

Coriolis and *I*-Type Interactions in the ν_2 , $2\nu_2$, and ν_4 States of $^{14}\text{NH}_3$

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High-resolution infrared spectra have been remeasured for the ν_2 , $2\nu_2$, and ν_4 bands of $^{14}\text{NH}_3$ using a vacuum grating infrared spectrometer and a diode laser spectrometer. Far-infrared spectra of $^{14}\text{NH}_3$ have been measured with microwave accuracy in the 700–1100 GHz region by employing a submillimeter wave spectrometer (RAD) with acoustic detection. The pure inversion and inversion–rotation transition frequencies in the ν_2 excited state of $^{14}\text{NH}_3$ have been determined for the first time. The vibration–inversion–rotation Hamiltonian of ammonia [Špirko, Stone, and Papoušek, *J. Mol. Spectrosc.* **60**, 159–178 (1976)] has been used for a precise parameterization of the energy levels of ammonia. The ground state rotational and centrifugal constants of $^{14}\text{NH}_3$ have been determined using a modified method of combination differences. Coriolis and *I*-type interactions between ν_2 , ν_4 , $2\nu_2$, $\nu_2 + \nu_4$, and $3\nu_2$ states have been analyzed and the band parameters have been obtained which reproduce the transition frequencies within the accuracy of the experimental data.

I. INTRODUCTION

In previous papers (*I–5*) a new vibration–inversion–rotation Hamiltonian for ammonia has been developed and applied to the available experimental transition frequencies in the infrared, submillimeter, and microwave regions for $^{14}\text{NH}_3$, $^{15}\text{NH}_3$, $^{14}\text{NH}_2\text{D}$, $^{14}\text{ND}_2\text{H}$, $^{14}\text{ND}_3$, and $^{14}\text{NT}_3$. The main purpose of this work is to

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obtain an accurate value of the inversion barrier in ammonia and to discuss certain anomalies in the spectra of this classic example of a nonrigid molecule (5).

In the present paper we have used this Hamiltonian for a precise parameterization of the energy levels of ammonia in the sense of obtaining the effective values of molecular parameters which reproduce the high-resolution infrared, submillimeter, and microwave data to within the accuracy of the experiments. Formulas which are obtained from this Hamiltonian to fit the experimental data are formally identical with those that would be obtained from the standard Darling–Dennison vibrational–rotational Hamiltonian. There are however two main advantages of our approach (Section II): (i) higher-order formulas can be obtained from the lower-order terms in the expansion of our Hamiltonian in terms of Q [cf. (6)]; and (ii) relations of the effective parameters to the basic molecular constants such as the molecular geometry and the potential energy function of ammonia are clearly defined in our treatment.

In the present paper we apply this treatment to the infrared data on $^{14}\text{NH}_3$ measured with the vacuum grating spectrometer at the Ohio State University in Columbus, Ohio, with the diode laser spectrometer at the Los Alamos Scientific Laboratory, and with the submillimeter wave spectrometer RAD at the Institute for Applied Physics at the Academy of Sciences USSR in Gorkii, (Section III). Although the infrared spectrum of ammonia has been studied in considerable detail (7–23), previous measurements (7–13) have been done with much lower resolution than achieved here. With the grating spectrometer, we have measured with resolution of about $0.03\text{--}0.06\text{ cm}^{-1}$ the ν_1 , ν_2 , ν_3 , and ν_4 fundamental bands, the $2\nu_2$ and $2\nu_4$ overtone bands, and the “hot” bands for transitions from the ν_2 level to the $\nu_1 + \nu_2$, $\nu_2 + \nu_3$, ν_4 , and $2\nu_2$ levels of $^{14}\text{NH}_3$. The 10^{-4}-cm^{-1} resolution of the diode laser spectrometer has made it possible to resolve certain features in the ν_2 band that remained unresolved in the grating measurements. We report here also for the first time the measured frequencies of the pure inversion and rotation–inversion transitions in the ν_2 state of $^{14}\text{NH}_3$ at 700–1100 GHz.

Combining these data with some other high- and ultra-high-resolution submillimeter and infrared data on the ν_2 (or $2\nu_2$) band of ammonia (14, 16–20, 22–24), we have determined the ground-state rotational and centrifugal distortion constants of $^{14}\text{NH}_3$ using a modified method of combination differences (Section IV). We have also analyzed in detail the Coriolis and l -type interactions between the ν_2 , ν_4 , $2\nu_2$, $\nu_2 + \nu_4$, and $3\nu_2$ states of ammonia (Section V). The results of analysis of the ν_1 , ν_3 , and $2\nu_4$ states including the perturbation-allowed transitions to the $2\nu_4$ level will be presented in a subsequent paper.

II. PARAMETERIZATION OF THE ENERGY LEVELS OF AMMONIA

If we expand the vibration–inversion–rotation Hamiltonian for NH_3 (1, 4) in the vibrational coordinates Q , and retain only terms of order of magnitude $\kappa^2 T_v$, we obtain

$$H = T_i^0 + T_r^0 + T_{\text{Cent}} + T_{\text{Cor}} + T_{\text{vib}} + V, \quad (1)$$

where

$$T_i^0 = (1/2)\mu_{\rho\rho}^0 J_\rho^2 + (1/2)(J_\rho \mu_{\rho\rho}^0) J_\rho + (1/2)(\mu^0)^{1/4} \{ J_\rho \mu_{\rho\rho}^0 (\mu^0)^{-1/2} [J_\rho (\mu^0)^{1/4}] \} + U_0(\rho), \quad (2)$$

$$T_r^0 = (1/2)\mu_{xx}^0(J_x^2 + J_y^2) + (1/2)\mu_{zz}^0J_z^2, \quad (3)$$

$$T_{\text{Cent}} = (1/2) \sum_{\alpha, \beta=x, y, z, \rho} [\sum_k X_k^{\alpha\beta} Q_k + \sum_{k, l} Y_{kl}^{\alpha\beta} Q_k Q_l] J_\alpha J_\beta \\ + (1/2) \sum_{\alpha=x, y, z, \rho} [\sum_k (J_\rho X_k^{\rho\alpha}) Q_k + \sum_{k, l} (J_\rho Y_{kl}^{\rho\alpha}) Q_k Q_l] J_\alpha, \quad (4)$$

$$T_{\text{Cor}} = -(1/2) \sum_{\alpha=x, y, z, \rho} \mu_{\alpha\alpha}^0 (J_\alpha P_\alpha + P_\alpha J_\alpha) - (1/2) (J_\rho \mu_{\rho\rho}^0) P_\rho, \quad (5)$$

$$T_{\text{Vib}} = (1/2) \sum_k P_k^2 + (1/2) \sum_{\alpha=x, y, z, \rho} \mu_{\alpha\alpha}^0 P_\alpha^2, \quad (6)$$

$$V = V_0(\rho) + \sum_k \kappa_k(\rho) Q_k + (1/2) \sum_k \lambda_k(\rho) Q_k^2 \\ + \sum_{klm} k_{klm}(\rho) Q_k Q_l Q_m + \cdots \quad (7)$$

All the symbols have the same meaning as in Refs. (1, 4, 5); k, l, m take on the values 1, 3a, 3b, 4a, 4b. It should be emphasized that all parameters occurring in Eqs. (2)–(7) are functions of the coordinate measuring the large-amplitude inversion motion.

In the theory of centrifugal distortion described in Ref. (4) we used second-order perturbation theory and evaluated the matrix elements of the vibrational and rotational operators occurring in T_r^0 , T_{Cent} , T_{Vib} , and V . Together with T_i^0 , this gives an effective vibration–inversion–rotation Hamiltonian for NH_3 that contains only functions of ρ and the operator $J_\rho = -i\hbar\partial/\partial\rho$ [Eqs. (14)–(16) in (4)]. If the resulting Schrödinger equation is solved numerically as an “inverse” eigenvalue problem, we can obtain physically reliable information on the molecular potential function of ammonia including the “true” double-minimum potential function for the inversion motion (5). This is, however, a treatment which is not suitable for fitting experimental data with an accuracy comparable to that of the high-resolution infrared and microwave data.

We have now modified the treatment so that the parameterization of the energy levels can be achieved relatively easily. We do not obtain direct information on the whole potential function of ammonia, but effective molecular parameters such as rotational constants, band origins, and interaction parameters are obtained by a least-squares fit.

The basic idea of our treatment consists in the expansion of the ρ -dependent parameters in Eqs. (3)–(7) as a power series in the large-amplitude coordinate ρ in the point of the planar reference configuration of the atomic nuclei ($\rho = \pi/2$). The choice of the planar reference configuration in this expansion is the most natural from the point of view of the symmetry of the problem. All the ρ -dependent terms are either even or odd functions of $\bar{\theta} = \rho - \pi/2$ [A_1' or A_2'' species in the D_{3h} permutation-inversion group of NH_3 (1, 5)]. Let us denote these parameters in general as $M_p^{(A_1')}$ and $M_p^{(A_2')}$. We can write

$$M_p^{(A_1')} = {}^{(0)}M_p^{(A_1')} + {}^{(1)}M_p^{(A_1')}\bar{\theta}^2 + {}^{(2)}M_p^{(A_1')}\bar{\theta}^4 + \cdots, \quad (8a)$$

$$M_p^{(A_2')} = {}^{(1)}M_p^{(A_2')}\bar{\theta} + {}^{(2)}M_p^{(A_2')}\bar{\theta}^3 + \cdots, \quad (8b)$$

where ${}^{(s)}M_p$ are ρ -independent coefficients depending only on the molecular geometry and atomic masses.

If we substitute Eq. (8) into Eqs. (3)–(7), Eq. (1) can be written in the following form:

$$H = [T_i^0 + V_0(\bar{\theta})] + [(1/2) \sum_k P_k^2 + (1/2) \sum_k {}^{(0)}\lambda_k Q_k^2] \\ + [(1/2){}^{(0)}\mu_{xx}^0(J_x^2 + J_y^2) + (1/2){}^{(0)}\mu_{zz}^0 J_z^2] + H' \\ = H_0 + H', \quad (9)$$

where

$$H' = (1/2) \sum_{s=1} [{}^{(s)}\mu_{xx}^0 \bar{\theta}^{2s}(J_x^2 + J_y^2) + {}^{(s)}\mu_{zz}^0 \bar{\theta}^{2s} J_z^2] + T_{\text{Cent}} + T_{\text{Cor}} \\ + (1/2) \sum \mu_{\alpha\alpha}^0 p_\alpha^2 + \sum_k \sum_s {}^{(s)}\lambda_k \bar{\theta}^{2s} Q_k^2 + \sum_{klm} k_{klm} Q_k Q_l Q_m. \quad (10)$$

Wavefunctions ψ_0 that are solutions of the Schrödinger equation

$$H_0 \psi_0 = E_0 \psi_0 \quad (11)$$

can be written as the product functions

$$\psi_0(\bar{\theta}; \theta, \Phi, \chi; Q) = [\psi_i(\bar{\theta})][S_{Jkm}(\theta, \Phi) \exp(ik\chi)][\prod_v \psi_v^0(Q)], \quad (12)$$

where v is summed over 1, 3a, 3b, 4a, 4b; here $\psi_i(\bar{\theta})$ are the inversion wavefunctions, $S_{Jkm}(\theta, \Phi) \exp(ik\chi)$ the symmetric rotor wavefunctions, and $\psi_v^0(Q)$ the harmonic oscillator wavefunctions. The inversion wavefunctions $\psi_i(\bar{\theta})$ are not obtained in the present treatment by a numerical integration of the Schrödinger equation with the operator $T_i^0 + V_0(\bar{\theta})$; they are assumed to be known.

The product functions (12) are basis functions in which the Schrödinger problem with the Hamiltonian H is solved either by standard perturbation methods or by a variational approach (if there is a close coincidence of the interacting levels). In this Section, only a simple example will be discussed to demonstrate the usefulness of this approach.

