')]/h$ are theoretical expressions for the corresponding inversion and inversion-rotation transition frequencies which can be used to fit the molecular parameters of the ν_2 state.

Molecular parameters which can be obtained by combining our submillimeter-wave data with the precise infrared data on the ν_2 band (20–22) are given in Table VII. The frequencies of the pure inversion transitions in the ν_2 state provide information on the differences between the upper (a) and lower (s) state rotational and centrifugal distortion constants $\Delta X = X^{(a)} - X^{(s)}$ in the polynomial defined by Eq. (12). Furthermore, these data determine—in principle at least—also parameters $X^{(i)}$, where $X^{(i)}$ has a coefficient depending on K , e.g., $(C_i - B_i)$, $D_K^{(i)}$ or $D_{JK}^{(i)}$. This is of course the consequence of the fact that in our treatment neither k (nor $k - l_i$) are good quantum numbers.¹ Much stronger information on the “spectroscopically forbidden” molecular constants such as $(C_i - B_i)$ or $D_K^{(i)}$ can of course be obtained from the frequencies of the $\Delta k = \pm 3$ perturbation-allowed transitions.

¹ A simple analysis of the theoretical expressions for $E_{ir}(J', K') - E_{ir}(J'', K'')$ shows that molecular constants such as, e.g., $(C_i - B_i)$ or $D_K^{(i)}$ are numerically determinable by this treatment if the inversion and rotation spacings are of the same order of magnitude and a suitable set of very precise frequencies is available. We have found by a numerical analysis rather large dispersions of values of those constants fitted only to the inversion frequencies. However, with the still more precise frequencies which could be obtained, e.g., by saturation spectroscopy, determination of those constants from the frequencies of transitions allowed by usual selection rules seems to be possible.

TABLE VII
Effective Parameters of the ν_2 Band of $^{14}\text{NH}_3$ (in MHz)^a

Parameter	Our theory	Nielsen-Dennison approximation (13)	Polynomial approximation
$\Delta E^0 \times 10^{-6}$	1.06990261(11)	1.0699016(72)	1.069901(13)
$\Delta B \times 10^{-3}$	- 5.400881(30)	- 5.4045(19)	- 5.4050(32)
$\Delta(C-B) \times 10^{-3}$	7.544906(58)	7.5529(36)	7.5538(63)
$\Delta D_J \times 10^{-1}$	- 1.30075(14)	- 1.3202(89)	- 1.327(14)
$\Delta D_{JK} \times 10^{-1}$	3.56275(45)	3.639(28)	3.660(46)
$\Delta D_K \times 10^{-1}$	- 2.41748(40)	- 2.479(25)	- 2.494(43)
$\Delta H_{JJJ} \times 10^2$	- 1.8310(21)	- 2.12(13)	- 2.25(20)
$\Delta H_{JJK} \times 10^2$	7.3240(89)	8.39(56)	9.00(89)
$\Delta H_{JKK} \times 10^2$	- 9.643(13)	-10.37(82)	-11.3(14)
$\Delta H_{KKK} \times 10^2$	4.1813(68)	3.91(42)	4.40(72)
$\Delta G_{JJJJ} \times 10^5$	1.3215(82)	2.21(51)	2.84(77)
$\Delta G_{JJJK} \times 10^5$	- 6.760(45)	-10.1(28)	-13.8(43)
$\Delta G_{JJKK} \times 10^4$	1.269(11)	1.49(70)	2.3(11)
$\Delta G_{JKKK} \times 10^4$	- 1.036(16)	- 1.0(11)	- 1.8(18)
$\Delta G_{KKKK} \times 10^5$	3.091(99)	4.0(63)	7.0(11)
$B_8 \times 10^{-5}$	3.01896503(71)	3.018980(45)	3.018978(82)
$(C_8 - B_8) \times 10^{-5}$	- 1.1957024(14)	- 1.196012(86)	- 1.19601(15)
$D_J^{(s)} \times 10^{-1}$	3.39019(46)	3.470(28)	3.469(51)
$D_{JK}^{(s)} \times 10^{-1}$	- 7.2604(13)	- 7.652(71)	- 7.65(13)
$D_K^{(s)} \times 10^{-1}$	2.337 ^b	2.337 ^b	2.337 ^b
$H_{JJJ}^{(s)} \times 10^2$	1.6441(69)	2.61(43)	2.55(78)
$H_{JJK}^{(s)} \times 10^2$	- 6.564(33)	- 9.9(21)	- 9.6(38)
$H_{JKK}^{(s)} \times 10^2$	8.799(70)	6.8(45)	6.3(82)
$H_{KKK}^{(s)} \times 10^2$	- 7.315 ^b	- 7.315 ^b	- 7.315 ^b
$\eta_3^0 \times 10^5$	7.94(14)	41.1(62)	-
$(\eta_3^J + 9\eta_3^K) \times 10^7$	- 2.592(81)	- 10.4(51)	-
$\eta_6^0 \times 10^{13}$	- 1.54	- 29.(61)	-
α	- 3.875(19)	-	-
β	- 0.023(50)	-	-
Standard deviation of the fit	0.104	435.7	1506.4

Due to a close coincidence between the $s(3,0)$ and $a(3,3)$ levels in the ν_2 state of $^{14}\text{NH}_3$ (Fig. 5), the $a(3,3)-a(2,0)$ and $s(3,0)-s(3,3)$ transitions in the ν_2 state should have intensities comparable to those of the usual inversion and inversion-rotation transitions (cf. Fig. 6). We detected both perturbation-allowed transitions (Table IV).

The energy difference between the perturbed energy levels $\Delta = a(3,3) - s(3,0)$ can be obtained by combining the frequencies of the "forbidden" and usual inversion-rotation and pure inversion transitions:

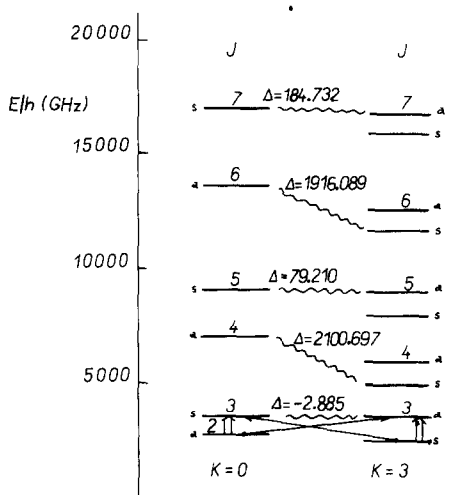


FIG. 5. Vibration-inversion-rotation energy levels with $K = 0$ and 3 of ortho NH_3 in the ν_2 state relatively to the $s(0,0)$ ν_2 energy level; $\Delta = (\frac{s}{a})(J,0) - (\frac{a}{s})(J,3)$.

$$\Delta = [a(3,3) - s(3,3)] - [s(3,0) - s(3,3)] = 2884.1 \text{ MHz} \quad (\equiv 0.096203 \text{ cm}^{-1}), \quad (18a)$$

or

$$\Delta = [a(3,3) - s(2,0)] - [s(3,0) - a(2,0)] = 2884.7 \text{ MHz} \quad (\equiv 0.096223 \text{ cm}^{-1}). \quad (18b)$$

Both values of Δ are in excellent agreement; the difference of 0.6 MHz between the value of Δ obtained from Eqs. (18a) and (18b) is due to the pressure dependence of the line frequencies (cf. Section II).

The $\Delta k = \pm 3$ "forbidden" vibration-inversion-rotation transitions were measured on the ν_2 band of NH_3 by Laughton *et al.* (34) by using infrared-microwave two-photon spectroscopy. As far as we know, our submillimeterwave measurements of the $\Delta k = \pm 3$ transitions are the first measurements of "forbidden" transitions in an excited molecular vibration-rotation state.