Let us consider the so-called rigid bender approximation which has been treated numerically in Refs. (1, 2) to obtain information on the inversion potential function in ammonia. The rigid bender Hamiltonian H_{rb}^0 can be written in the form (1)

$$H_{\text{rb}}^0 = [T_i^0 + V_0(\bar{\theta})] + (1/2)\mu_{xx}^0(J^2 - J_z^2) + (1/2)\mu_{zz}^0 J_z^2. \quad (13)$$

If we expand μ_{xx}^0 and μ_{zz}^0 in a power series according to Eq. (8a), H_{rb}^0 has diagonal and off-diagonal matrix elements in $\psi_i(\bar{\theta})(\equiv |i\rangle)$:

$$(hc)^{-1} \langle v; J, k, m; i | H_{\text{rb}}^0 | v; J, k, m; i \rangle \\ = E_i^0/hc + (h/4\pi^2c)[{}^{(0)}\mu_{xx}^0 + \sum_{s=1} {}^{(s)}\mu_{xx}^0 \langle i | \bar{\theta}^{2s} | i \rangle][J(J+1) - k^2] \\ + (h/4\pi^2c)[{}^{(0)}\mu_{zz}^0 + \sum_{s=1} {}^{(s)}\mu_{zz}^0 \langle i | \bar{\theta}^{2s} | i \rangle]k^2 \\ = E_i^0/hc + B_i J(J+1) + (C_i - B_i)k^2, \quad (14)$$

$$(hc)^{-1} \langle v; J, k, m; i | H_{\text{rb}}^0 | v; J, k, m; i+2 \rangle \\ = (h/4\pi^2c)[\sum_{s=1} {}^{(s)}\mu_{xx}^0 \langle i | \bar{\theta}^{2s} | i+2 \rangle][J(J+1) - k^2] \\ + (h/4\pi^2c)[\sum_{s=1} {}^{(s)}\mu_{zz}^0 \langle i | \bar{\theta}^{2s} | i+2 \rangle]k^2. \quad (15)$$

If we treat this problem by the standard perturbation theory up to third order, we obtain the well-known formula for the energy levels of a nondegenerate vibrational state and the i th inversion state including sextic centrifugal distortion coefficients:

$$\left(\frac{E_i}{hc}\right) = \left(\frac{E_i^0}{hc}\right) + B_i J(J+1) + (C_i - B_i)k^2 - D_J^{(i)} J^2(J+1)^2 - D_{JK}^{(i)} J(J+1)k^2 - D_K^{(i)} k^4 + H_{JJJ}^{(i)} J^3(J+1)^3 + H_{JJK}^{(i)} J^2(J+1)^2 k^2 + H_{JKK}^{(i)} J(J+1)k^4 + H_{KKK}^{(i)} k^6. \quad (16)$$

It should be mentioned that from the mathematical point of view such a treatment is correct if the series expansions (8) are convergent. We have verified a rapid convergence of the series expansions of all parameters occurring in the Hamiltonian H in Eq. (1), which justifies our procedure.

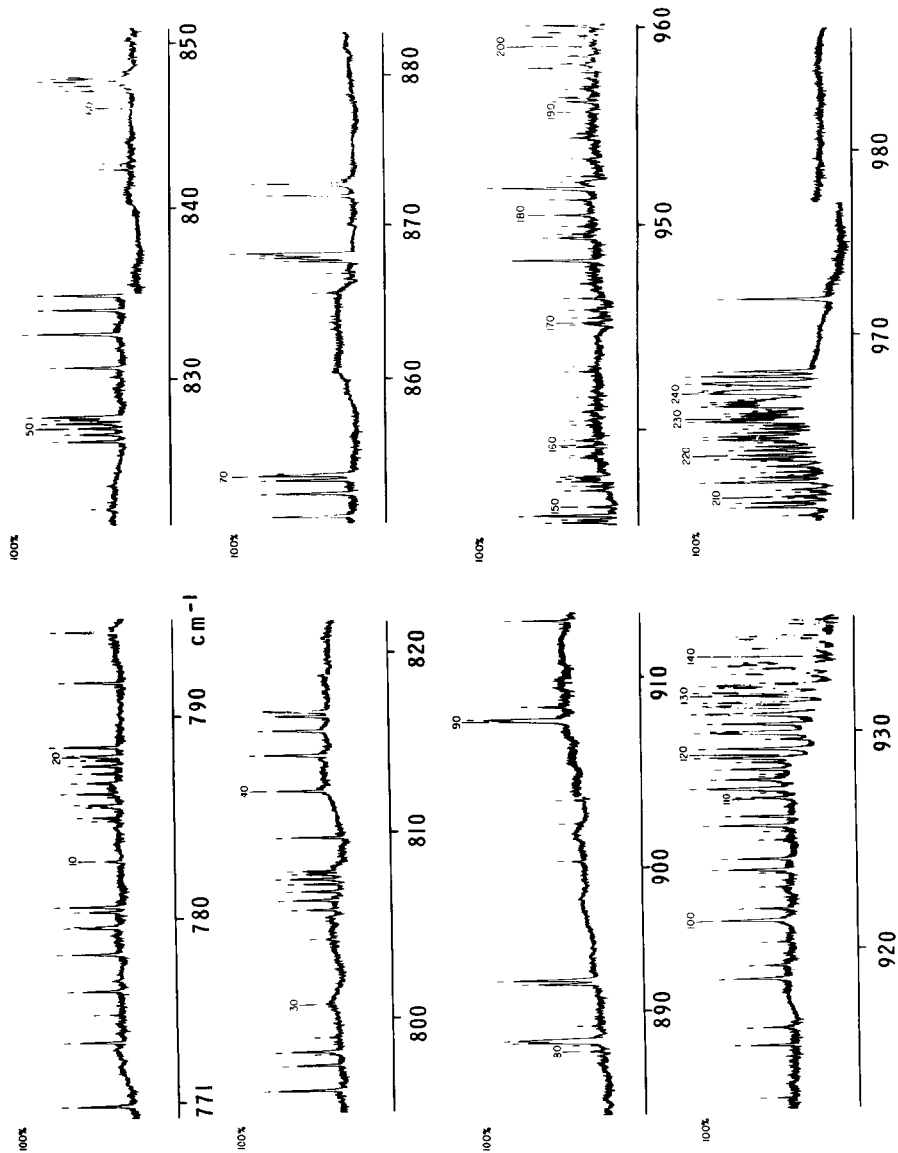
Rotational and centrifugal distortion coefficients in Eq. (16), and in other relations which could be obtained from higher-order terms in the Hamiltonian by perturbation treatment, are effective parameters for the i th inversion state. Their relation to the coefficients of the expansion (8a) could be found in explicit form. The algebra involved in such a treatment is straightforward but rather lengthy and will not be carried out in this paper. Instead we concentrate on the determination of the effective molecular parameters by a least-squares fit to the experimental data (Sections IV–VI).

It should be noted that in our approach to the parameterization of the energy levels, NH_3 is treated as a planar molecule of D_{3h} symmetry with a large-amplitude motion. Because we use the model Hamiltonian described in Refs. (1, 4, 5), such an approach is physically correct and its advantage is that higher-order effects can be described in a lower-order treatment (see the above discussion of the rigid bender approximation). Previous approaches (e.g., (7, 25)) considered ammonia as a molecule of C_{3v} symmetry and the vibration–rotation Hamiltonian was expanded in terms of Q in the point group of the equilibrium configuration. Strictly speaking this is not physically correct, and the relation between the effective molecular parameters and the true physical parameters is not clear in such a treatment, especially for the excited vibrational–rotational states.

III. HIGH-RESOLUTION INFRARED MEASUREMENTS

The ν_2 and ν_4 bands of ammonia in the infrared were recorded with a 3.5-m focal length vacuum grating infrared spectrometer at the Ohio State University equipped with a 9 in. \times 6 in. (22½ cm \times 15 cm) Bausch and Lomb grating with 40 grooves per millimeter and used echelle fashion. The gas sample used was supplied by Matheson and Company and was quoted to have a purity of 99.4% of $^{14}\text{NH}_3$. The source of continuous radiation was a carbon rod furnace. The measurements were made relative to the 1–0 band lines of CO and the accuracy is believed to be about 0.005 cm^{-1} . Other experimental details have been given in detail by Curtis (26). Figures 1a, 1b, and 1c display the spectra recorded, along with pressures and path lengths used for the ammonia gas.

Portions of the ν_2 band were examined under Doppler-limited resolution using the diode laser spectrometer at Los Alamos Scientific Laboratory (27). This was



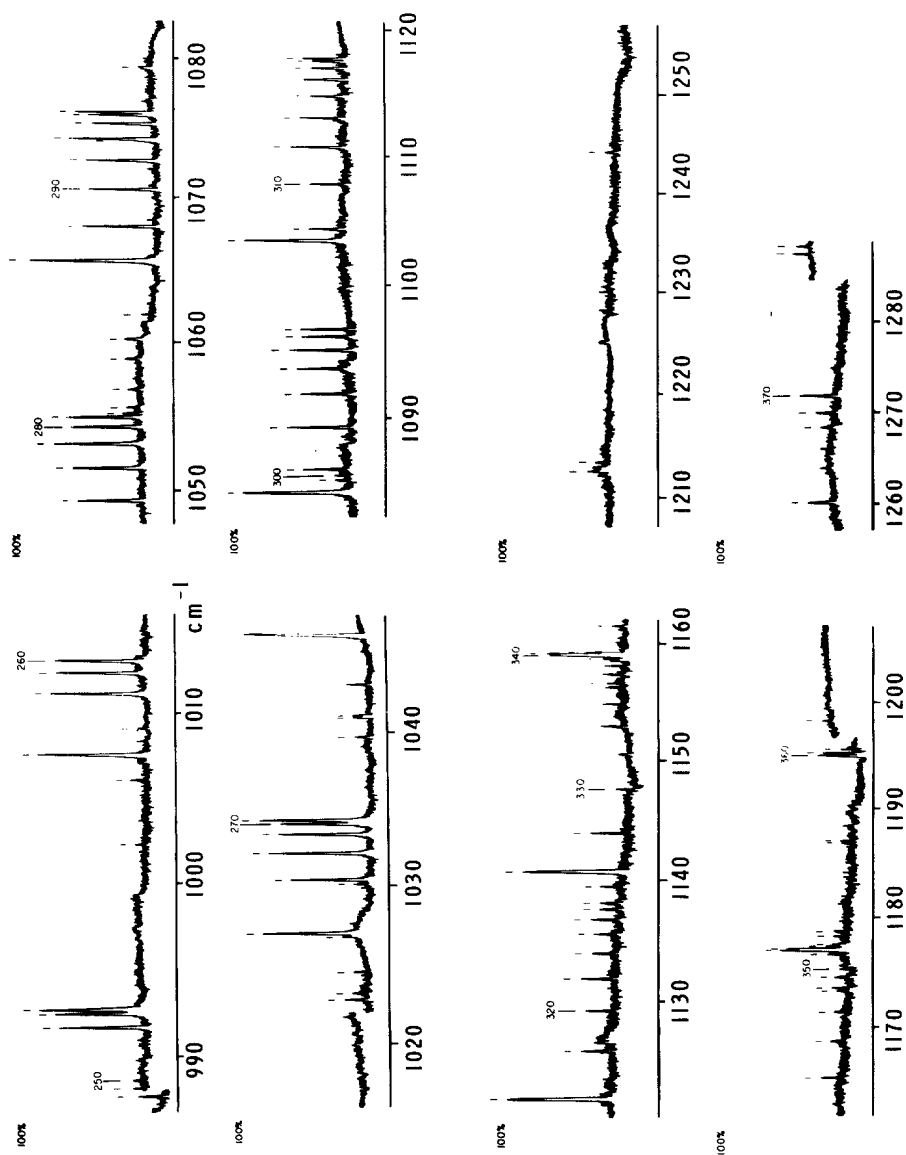
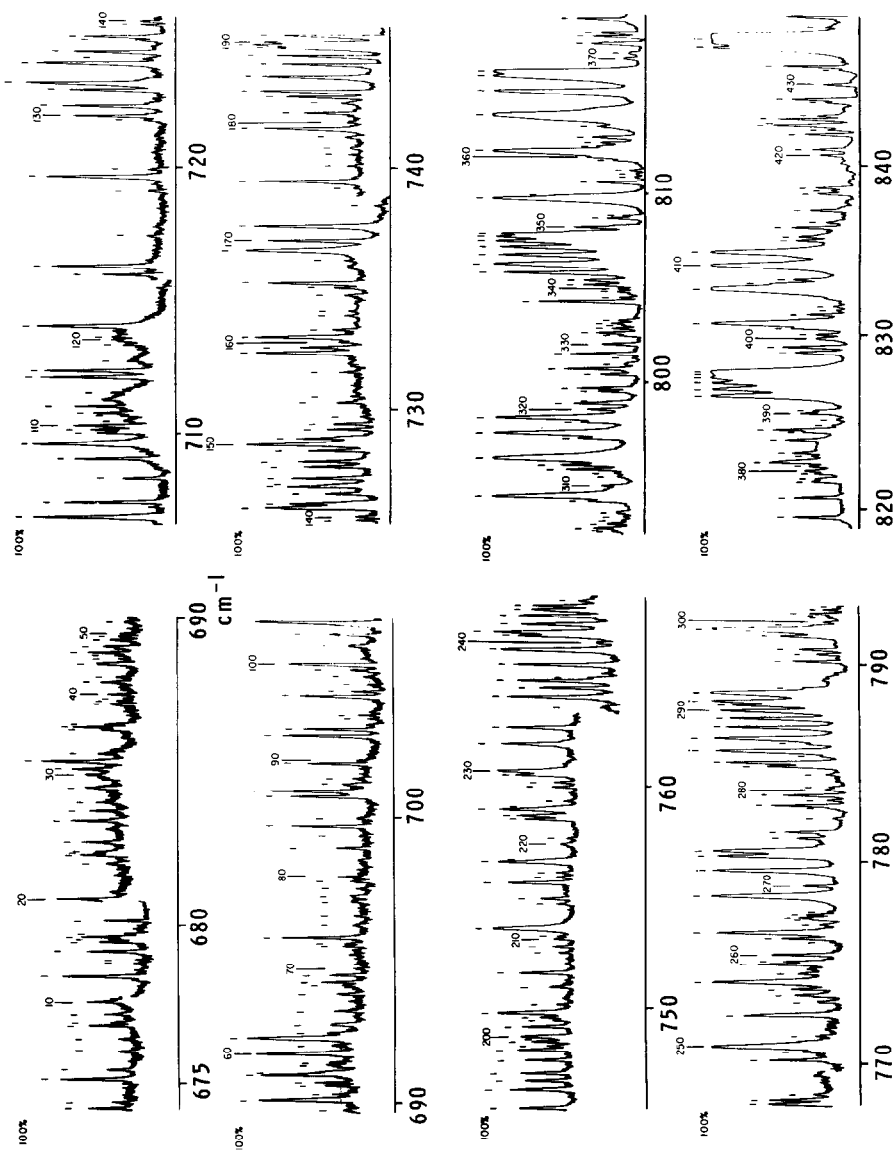