We used the precise infrared-microwave two-photon (20, 21), infrared heterodyne measurements (22) of the ν_2 band of $^{14}\text{NH}_3$, and our submillimeterwave

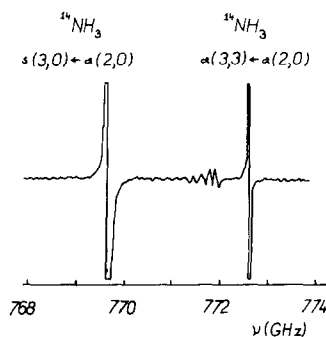


FIG. 6. The lines of the $s(3,0)$ - $a(2,0)$ allowed inversion-rotation transition and the $a(3,3)$ - $a(2,0)$ "forbidden" transition of $^{14}\text{NH}_3$ in the ν_2 state.

frequencies as the data which provide information on the rotational and centrifugal distortion constants of the ν_2 state, such as B_i , $D_J^{(i)}$, $D_{JK}^{(i)}$, etc. These data were used in the method of combination differences, i.e., transitions originating from the same ground-state inversion-rotation level were used to provide information on the upper-state molecular constants.

A simultaneous least-squares fit of our submillimeterwave data and precise infrared data (20–22) was carried out using CDC Cyber 172 computer with double-precision arithmetics (120 bits). The converged values of molecular parameters of the ν_2 state of $^{14}\text{NH}_3$ are given in Table VII. The calculated transition frequencies are compared with the experimental frequencies in Tables III and IV.

We also fitted the experimental data by constraining the parameters α and β [Eq. (16)] at zero values (cf. Tables III and VII). This is essentially equivalent to the use of the theory of Nielsen and Dennison (13); as could be expected, a significantly worse fit to the experimental data was obtained. In the corresponding columns of Tables III and VII, we give the results of the fit in which a simple polynomial approximation including the octic centrifugal distortion constants [cf. Eq. (12)] was used. It is obvious from these results that there is an alternation of the signs of the differences between the experimental and calculated inversion frequencies, $\nu_{\text{obs}} - \nu_{\text{calc}}$, depending on the parity of the rotational quantum number J for $K = 3$, except $J = 3$, $K = 3$ (Table III). This alternation can easily be explained by taking into account that depending on the parity of J , only the upper or lower component of the J , $K = 3$ level is perturbed (Fig. 5). This is analogous to the effect of the $\Delta k = \pm 3$ interaction observed in the ground-state inversion frequencies of ammonia [see, e.g. Ref. (11)]. The anomaly in the $J = 3$, $K = 3$ inversion frequency in the ν_2 state is due to the interlevel crossing of the $J = 3$, $K = 0$ and $J = 3$, $K = 3$ levels (Fig. 5).

In the last column of Table III, the values of $\nu_{\text{obs}} - \nu_{\text{calc}}$ are given where ν_{calc} are transition frequencies between the unperturbed energy levels of the ν_2 state. It is obvious that besides the J , $K = 3$ levels, also other levels are significantly perturbed by the $\Delta k = \pm 3$ interactions. Thus these interactions should be considered as spread over the whole set of energy levels rather than considered as predominantly "local" perturbations of the J , $K = 3n$ levels. Essentially, the same holds for the ground state of NH_3 and this explains the difficulties in fitting the ground-state ammonia spectrum using the standard power series expansion in the rotational quantum numbers J , K (11, 12).

It can be concluded that there are now precise microwave data on the inversion and inversion-rotation transitions in the ground state of ammonia (4–10), as well as precise infrared data on the ν_2 band (20–22, 34), and submillimeterwave data on the inversion and inversion-rotation transitions in the ν_2 excited state of $^{14}\text{NH}_3$ (our measurements). A simultaneous analysis of all these data including the $\Delta k = \pm 3n$ interactions is therefore possible. Such an analysis of data would provide a consistent set of ground-state and ν_2 excited-state NH_3 molecular parameters. Predictions of the so far not measured microwave, infrared, and submillimeter transition frequencies (with the accuracy of experiment) would be another useful result of such work.

This is a formidable numerical task of a least-squares refinement of approximately 80 molecular constants which is now solved in our laboratories.

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