FIG. 1a. Low-pressure grating spectra in the ν_2 region of ammonia. Gas pressure used was 2 mm Hg in a 1-m-long absorption cell. At the upper and lower ends of the spectrum some data were observed with a sample pressure of 5.5 mm Hg.



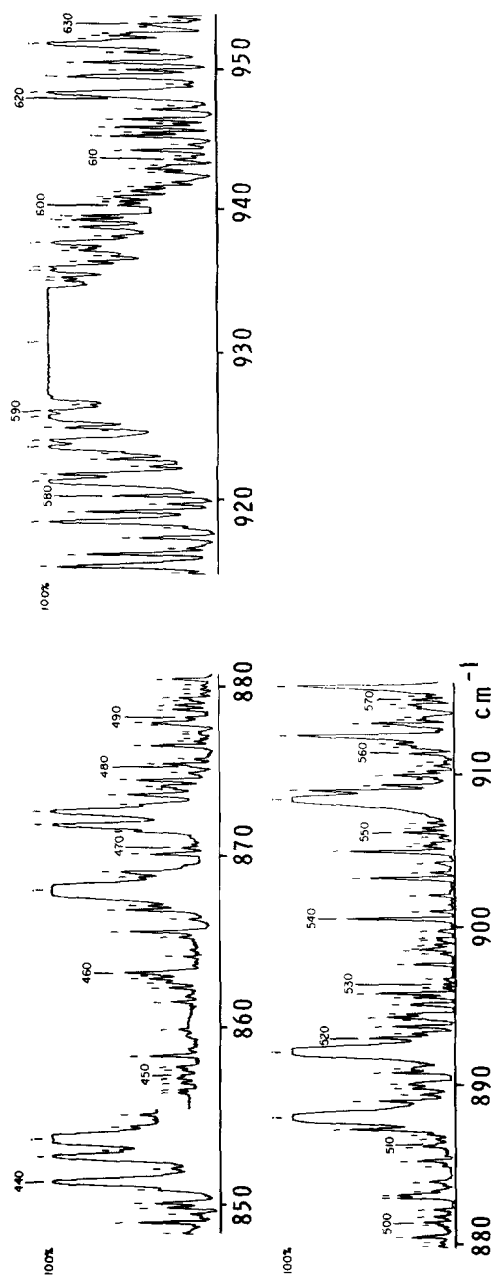
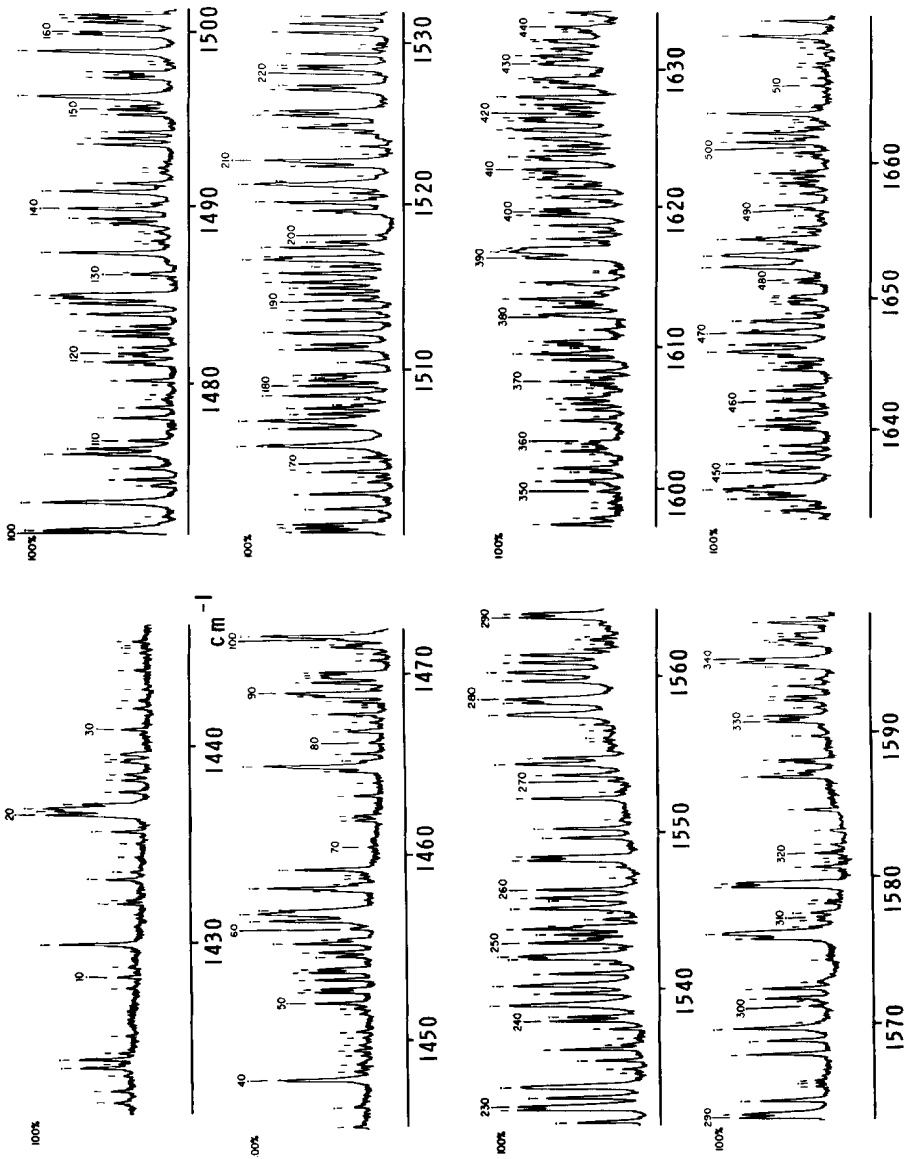


FIG. 1b. High-pressure grating spectra in the ν_2 region of ammonia. Gas pressure used was 1 cm Hg in an 11-m path. A line that has a dot over it is a blend of lines that are resolved in the low-pressure data.



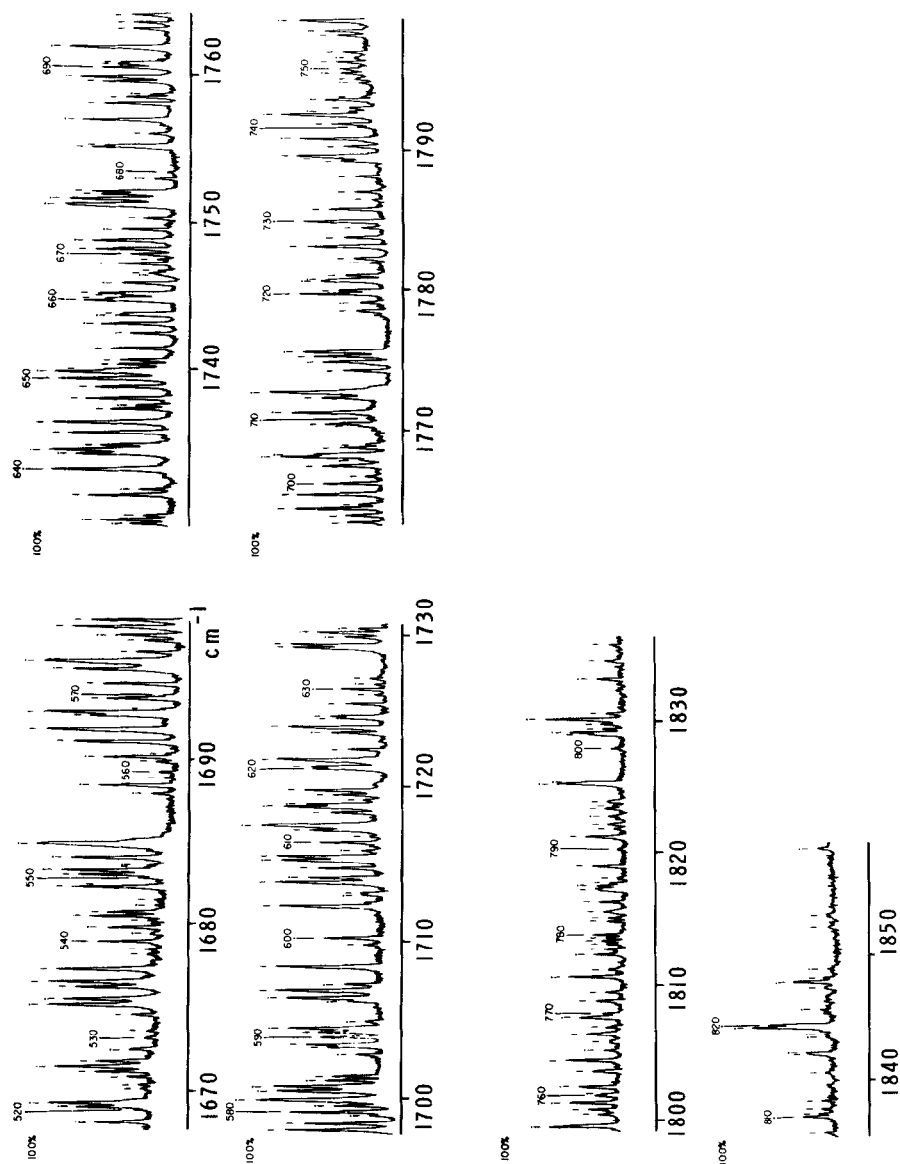


FIG. 1c. Grating spectra of the ν_4 region of ammonia. Gas pressure used was 1 cm Hg in a 1-m-long absorption cell. Line with a dot over it is an H_2O line or a blend with an H_2O line.

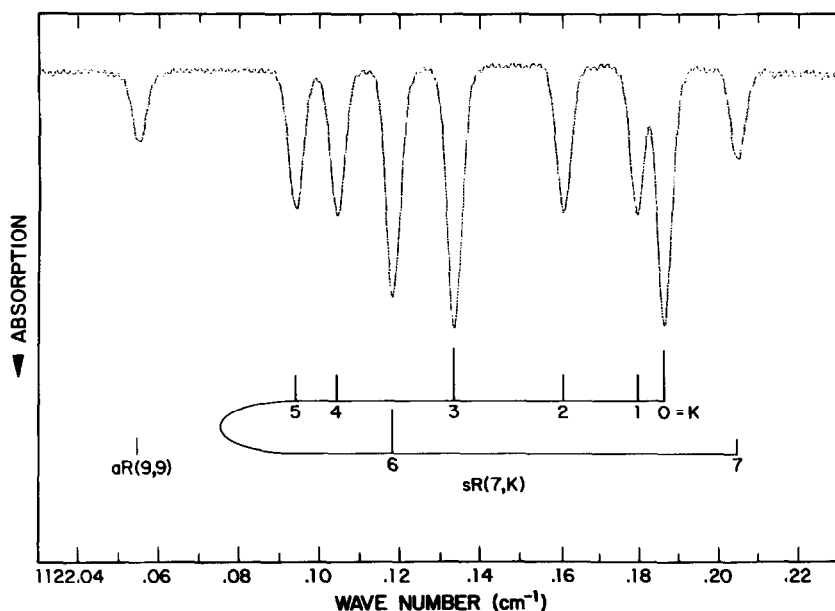


FIG. 2. The spectrum of $^{14}\text{NH}_3$ between 1122.03 and 1122.23 cm^{-1} as recorded with a tunable semiconductor diode laser, showing $sR(7,K)$ and $aR(9,9)$. Sample pressure was ~ 0.1 Torr in a 40-cm cell.

particularly useful for resolving the $sR(J,K)$ groupings; $sR(7,K)$ is shown as an example in Fig. 2. Relative line separations in these spectra were measured against simultaneously recorded interference fringes from a germanium etalon. Absolute wavenumbers were then obtained by referencing the lines to one transition in each group whose wavenumber had been very accurately determined as described in the next paragraph.

Experimental transition wavenumbers for the ν_2 , $2\nu_2$, and ν_4 bands together with their assignments are given in Tables I to III. In the case of the ν_2 band, we have also used the precise values of the pure inversion transition frequencies and inversion-rotation transition frequencies in the ν_2 excited state as measured by a submillimeter wave spectrometer, RAD³ (28–30), the infrared-microwave two-photon measurements (16, 17, 31) of the vibration-inversion-rotation transitions to the ν_2 state, and the ground-state pure inversion transition frequencies (32) to obtain precise frequencies of certain vibration-inversion-rotation transitions to the ν_2 state (see Fig. 3 and Table I).

The submillimeter-wave line centers of $^{14}\text{NH}_3$ were found to depend linearly on the pressure of the ammonia gas in the range 0.2–2 Torr (e.g., the slopes of the $J,K = 1,1$ and $2,2$ pure inversion transitions in the ν_2 state of $^{14}\text{NH}_3$ were found to be -2.4 MHz/Torr and $+1.5$ MHz/Torr, respectively). Most of the transition frequencies in Table IV were measured at a single value of pressure (in the range

³ The particular system of frequency stabilization of the backward wave oscillator used (Belov, Gershstein, and Maslovskii, in "Proceedings of the IV All Union Symposium on Molecular Spectroscopy of High and Superhigh Resolution, Tomsk-Novosibirsk, 1978") makes it possible to measure frequencies to a very high degree of accuracy.

TABLE I

Observed and Calculated Transition Wavenumbers in the ν_2 Band of $^{14}\text{NH}_3$ (cm^{-1})^a

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$
sP				aP			
1	0	948.2328 ⁱ 948.232	948.2323	-0.0005
2	0	892.158	892.1570	-0.001
2	1	928.230	928.2322	0.002	891.884	891.8825	-0.001
3	0	908.190	908.1988	0.009
3	1	908.1785 ^h	908.1767	-0.0018	872.565	872.5667	0.002
3	2	908.115	908.1124	-0.002	871.737	871.7371	0.000
4	0	*853.817	853.8186	0.002
4	1	888.0779 ^f 888.035 ^b	888.0788	0.0009	853.5467 ^h 853.549	853.5472	0.0005
4	2	887.9988 ^f	887.9995	0.0007	852.7237 ^h 852.727	852.7239	0.0002
4	3	*887.87683 ^g 887.8773 ^f 887.878	887.8746	-0.0022	*851.32692 ^h 851.330	851.3271	0.0002
5	0	*867.980 ^b	868.0003	0.020
5	1	*867.980 ^b	867.9682	-0.012	834.826	834.8230	-0.003
5	2	*867.882 ^b	867.8723	-0.010	834.013	834.0112	-0.002
5	3	*867.717	867.7193	0.002	*832.635	832.6338	-0.001
5	4	867.517	867.5204	0.003	830.654	830.6533	-0.001
6	0	*816.649	816.6459	-0.003
6	1	847.876	847.8756	-0.000	816.388	816.3864	-0.002
6	2	847.765	847.7622	-0.003	815.585	815.5911	0.006
6	3	*847.578	847.5795	0.002	*814.239	814.2418	0.002
6	4	847.336	847.3375	0.001	812.297	812.3002	0.003
6	5	847.053	847.0517	-0.001	809.714	809.7151	0.001
7	0	*827.857 ^b	827.8748	0.018
7	1	*827.857 ^b	827.8329	-0.024	798.228	798.2239	-0.004
7	2	827.703	827.7014	-0.002	797.451	797.4491	-0.002
7	3	*827.491	827.4878	-0.003	*796.131	796.1347	0.004
7	4	827.202	827.2012	-0.001	794.240	794.2444	0.004
7	5	826.854	826.8553	0.001	791.723	791.7261	0.003
7	6	826.470	826.4705	0.000	788.506	788.5112	0.005
8	0	*780.565 ^b	780.5523	-0.013
8	1	807.873	807.8714	-0.002	780.309	780.3161	0.007
8	2	807.716	807.7216	0.006	779.564	779.5657	0.002
8	3	*807.468	807.4768	0.009	*778.290	778.2932	0.003
8	4	807.148	807.1449	-0.003	776.458	776.4637	0.006
8	5	806.744	806.7382	-0.006	774.020	774.0264	0.006
8	6	806.281	806.2744	-0.007	770.913	770.9130	-0.000
8	7	805.775	805.7788	0.004	767.037	767.0387	0.002
9	0	*788.079 ^b	788.0707	-0.008
9	1	*788.034 ^b	788.0213	-0.013	762.639	762.6409	0.002
9	2	787.853	787.8533	0.000	761.921	761.9176	-0.003
9	3	*787.572	787.5776	0.006	*760.695	760.6919	-0.003
9	4	787.197	787.2009	0.004	758.927 ^b	758.9313	0.004
9	5	786.728	786.7334	0.006	756.586	756.5871	0.001
9	6	786.184 ^b	786.1914	0.007	753.590	753.5922	0.002
9	7	785.594	785.5964	0.002	749.862	749.8612	-0.001
9	8	784.976	784.9790	0.003	745.295	745.2938	-0.001

^a Our infrared grating measurements unless stated otherwise; asterisk denotes that this value has not been used in the fit.^b Blended line.^c Ref. (16).^d Ref. (14).^e Ref. (31).^f Ref. (17).^g Ref. (19).

TABLE I—Continued

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$
sP				aP			
10	0	*745.409 ^b	745.3761	-0.033
10	1	*768.309 ^b	768.3114	0.002	*745.194 ^b	745.1760	-0.018
10	2	*768.107 ^b	768.1258	0.019	744.490 ^b	744.4809	-0.009
10	3	*767.812	767.8199	0.008	*743.312	743.3047	-0.007
10	4	767.408	767.3994	-0.009	741.622	741.6179	-0.004
10	5	766.877	766.8733	-0.004	739.384	739.3754	-0.009
10	6	766.241 ^b	766.2545	0.013	736.513	736.5129	-0.000
10	7	765.565	765.5621	-0.003	732.949	732.9456	-0.003
10	8	764.824	764.8227	-0.001	728.580 ^b	728.5700	-0.010
10	9	764.074	764.0734	-0.001	723.275	723.2714	-0.004
11	0	*748.810 ^b	748.8207	0.011
11	1	*748.810 ^b	748.7689	-0.041	727.910	727.9026	-0.007
11	2	748.574 ^b	748.5663	-0.008	727.251	727.2350	-0.016
11	3	*748.228 ^b	748.2313	0.003	*726.109 ^b	726.1077	-0.001
11	4	747.765	747.7687	0.004	724.517	724.4956	-0.021
11	5	747.179	747.1858	0.007	722.368	722.3585	-0.009
11	6	746.492	746.4935	0.001	719.647	719.6368	-0.010
11	7	745.703	745.7076	0.005	716.248	716.2486	0.001
11	8	744.849	744.8512	0.002	712.095	712.0894	-0.006
11	9	743.961	743.9555	-0.006	707.051	707.0372	-0.014
11	10	743.078	743.0644	-0.014	700.965	700.9650	0.000
12	0	*711.029	710.9625	-0.066
12	1	729.419	729.4196	0.001	*710.796 ^b	710.8116	0.016
12	2	729.209	729.2006	-0.008	710.175	710.1682	-0.007
12	3	*728.822	728.8378	0.016	*709.098 ^b	709.0851	-0.013
12	4	728.331	728.3350	0.004	*707.585 ^b	707.5430	-0.042
12	5	727.699	727.6980	-0.001	*705.550 ^b	705.5084	-0.042
12	6	726.943	726.9357	-0.007	702.943	702.9287	-0.014
12	7	*726.109 ^b	726.0615	-0.047	699.727	699.7273	0.000
12	8	725.101	725.0940	-0.007	695.790	695.8018	0.012
12	9	724.052 ^b	724.0600	0.008	691.030	691.0257	-0.004
12	10	723.007	722.9965	-0.011	685.281	685.2589	-0.022
12	11	721.978	721.9546	-0.023	678.376	678.3670	-0.009
13	0	*710.329 ^b	710.3367	0.008
13	1	*710.329 ^b	710.2892	-0.040	*698.811 ^b	693.9096	0.099
13	2	*710.069 ^b	710.0545	-0.015	*693.233 ^b	693.2841	0.051
13	3	*709.669 ^b	709.6649	-0.003	*692.298 ^b	692.2358	-0.062
13	4	*709.098 ^b	709.1235	0.026	690.767	690.7523	-0.017
13	5	708.420	708.4349	0.015	*688.849 ^b	688.8087	-0.040
13	6	*707.585 ^b	707.6063	0.021	*686.391 ^b	686.3621	-0.029
13	7	706.645	706.6485	0.003	*683.356 ^b	683.3448	-0.011
13	8	*705.550 ^b	705.5769	0.027	679.653	679.6597	0.007
13	9	704.411	704.4136	0.003	*675.156 ^b	675.1800	0.024
13	10	703.197	703.1896	-0.006		669.7556	
13	11	701.962	701.9477	-0.014		663.2297	
13	12	700.774 ^b	700.7468	-0.027		655.4683	
sQ				aQ			
1	1	967.99774 ^c 967.995	967.9980	0.0003	931.62776 ^h 931.6280 ^f 931.632	931.6286	0.0008

^b Value calculated from the microwave ground state inversion frequencies, the submillimeter ν_2 inversion frequencies, and the high-resolution infrared vibration-inversion-rotation transition frequencies (see text).

^c Ref. (20).

^d Value calculated from the frequency difference (resolved K structure) in Ref. (18).

^e Value calculated from the microwave ground-state inversion frequencies, the submillimeter ν_2 inversion-rotation frequencies, and the high-resolution infrared vibration-inversion-rotation transition frequencies (see text).

^f Our diode laser measurements.

TABLE I—Continued

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$
sQ				aQ			
2	1	967.77467 ^h 967.777 ^d	967.7748	0.0001	932.13610 ^c 932.107 ^b	932.1361	0.0000
2	2	967.73860 ^h 967.73859 ^c 967.73841 ^g 967.749	967.7386	0.0000	931.33342 ^g 931.33348 ^f 931.3336 ^c 931.332	931.3338	0.0004
3	1		967.4490		932.886	932.8806	-0.005
3	2	967.40680 ^h 967.4073 ^c	967.4067	-0.0001	932.09402 ^c 932.107 ^b	932.0936	-0.0005
3	3	*967.34632 ^c 967.367	967.3441	-0.0022	*930.75697 ^h 930.7557 ^c 930.760	930.7574	0.0004
4	1	967.0302 ^h 966.965 ^b	967.0307	0.0005	933.8419 ^f 933.833 ^b	933.8422	0.0003
4	2	966.9814 ^h 966.965 ^b	966.9808	-0.0006	933.0762 ^c 933.063	933.0753	-0.0009
4	3	*966.908 ^d 966.898	966.9049	-0.003	*931.773	931.7729	-0.000
4	4	966.8150 ^h 966.816 ^d 966.814	966.8148	-0.0002	929.8982 ^f 929.8984 ^c 929.894	929.8984	0.0002
5	1	966.530	966.5324	0.002	934.999	934.9948	-0.004
5	2	966.4739 ^h 966.475 ^d 966.476	966.4735	-0.0004	934.2524 ^f 934.244 ^b	934.2526	0.0002
5	3	*966.37987 ^h 966.3804 ^c 966.379	966.3821	0.0022	*932.99243 ^c 932.99226 ^g 932.994	932.9919	-0.0005
5	4	966.26931 ^c 966.26935 ^g 966.268	966.2691	-0.0002	931.17745 ^h 931.17735 ^c 931.1776 ^f 931.165	931.1766	-0.0009
5	5	966.15100 ^c 966.151	966.1512	0.0002	928.7543 ^f 928.7547 ^c 928.755	928.7549	0.0006
6	1	*965.982 ^b	965.9678	-0.014	936.311	936.3068	-0.004
6	2	965.904	965.8989	-0.005	935.592	935.5933	0.001
6	3	*965.792 ^d 965.787	965.7904	-0.002	*934.377	934.3814	0.004
6	4	965.65222 ^h 965.6520 ^c 965.649	965.6521	-0.0001	932.63589 ^f 932.63582 ^g 932.634	932.6359	0.0000
6	5	965.49939 ^h 965.501 ^d 965.496	965.4993	-0.0001	930.30653 ^c 930.309	930.3058	-0.0007
6	6	965.355 ^d 965.352	965.3540	-0.001	927.32328 ^f 927.32323 ^g 927.3234 ^c 927.326	927.3240	0.0008
7	1	*965.360 ^b	965.3515	-0.008	937.736	937.7424	0.006
7	2		965.2720		937.063	937.0609	-0.002
7	3	*965.1373 ^c	965.1452	0.0079	*935.9034 ^h	935.9038	0.0004

TABLE I—Continued

J	K	v_{obs}	v_{calc}	$v_{\text{calc}} - v_{\text{obs}}$	v_{obs}	v_{calc}	$v_{\text{calc}} - v_{\text{obs}}$
		sQ			aQ		
7	4	965.140 964.9797 ^h 964.982 ^d 964.982	964.9800	0.0003	935.914 ^b 934.2358 ^f 934.244 ^b	934.2372	0.0014
7	5	964.79006 ^c 964.790	964.7903	0.0002	932.01111 ^h 932.014	932.0117	0.0006
7	6	964.5954 ^c 964.596 ^b	964.5957	0.0003	929.1616 ^f 929.161	929.1607	-0.0009
7	7	964.42410 ^c 964.428 ^b	964.4241	0.0000	*925.5977 ^f 925.598	925.6016	0.0039
8	1		964.6981		939.256 ^b	939.2637	0.008
8	2	*964.596 ^b	964.6077	0.012	*938.625 ^b	938.6164	-0.009
8	3	*964.428 ^b	964.4621	0.034	*937.516	937.5182	0.002
8	4	964.271	964.2692	-0.002	*935.914 ^b	935.9376	0.024
8	5	964.04115 ^h 964.044	964.0413	0.0002	933.82600 ^c 933.8265 ^f 933.833 ^b	933.8275	0.0015
8	6	963.79607 ^h 963.651 ^d 963.787	963.7962	0.0001	931.12190 ^c 931.1227 ^f 931.124 ^b	931.1227	0.0008
8	7	963.55939 ^h 963.5582 ^c 963.555	963.5587	-0.0007	927.74196 ^c 927.739	927.7403	-0.0017
8	8	963.36262 ^c 963.362	963.3627	0.0001	923.582	923.5827	0.001
9	1		964.0219		*940.850 ^b	940.8335	-0.016
9	2		963.9206		*940.235 ^b	940.2212	-0.014
9	3		963.7560		*939.197	939.1837	-0.013
9	4	963.5343 ^h	963.5352	0.0009	937.6989 ^f 937.701	937.6929	-0.0060
9	5	963.276 ^b	963.2691	-0.007	935.710	935.7053	-0.005
9	6	962.97368 ^c 962.975	962.9733	-0.0003	933.15745 ^h 933.1571 ^c 933.152	933.1588	0.0013
9	7	962.6705 ^h 962.6736 ^c 962.673	962.6698	-0.0007	929.9711 ^f 929.969 ^d 929.954	929.9712	0.0001
9	8	962.38850 ^h 962.3878 ^c 962.389	962.3888	0.0003	926.04584 ^c 926.047	926.0424	-0.0034
9	9	962.167	962.1715	0.004	921.255	921.2611	0.006
10	1		963.3374		942.4206 ⁱ	942.4201	-0.0005
10	2		963.2250		*941.872 ^b	941.8415	-0.030
10	3		963.0415		*940.850 ^b	940.8632	0.013
10	4		962.7931		*939.488 ^b	939.4618	-0.026
10	5	962.4895 ^h	962.4892	-0.0003	937.6119 ^f 937.605	937.5988	-0.0132
10	6	962.1448 ^h	962.1435	-0.0013	935.2216 ^f 935.223	935.2169	-0.0047
10	7	*961.760 ^b	961.7752		932.233 ^d 932.233	932.2373	0.004
10	8	961.4113 ^h 961.409	961.4110	-0.0003	928.5581 ^f 928.559	928.5590	0.0009

TABLE I—Continued

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{ob}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{ob}}$
				SQ			
10	9	961.086	961.0870	0.001	924.068	924.0639	-0.004
10	10	960.85232 ^c 960.857	960.8522	-0.0001	918.6209 ^f 918.620	918.6296	0.0087
11	1		962.6590			944.0025	
11	2		962.5357		943.4481 ⁱ 943.486 ^b	943.4536	0.0054
11	3		963.3334		*942.5667 ⁱ 942.569	942.5290	-0.0377
11	4		962.0576		*941.255 ^b	941.2108	-0.044
11	5		961.7165		*939.488 ^b	939.4676	-0.020
11	6	*961.325 ^b	961.3219	-0.003	937.273 ^b	937.2494	-0.024
11	7	*960.857 ^b	960.8908	0.034	934.471 ^b	934.4829	0.011
11	8	960.446	960.4463	0.000	*931.124 ^b	931.0693	-0.055
11	9	960.01990 ^c 960.019	960.0199	0.0000	926.88456 ^h 926.8844 ^c 926.887	926.8868	0.0022
11	10	959.656	959.6544	-0.002	921.8120 ^f 921.810	921.7999	-0.0121
11	11	959.408	959.4071	-0.001	915.665	915.6800	0.015
12	1		962.0032			945.5772	
12	2		961.8687		*945.0918 ^{ib}	945.0511	-0.0407
12	3		961.6475		*944.1835 ⁱ	944.1696	-0.0141
12	4		961.3442		*942.9368 ^{ib}	942.9217	-0.0151
12	5		960.9662			941.2849	
12	6		960.5237			939.2191	
12	7		960.0315			936.6600	
12	8		959.5098		*933.501 ^b	933.5147	0.014
12	9	958.975	958.9858	0.011		929.6612	
12	10	958.499	958.4968	-0.002	924.9499 ^e 924.942	924.9547	0.0048
12	11	958.089	958.0924	0.003	919.264	919.2443	-0.020
12	12	957.835	957.8390	0.004	912.385	912.4029	0.018
				SR			
0	0	951.7794 ⁱ 951.775	951.7769	-0.0025
1	0	1007.5474 ^j 1007.544 ^b	1007.5471	-0.0003
1	1	1007.54068 ^h 1007.544 ^b	1007.5406	-0.0001	971.88224 ^g 971.88204 ^c 971.882	971.8821	-0.0001
2	0	*992.694	992.7003	0.006
2	1	1027.0467 ^f 1027.040 ^b	1027.0471	0.0004	992.45019 ^k 992.452	992.4500	-0.0002
2	2	1027.0331 ^h 1027.0335 ^f 1027.040 ^b	1027.0329	-0.0002	991.69069 ^k 991.6914 ^c 991.690	991.6903	-0.0004
3	0	*1046.4056 ^l 1046.392 ^b	1046.4053	-0.0003
3	1	1046.4008 ^l 1046.392 ^b	1046.4009	0.0001	1013.1758 ^h 1013.174	1013.1757	-0.0001

TABLE I—Continued

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{ob}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{ob}}$
		sR			aR		
3	2	1046.3881 ^l 1046.392 ^b	1046.3881	0.0000	1012.4452 ^h 1012.442	1012.4449	-0.0003
3	3	*1046.37450 ^h 1046.375 ^d 1046.392 ^b	1046.3745	0.0000	*1011.20350 ^e 1011.2035 ^c 1011.202	1011.2032	-0.0003
4	0	*1034.245	1034.2409	-0.004
4	1	1065.5944 ^f 1065.576 ^b	1065.5950	0.0006	1034.0128 ^h 1034.011	1034.0141	0.0013
4	2	1065.5824 ^f 1065.576 ^b	1065.5820	-0.0004	1033.3165 ^h 1033.316	1033.3166	0.0001
4	3	*1065.5655 ^f 1065.576 ^b	1065.5677	0.0022	*1032.1311 ^h 1032.129	1032.1311	0.0000
4	4	1065.5636 ^f 1065.576 ^b	1065.5636	0.0000	1030.4222 ^h 1030.421	1030.4217	-0.0005
5	0	*1084.6296 ^l	1084.6276	-0.0020
5	1	1084.6244 ^l 1084.608 ^b	1084.6246	0.0002	1054.916	1054.9152	-0.001
5	2	1084.6082 ^c 1084.608 ^b	1084.6102	0.0020	1054.2511 ^h 1054.254	1054.2548	0.0037
5	3	*1084.59306 ^c 1084.608 ^b	1084.5930	-0.0001	*1053.13044 ^h 1053.135	1053.1320	0.0016
5	4	1084.58371 ^c 1084.608 ^b	1084.5837	0.0000	1051.51207 ^h 1051.517	1051.5123	0.0002
5	5	1084.59924 ^c 1084.608 ^b	1084.5988	-0.0004	1049.34632 ^h 1049.349	1049.3456	-0.0007
6	0	*1076.033	1076.0184	-0.015
6	1	1103.4846 ^l 1103.452 ^b	1103.4864	0.0018	1075.8218 ^h 1075.824	1075.8254	0.0036
6	2	1103.4686 ^l 1103.452 ^b	1103.4696	0.0010	1075.2024 ^f 1075.207	1075.2051	0.0027
6	3	*1103.4397 ^l 1103.452 ^b	1103.4478	0.0081	*1074.1477 ^h 1074.152	1074.1505	0.0026
6	4	1103.4293 ^l 1103.452 ^b	1103.4310	0.0017	1072.6262 ^h 1072.631	1072.6288	0.0026
6	5	1103.4324 ^l 1103.452 ^b	1103.4342	0.0018	1070.5909 ^f 1070.594	1070.5914	0.0005
6	6	1103.4784 ^l 1103.452 ^b	1103.4792	0.0008	1067.9733 ^h 1067.976	1067.9735	0.0002
7	0	*1122.1861 ^l 1122.132 ^b	1122.1784	-0.0077
7	1	1122.1792 ^l 1122.132 ^b	1122.1783	-0.0009	1096.6906 ^h 1096.682	1096.6900	-0.0006
7	2	1122.1606 ^l 1122.132 ^b	1122.1582	-0.0024	1096.1132 ^f 1096.112	1096.1117	-0.0015
7	3	*1122.1332 ^l 1122.132 ^b	1122.1305	-0.0027	*1095.1296 ^h 1095.124	1095.1288	-0.0008
7	4	1122.1042 ^l 1122.132 ^b	1122.1043	0.0001	1093.7119 ^f 1095.715	1093.7111	-0.0008
7	5	1122.0937 ^l 1122.132 ^b	1122.0934	-0.0003	1091.8120 ^h 1091.816	1091.8128	0.0008
7	6	1122.1181 ^l 1122.132 ^b	1122.1175	-0.0006	1089.3704 ^h 1089.370	1089.3704	0.0000

TABLE I—*Continued*

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$
		sR			aR		
7	7	1122.2046 ^l 1122.132 ^b	1122.2039	-0.0007	1086.3044 ^h 1086.295	1086.3032	-0.0012
8	0	*1117.642	1117.6036	-0.038
8	1	1140.697 ^l 1140.628 ^b	1140.6988	0.002	*1117.453 ^b	1117.4563	0.003
8	2	1140.677 ^l 1140.628 ^b	1140.6749	-0.002	1116.922	1116.9200	-0.002
8	3	*1140.624 ^l 1140.628 ^b	1140.6404	0.016	*1116.015	1116.0100	-0.005
8	4	1140.601 ^l 1140.628 ^b	1140.6036	0.003	1114.703	1114.6992	-0.004
8	5	1140.575 ^{b,l} 1140.628 ^b	1140.5768	0.002	1112.941 ^b	1112.9457	0.005
8	6	1140.575 ^{b,l} 1140.628 ^b	1140.5781	0.003	1110.687	1110.6893	0.002
8	7	1140.630 ^l 1140.628 ^b	1140.6322	0.002	1107.843	1107.8503	0.007
8	8	1140.768 ^l 1140.628 ^b	1140.7725	0.004	1104.329	1104.3313	0.002
9	0		1159.0418	
9	1		1159.0479		1138.081	1138.0777	-0.003
9	2		1159.0198		1137.597	1137.5818	-0.015
9	3		1158.9776		*1136.759 ^b	1136.7423	-0.017
9	4	*1159.165 ^b	1158.9289		1135.559	1135.5368	-0.022
9	5	*1158.910 ^b	1158.8851		1133.944	1133.9287	-0.015
9	6		1158.8624		1131.868	1131.8628	-0.005
9	7		1158.8830		1129.259	1129.2630	0.004
9	8		1158.9771		1126.025	1126.0314	0.006
9	9		1159.1851		*1122.132 ^b	1122.0536	-0.078
10	0	*1158.663 ^b	1158.6099	-0.053
10	1		1177.2275		*1158.493 ^b	1158.5200	0.027
10	2		1177.1944		*1158.049 ^b	1158.0600	0.011
10	3		1177.1436		*1157.301	1157.2846	-0.016
10	4		1177.0820		1156.209 ^b	1156.1770	-0.032
10	5	*1176.999 ^b	1177.0199		1154.734 ^b	1154.7079	-0.026
10	6	*1177.131 ^b	1176.9719		1152.851 ^b	1152.8295	-0.022
10	7		1176.9583		1150.485	1150.4716	-0.013
10	8		1177.0061		1147.535	1147.5389	0.004
10	9		1177.1515		1143.908	1143.9135	0.005
10	10		1177.4422		1139.471	1139.4646	-0.006
11	0		1195.2250	
11	1		1195.2426		*1178.703 ^b	1178.7681	0.065
11	2		1195.2038		1178.319	1178.3365	0.018
11	3		1195.1431		*1177.591 ^b	1177.6135	0.023
11	4	*1195.176 ^b	1195.0669		*1176.618 ^b	1176.5895	-0.028
11	5	*1195.531 ^b	1194.9847		*1175.293 ^b	1175.2441	-0.049
11	6	*1194.923 ^b	1194.9099		*1173.583 ^b	1173.5398	-0.043
11	7		1194.8609		1171.435	1171.4156	-0.019
11	8		1194.8620		1168.781	1168.7823	0.001
11	9		1194.9458		*1165.497 ^b	1165.5222	0.025
11	10		1195.1547		*1161.483 ^b	1161.4957	0.013
11	11		1195.5449		1156.555	1156.5574	0.002

Note added in proof: ν_{obs} for aR(9,9) is 1122.0555 cm^{-1} from our diode laser measurements (see Fig. 2).

TABLE II

Observed and Calculated Transition Wavenumbers in the $2\nu_2$ Band of $^{14}\text{NH}_3$ (cm^{-1})^a

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$
		SP			aP		
1	0	1862.285 ^c	1862.2852	0.000
2	0	1557.4402	...
2	1	1842.099 ^c	1842.0978	-0.001	1556.904	1556.8966	-0.007
3	0	...	1821.0697
3	1	1821.255 ^c	1821.2542	-0.001	*1538.012 ^b	1538.0872	0.075
3	2	1821.814 ^c	1821.8138	0.000	1536.458	1536.4411	-0.017
4	0	1520.442 ^b	1520.4775	0.036
4	1	1799.9991 ^d	1799.9994	0.0003	...	1519.8926	...
4	2	1800.5218 ^d	1800.5246	0.0028	1518.205	1518.1647	-0.040
4	3	1801.4303 ^d	1801.4327	0.0024	*1515.337 ^b	1515.4286	0.092
5	0	*1778.244 ^c	1778.2226	-0.021
5	1	1778.399 ^c	1778.3929	-0.006	...	1502.3794	...
5	2	1778.876 ^c	1778.8763	0.000	1500.522 ^b	1500.5565	0.034
5	3	1779.714 ^c	1779.7129	-0.001	*1497.672 ^b	1497.6352	-0.037
5	4	1780.958 ^c	1780.9556	-0.002	1493.875	1493.8663	-0.009
6	0	1486.245 ^b	1486.2533	0.008
6	1	1756.508 ^c	1756.5051	-0.003	...	1485.6175	...
6	2	1756.935 ^c	1756.9399	0.004	...	1483.6886	...
6	3	1757.689 ^c	1757.6934	0.004	...	1480.5728	...
6	4	1758.812 ^c	1758.8155	0.003	1476.431 ^b	1476.4561	0.025
6	5	1760.390 ^c	1760.3883	-0.002	...	1471.7713	...
7	0	*1734.303 ^c	1734.2412	-0.062
7	1	...	1734.4161	1469.6770	...
7	2	1734.804 ^c	1734.7962	-0.008	1467.645	1467.6287	-0.016
7	3	1735.460 ^c	1735.4564	-0.004	...	1464.3072	...
7	4	...	1736.4429	1459.8671	...
7	5	...	1737.8324	...	1454.585 ^b	1454.5813	-0.003
7	6	1739.739 ^c	1739.7455	0.007	1449.227	1449.1740	-0.052
8	0	1455.3213	...
8	1	1712.225 ^c	1712.2137	-0.012	...	1454.6262	...
8	2	1712.531 ^c	1712.5341	0.003	...	1452.4369	...
8	3	1713.084 ^c	1713.0923	0.008	...	1448.8888	...
8	4	1713.928 ^c	1713.9301	0.003	...	1444.1324	...
8	5	...	1715.1188	1438.3818	...
8	6	1716.780 ^c	1716.7706	-0.009	...	1431.9797	...
8	7	1719.039 ^c	1719.0563	0.017	...	1426.1235	...
9	0	...	1689.7693
9	1	*1690.006 ^b	1689.9922	-0.014	...	1440.5309	...
9	2	1690.215 ^b	1690.2488	0.034	...	1438.1608	...
9	3	1690.664 ^b	1690.6977	0.034	1434.318	1434.3468	0.029
9	4	1691.357 ^b	1691.3764	0.019	...	1429.2631	...
9	5	1692.354	1692.3494	-0.005	...	1423.1118	...
9	6	1693.736	1693.7206	-0.015	...	1416.1252	...
9	7	1695.6462 ^d	1695.6492	0.0030	...	1408.6683	...
9	8	...	1698.3710	1402.6953	...
10	0	1428.2666	...
10	1	...	1667.8509	1427.4485	...
10	2	...	1668.0405	1424.8197	...
10	3	...	1668.3745	1420.6748	...
10	4	...	1668.8856	1415.2408	...

^a Our infrared grating measurements unless stated otherwise; asterisk denotes that this value has not been used in the fit.

^b Blended line.

^c Calculated from the frequency of the hot band $2\nu_2 \leftarrow \nu_2$ transition (our measurements), ν_2 frequency, and the ground-state pure inversion transition.

TABLE II—Continued

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{ob}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{ob}}$
				sP			
10	5		1669.6316			1408.7246	
10	6		1670.7066			1401.3108	
10	7		1672.2579			1393.1949	
10	8		1674.5058			1384.7213	
10	9		1677.7695			1378.9995	
11	0		1645.5558	
11	1		1645.8935			1415.3953	
11	2		1646.0135			1412.3535	
11	3		1646.2283			1407.8008	
11	4		1646.5658			1415.2370	
11	5		1647.0759			1409.8936	
11	6		1647.8432			1402.8204	
11	7		1649.0019			1393.9842	
11	8		1650.7560			1383.3645	
11	9		1653.4042			1370.7866	
11	10		1657.3703			1355.1920	
12	0		1405.7387	
12	1		1624.2283			1404.1348	
12	2		1624.2769			1407.5765 ^f	
12	3		1624.3694			1405.7684	
12	4		1624.5284			1402.4624	
12	5		1624.7966			1397.5366	
12	6		1625.2479			1390.8810	
12	7		1626.0030			1382.4472	
12	8		1627.2489			1372.2658	
12	9		1629.2630			1360.3733	
12	10		1632.4426			1346.6781	
12	11		1637.3413			1331.4857	
				sQ			
1	1	1881.8646 ^d	1881.8637	-0.0009	1596.634	1596.6426	0.008
2	1	1880.8542 ^d	1880.8523	-0.0019	*1597.594 ^b	1597.6566	0.063
2	2	1881.4389 ^d	1881.4400	0.0011	1596.046 ^b	1596.0378	-0.008
3	1	1879.368 ^c	1879.3695	0.001		1599.2261	
3	2	1879.9299 ^d	1879.9319	0.0020	*1597.594 ^b	1597.5343	-0.060
3	3	1880.8999 ^d	1880.9022	0.0023	*1594.810 ^b	1594.8588	0.049
4	1	1877.4586 ^d	1877.4555	-0.0031		1601.3986	
4	2	1877.9836 ^d	1877.9848	0.0012		1599.6205	
4	3	1878.8987 ^d	1878.8985	-0.0002	1596.790 ^c	1596.7743	-0.016
4	4	1880.2514 ^d	1880.2501	-0.0013	1593.157 ^b	1593.1115	-0.046
5	1	1875.168 ^c	1875.1619	-0.006	1604.181 ^b	1604.2259	0.045
5	2	1875.648 ^c	1875.6511	0.003	1602.347 ^c	1602.3501	0.003
5	3	1876.4937 ^d	1876.4960	0.0023		1599.3234	
5	4	1877.74712 ^e	1877.7471	0.0000	1595.341 ^c	1595.3325	-0.008
5	5	1879.4923 ^d	1879.4879	-0.0044	1590.859 ^b	1590.8111	-0.048
6	1	*1872.561 ^c	1872.5510	-0.010	1607.775	1607.7600	-0.015
6	2	1872.994 ^c	1872.9937	0.000	1605.778 ^c	1605.7729	-0.005
6	3	1873.7638 ^d	1873.7590	-0.005	1602.543 ^c	1602.5540	0.011
6	4	1874.887 ^c	1874.8938	0.007	1598.248 ^c	1598.2586	0.011
6	5	1876.4821 ^d	1876.4764	-0.0057	1593.167 ^c	1593.1610	-0.006
6	6	1878.6270 ^d	1878.6290	0.0020	1588.016	1587.9868	-0.029

^d Calculated as indicated in footnote c but the diode laser measurements of the $2\nu_2 \leftarrow \nu_2$ frequency (20) have been used.

^e Ref. (22).

^f Assigned as the $2\nu_2$ frequency although the corresponding upper state has the largest contribution from the $\nu_4(-l)$ state (see Section VI and Table XIII).

TABLE II—Continued

J	K	v_{obs}	v_{calc}	$v_{\text{calc}} - v_{\text{ob}}$	v_{obs}	v_{calc}	$v_{\text{calc}} - v_{\text{ob}}$
sQ				aQ			
7	1		1869.6938		1612.064 ^c	1612.0526	-0.011
7	2	1870.081 ^c	1870.0846	0.003	1609.950 ^c	1609.9321	-0.018
7	3	1870.735 ^c	1870.7607	0.026	1606.501 ^c	1606.4994	-0.002
7	4	1871.763 ^c	1871.7653	0.002	1601.909 ^c	1601.9059	-0.003
7	5		1873.1709		1596.373 ^b	1596.3671	-0.006
7	6	1875.102 ^c	1875.0919	-0.010	1590.225 ^c	1590.2274	0.002
7	7	1877.681 ^c	1877.7015	0.020	1584.615	1584.6865	0.072
8	1	1866.660 ^c	1866.6690	0.009		1617.1537	
8	2	1866.979 ^c	1867.0032	0.024		1614.8596	
8	3	1867.559 ^c	1867.5822	0.024	1611.161	1611.1731	0.012
8	4	1868.410 ^c	1868.4447	0.035	*1606.297 ^b	1606.2694	-0.028
8	5	1869.661 ^c	1869.6571	-0.004	*1600.278 ^b	1600.3522	0.074
8	6	1871.343 ^c	1871.3254	-0.018	1593.652	1593.6557	0.004
8	7	1873.6087 ^d	1873.6116	0.0029	1586.534	1586.5474	0.013
8	8		1876.7547		1581.014 ^b	1580.9841	0.029
9	1	1863.530	1863.5615	0.031		1623.1060	
9	2	1863.846	1863.8353	-0.011	*1620.601 ^b	1620.5600	-0.041
9	3	1864.390 ^b	1864.3105	-0.079		1616.5538	
9	4		1865.0214			1611.3158	
9	5		1866.0275		1605.018	1605.0545	0.037
9	6		1867.4255		1597.985	1597.9567	-0.028
9	7		1869.3657			1590.2206	
9	8		1872.0720		1582.219	1582.1937	-0.025
9	9		1875.8676			1576.9893	
10	1		1860.4619			1629.9128	
10	2		1860.6723			1626.9599	
10	3		1861.0386			1622.5564	
10	4		1861.5902		*1630.288 ^b	1630.2032	-0.085
10	5		1862.3794			1625.1338	
10	6		1863.4932			1618.4005	
10	7		1865.0694			1609.9729	
10	8		1867.3158		1599.837	1599.8341	-0.003
10	9		1870.5357		1587.831	1587.8133	-0.017
10	10		1875.1581		1572.886	1572.8566	-0.029
11	1		1857.4677			1637.3257	
11	2		1857.6119		*1640.823 ^b	1640.8619 ^f	0.039
11	3		1857.8650			1639.2122	
11	4		1858.2510			1636.1302	
11	5		1858.8151			1631.4958	
11	6		1859.6341			1625.2017	
11	7		1860.8324			1617.2028	
11	8		1862.6012		*1607.502 ^b	1607.5333	0.031
11	9		1865.2229			1596.2344	
11	10	1869.1010 ^d	1869.1005	-0.0005	1583.192	1583.2191	0.027
11	11		1874.7939				
sR				aR			
0	0	1616.980 ^b	1617.0601	0.080
1	0		1920.4180	
1	1	1920.6200 ^d	1920.6181	-0.0019		1637.4027	

TABLE II—Continued

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$
sR				aR			
2	0	1659.336	1659.3593	0.024
2	1	1938.9681 ^d	1938.9676	-0.0005	1658.777	1658.7954	0.018
2	2	1939.5562 ^d	1939.5580	0.0018	1657.128 ^b	1657.1310	0.003
3	0	...	1956.6277
3	1	1956.8292 ^d	1956.8256	-0.0036	1680.700	1680.7321	0.032
3	2	1957.3904 ^d	1957.3920	0.0016	1678.964	1678.9902	0.026
3	3	1958.3681 ^d	1958.3680	-0.0001	1676.219	1676.2046	-0.014
4	0	1703.863	1703.8483	-0.014
4	1	...	1974.2245	...	1703.236	1703.2451	0.009
4	2	...	1974.7596	...	1701.399 ^b	1701.4142	0.015
4	3	1975.6790 ^d	1975.6816	0.0026	1698.441 ^b	1698.4626	0.022
4	4	1977.0421 ^d	1977.0416	-0.0005	1694.590	1694.5776	-0.012
5	0	...	1990.9939
5	1	...	1991.2078	...	1726.390 ^b	1726.3683	-0.022
5	2	...	1991.7050	...	1724.444	1724.4344	-0.010
5	3	...	1992.5616	...	1721.289	1721.3046	0.016
5	4	...	1993.8254	...	1717.132	1717.1350	0.003
5	5	1995.5818 ^d	1995.5760	-0.0058	1712.196 ^b	1712.2008	0.005
6	0	1750.7875	...
6	1	...	2007.8287	...	1750.154	1750.1356	-0.019
6	2	...	2008.2821	...	1748.088 ^b	1748.0763	-0.012
6	3	...	2009.0633	...	1744.733	1744.7461	0.013
6	4	...	2010.2162	...	1740.312	1740.2974	-0.015
6	5	...	2011.8149	...	1734.952	1734.9469	-0.005
6	6	2013.9848 ^d	2013.9755	-0.0093	1729.028	1729.0403	0.012
7	0	...	2023.8772
7	1	...	2024.1492	1774.5801	...
7	2	...	2024.5537	...	*1772.334 ^b	1772.3548	0.021
7	3	...	2025.2506	...	1768.769	1768.7837	0.015
7	4	...	2026.2798	...	1764.034	1764.0429	0.009
7	5	...	2027.7092	...	1758.376	1758.3375	-0.039
7	6	...	2029.6467	...	1751.931	1751.9034	-0.028
7	7	...	2032.2568	...	1745.084	1745.1103	0.026
8	0	1800.503	1800.4941	-0.009
8	1	...	2040.2383	1799.7288	...
8	2	...	2040.5896	...	*1797.338 ^b	1797.2588	-0.079
8	3	...	2041.1950	1793.3801	...
8	4	...	2042.0897	1788.3221	...
8	5	...	2043.3352	...	1782.291	1782.2949	0.004
8	6	...	2045.0303	...	*1775.598 ^b	1775.4872	-0.111
8	7	...	2047.3281	...	*1768.133 ^b	1768.0996	0.033
8	8	...	2050.4556	...	1760.428	1760.4826	0.055
9	0	...	2055.7768
9	1	...	2056.1725	1825.5703	...
9	2	...	2056.4670	1822.7002	...
9	3	...	2056.9746	1818.4355	...
9	4	...	2057.7260	1826.2782	...
9	5	...	2058.7753	1821.4637	...
9	6	...	2060.2121	...	1815.080	1815.0464	-0.034
9	7	...	2062.1772	...	1806.919	1806.9986	0.080

TABLE II—Continued

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{ob}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{ob}}$
		sR			aR		
9	8		2064.8819		1797.338	1797.3065	-0.031
9	9		2068.6338		1785.824	1785.8030	-0.020
10	0		1853.3861	
10	1		2072.0362			1851.8432	
10	2		2072.2707			1855.4684 ^F	
10	3		2072.6752			1853.9678	
10	4		2073.2754			1851.0964	
10	5		2074.1185			1846.7360	
10	6		2075.2841			1840.7818	
10	7		2076.8999			1833.1915	
10	8		2079.1610			1824.0029	
10	9		2082.3544		*1813.351	1813.2611	-0.090
10	10		2086.8883		1800.850	1800.8838	0.034

0.3–0.6 Torr); the accuracy of those frequencies is about ± 1 MHz. The frequencies obtained by extrapolating to zero pressure from at least three measurements at different pressures are determined with the accuracy of ± 0.2 MHz (Table IV).

IV. GROUND-STATE ROTATIONAL AND CENTRIFUGAL DISTORTION CONSTANTS

Combination relations have been used in evaluating the molecular constants of the ground state of $^{14}\text{NH}_3$. In the standard application of this method to NH_3 , rotational and centrifugal distortion constants are obtained separately for the symmetric and antisymmetric components of the inversion doublet. We have modified this treatment so that all the infrared data are processed simultaneously with the microwave pure inversion transition frequencies, using the following equation in addition to the standard combination relations:

$$\begin{aligned} \Delta_i(J, K) = & 0.7934115 + [{}^{(a)}B_0 - ({}^{(s)}B_0)]J(J+1) \\ & - [{}^{(a)}D_J^0 - ({}^{(s)}D_J^0)]J^2(J+1)^2 - [{}^{(a)}D_{JK}^0 - ({}^{(s)}D_{JK}^0)]J(J+1)K^2 \\ & + [{}^{(a)}H_{JJ}^0 - ({}^{(s)}H_{JJ}^0)]J^3(J+1)^3 + [{}^{(a)}H_{JK}^0 - ({}^{(s)}H_{JK}^0)]J^2(J+1)^2K^2 \\ & + [{}^{(a)}H_{KK}^0 - ({}^{(s)}H_{KK}^0)]J(J+1)K^4 + \{[{}^{(a)}C_0 - ({}^{(a)}B_0) - [{}^{(s)}C_0 - ({}^{(s)}B_0)]\}K^2 \\ & - [{}^{(a)}D_K^0 - ({}^{(s)}D_K^0)]K^4 + [{}^{(a)}H_{KKK}^0 - ({}^{(s)}H_{KKK}^0)]K^6. \quad (17) \end{aligned}$$

The values of the molecular parameters obtained in this way are then consistent also with the experimental inversion frequencies; they are listed in Table V. In this and all other fits the weights of the experimental data have been chosen to be inversely proportional to the squares of their estimated dispersions.

V. CORIOLIS AND *l*-TYPE INTERACTIONS IN THE EXCITED VIBRATION-INVERSION STATES OF $^{14}\text{NH}_3$

The lowest-lying vibration–inversion energy levels of $^{14}\text{NH}_3$ (Fig. 4) form a complicated system of interacting levels. In order to keep the problem in a

TABLE III

Observed and Calculated Transition Wavenumbers in the ν_4 Band of $^{14}\text{NH}_3$ (cm^{-1})^a

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{ob}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{ob}}$
		s^{P}_{P}			a^{P}_{P}		
1	1	1610.089	1610.0987	0.010	*1610.361 ^b	1610.4571	0.096
2	1	1590.684	1590.6940	0.010	1591.085	1591.1419	0.057
2	2	1594.810 ^b	1594.7855	-0.024	1595.072 ^b	1595.1275	0.056
3	1	1571.823 ^b	1571.8419	0.019	1572.483	1572.5064	0.024
3	2	1575.852	1575.8580	0.006		1576.3409	
3	3	1579.364	1579.3528	-0.011	1579.621 ^b	1579.6732	0.052
4	1	1553.622 ^b	1553.6469	0.025	1554.725	1554.7387	0.014
4	2	*1557.532 ^b	1557.4948	-0.035	*1558.270 ^b	1558.2431	-0.027
4	3	1560.893	1560.8956	0.003	1561.373	1561.3889	0.016
4	4	1563.829	1563.8094	-0.020	1564.075	1564.1027	0.028
5	1	1536.207	1536.2316	0.025	1538.012 ^b	1538.0321	0.020
5	2	1539.756	1539.7715	0.016	1541.002	1540.9782	-0.024
5	3	1542.973	1543.0126	0.040	1543.844	1543.8055	-0.038
5	4	1545.796	1545.8165	0.020	1546.324	1546.3065	-0.018
5	5	1548.188	1548.1644	-0.024	1548.421	1548.4278	0.007
6	1	1519.659 ^b	1519.6938	0.035	1522.388	1522.4910	0.103
6	2	*1522.712 ^b	1522.7758	0.064	1524.736	1524.7068	-0.029
6	3	1525.761	1525.7670	0.006	1527.055	1527.0520	-0.003
6	4	1528.375	1528.4040	0.029	1529.287	1529.2215	-0.065
6	5	1530.613	1530.6304	0.017	1531.153	1531.1241	-0.029
6	6	1532.445	1532.4265	-0.018	1532.666	1532.6630	-0.003
7	1	1504.025	1504.0737	0.049		1508.1241	
7	2	*1506.604 ^b	1506.5935	-0.010		1509.5679	
7	3	*1509.138 ^b	1509.2316	0.094	1511.314	1511.2770	-0.037
7	4	1511.599	1511.6277	0.028	1513.054 ^b	1512.9703	-0.084
7	5	1513.654	1513.6786	0.025	1514.599	1514.5373	-0.062
7	6	1515.337	1515.3466	0.010	1515.871	1515.8837	0.012
7	7	*1516.663 ^b	1516.6045	-0.058	1516.840	1516.8229	-0.017
8	1	*1489.304 ^b	1489.3635	0.059		1494.9140	
8	2	1491.320	1491.2920	-0.028	1495.726 ^b	1495.6511	-0.075
8	3	1493.531	1493.4829	-0.048		1496.6293	
8	4	1495.527	1495.5537	0.027	1497.672 ^b	1497.7002	0.028
8	5	1497.332	1497.3607	0.029	*1498.822 ^b	1498.7882	-0.036
8	6	*1498.822 ^b	1498.8457	0.024	1499.806	1499.8198	0.014
8	7	1499.940	1499.9734	0.033	1500.522 ^b	1500.6392	0.117
8	8	1500.746	1500.7068	-0.039	1500.933	1500.9200	-0.013
9	1		1475.5394			1482.8682	
9	2	1476.879	1476.9114	0.032		1483.0076	
9	3		1478.5927		*1483.249 ^b	1483.2377	-0.011
9	4	1480.191	1480.2554	-0.064		1483.5720	
9	5	1481.718	1481.7408	0.023		1484.0286	
9	6	1482.955	1482.9743	0.019		1484.5927	
9	7	1483.911	1483.9131	0.002		1485.1588	
9	8	1484.496	1484.5187	0.023		1485.4564	
9	9	1484.779	1484.7417	-0.037	1484.950	1484.9608	0.011
10	1		1462.5856			1472.0371	
10	2		1463.4693		1471.623 ^b	1471.6845	0.062
10	3	1464.643	1464.6209	-0.022	*1471.147 ^b	1471.2078	0.061
10	4		1465.8093		*1470.754 ^b	1470.7456	-0.008
10	5	1466.939 ^b	1466.8940	-0.045		1470.4355	

^a Our infrared grating measurements unless stated otherwise; asterisk denotes that this value has not been used in the fit.

^b Blended line.

^c Assigned as the $\nu_4^R X$ ($X = P, Q, R$) frequency although the corresponding upper state has the largest contribution from the $\nu_4(-l)$ state (see Section VI and Table XIII).

TABLE III—Continued

J	K	ν_{obs}	ν_{calc}	$\nu_{calc} - \nu_{ob}$	ν_{obs}	ν_{calc}	$\nu_{calc} - \nu_{ob}$
		$s^P P$			$a^P P$		
10	6	1467.783	1467.7981	0.015		1470.3631	
10	7	1468.466	1468.4752	0.009		1470.5058	
10	8	*1468.920 ^b	1468.8873	-0.033		1470.6699	
10	9	*1468.920 ^b	1468.9890	0.069		1470.4116	
10	10	1468.753 ^b	1468.7170	-0.036	1468.920	1468.9406	0.021
11	1		1450.5043			1462.5162	
11	2		1450.9757			1461.7552	
11	3		1451.6141			1460.6378	
11	4		1452.2890			1459.3724	
11	5	*1452.828 ^b	1452.9040	0.076		1458.1999	
11	6	*1453.335 ^b	1453.3978	0.063		1457.3275	
11	7	1453.743 ^b	1453.7303	-0.013		1456.8519	
11	8	1453.907 ^b	1453.8682	-0.039		1456.6879	
11	9	1453.743 ^b	1453.7729	0.030		1456.4945	
11	10	*1453.335 ^b	1453.3899	0.055		1455.5894	
11	11	1452.662	1452.6405	-0.022	1452.828	1452.8387	0.011
12	1		1439.3178			1408.5551	
12	2		1439.4463			1453.3373	
12	3	*1439.621 ^b	1439.6113	-0.010		1451.6431	
12	4		1439.7628			1449.6013	
12	5		1439.8582			1447.5176	
12	6		1439.8673			1445.7100	
12	7		1439.7681			1444.4163	
12	8	*1439.621 ^b	1439.5399	-0.081		1443.6952	
12	9	*1439.208 ^b	1439.1554	-0.053		1443.3408	
12	10	1438.563	1438.5725	0.010		1442.8008	
12	11	1437.684	1437.7260	0.042		1441.0792	
12	12	*1436.483 ^b	1436.5199	0.037		1436.6113	
		$s^P Q$			$a^P Q$		
1	1	1630.444 ^b	1630.4598	0.016	1630.878	1630.8879	0.010
2	1	1631.427	1631.4400	0.013	1632.028 ^b	1632.0758	0.048
2	2	1635.520 ^b	1635.4842	-0.036	1635.896 ^b	1635.9376	0.042
3	1	1632.998	1633.0170	0.019	1634.076	1634.0721	0.004
3	2	1636.905	1636.9020	-0.003	*1637.544 ^b	1637.6128	0.069
3	3	1640.358	1640.3651	0.007	1640.823	1640.8191	-0.004
4	1	1635.268	1635.2942	0.027	1637.023 ^b	1637.0513	0.028
4	2	1638.881	1638.8801	-0.001	1640.075	1640.0422	-0.033
4	3	1642.176 ^b	1642.1982	0.022	1643.003	1642.9447	-0.058
4	4	1645.117	1645.1109	-0.006	1645.588	1645.5516	-0.036
5	1	1638.325	1638.3506	0.025		1641.0993	
5	2	1641.515	1641.4870	-0.028	1643.382	1643.3683	-0.014
5	3	1644.588	1644.5696	-0.018		1645.8026	
5	4	*1647.406 ^b	1647.3356	-0.070	1648.183	1648.0979	-0.085
5	5	1649.731	1649.7299	-0.001	1650.213	1650.1639	-0.049
6	1	*1642.176 ^b	1642.2086	0.033		1646.2071	
6	2	1644.827	1644.7910	-0.036		1647.7121	
6	3	*1647.592 ^b	1647.5341	-0.058	1649.582	1649.5238	-0.058
6	4	1650.062	1650.0786	0.017	1651.455	1651.3618	-0.093

TABLE III—Continued

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$
		s^P_Q			a^P_Q		
6	5	*1652.418 ^b	1652.3226	-0.095		1653.1170	
6	6	1654.217 ^b	1654.2301	0.013	1654.703	1654.6965	-0.007
7	1		1646.8437			1652.3403	
7	2	1648.857	1648.8425	-0.015		1653.1463	
7	3	1651.201	1651.1513	-0.050	*1654.217 ^b	1654.2399	0.023
7	4	*1653.311 ^b	1653.3888	0.078	*1655.431 ^b	1655.4737	0.043
7	5	*1655.431 ^b	1655.4128	-0.018	1656.839	1656.7735	-0.065
7	6	1657.128 ^b	1657.1670	0.039	1658.071	1658.0675	-0.003
7	7	1658.601	1658.6187	0.018		1659.2021	
8	1		1652.2163		*1659.528 ^b	1659.4910	-0.037
8	2		1653.6658			1659.7064	
8	3	*1655.431 ^b	1655.4772	0.046		1660.0640	
8	4		1657.3237			1660.5783	
8	5	1659.056 ^b	1659.0485	-0.007		1661.2690	
8	6	1660.560	1660.5791	0.019		1662.1232	
8	7	1661.833	1661.8755	0.043		1663.0379	
8	8	*1662.813 ^b	1662.9024	0.089		1663.7453	
9	1		1658.2962			1667.6946	
9	2		1659.2641			1667.4248	
9	3	1660.560	1660.5569	-0.003		1667.0869	
9	4	1662.038	1661.9451	-0.094		1666.8207	
9	5	1663.270	1663.2899	0.020		1666.7655	
9	6	1664.510	1664.5170	0.007		1667.0090	
9	7	1665.565 ^b	1665.5830	0.018		1667.5315	
9	8	1666.379 ^b	1666.4534	0.075		1668.1423	
9	9	1667.066	1667.0871	0.021		1668.4014	
10	1		1665.0728			1677.0337	
10	2	*1665.565 ^b	1665.6345	0.070		1676.3616	
10	3	*1666.379 ^b	1666.4244	0.045		1675.3933	
10	4	*1667.349 ^b	1667.3134	-0.036		1674.3386	
10	5		1668.2075			1673.4402	
10	6	1668.975 ^b	1669.0478	0.074		1672.9076	
10	7		1669.7978			1672.8407	
10	8	1670.423	1670.4280	0.005		1673.1575	
10	9	1670.873	1670.9044	0.031		1673.5212	
10	10	*1671.197 ^b	1671.1777	-0.019		1673.2540	
11	1		1672.5572			1641.2047	
11	2		1672.7814			1686.6227	
11	3		1673.1069			1685.0870	
11	4		1673.4854			1683.2691	
11	5		1673.8767			1681.4768	
11	6		1674.2535			1680.0308	
11	7		1674.5974			1679.1719	
11	8		1674.8921			1678.9627	
11	9		1675.1153			1679.2018	
11	10		1675.2304			1679.3418	
11	11		1675.1785			1678.3922	
		s^P_R			a^P_R		
1	1	1671.197 ^b	1671.2058	0.009	1671.793	1671.8218	0.029

TABLE III—Continued

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{ob}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{ob}}$
		$\text{s}^{\text{P}}\text{R}$			$\text{a}^{\text{P}}\text{R}$		
2	1	1692.615	1692.6151	0.000	1693.643	1693.6415	-0.001
2	2	1696.516	1696.5282	0.012	1697.224	1697.2095	-0.015
3	1	1714.639	1714.6643	0.025	1716.357	1716.3848	0.028
3	2	1718.281	1718.2873	0.006	1719.430	1719.4119	-0.018
3	3	*1721.728 ^b	1721.6678	-0.060	1722.425	1722.3749	-0.050
4	1	1737.388	1737.4132	0.025	*1739.982 ^b	1740.1186	0.137
4	2	1740.601	1740.5956	-0.006	1742.433	1742.4324	-0.001
4	3	1743.727	1743.7552	0.028	1744.978	1744.9418	-0.037
4	4	1746.605 ^b	1746.6301	0.025	1747.416	1747.3430	-0.073
5	1	*1760.802 ^b	1760.8654	0.063	1764.804 ^b	1764.8155	0.011
5	2	1763.527	1763.5022	-0.024	*1766.253 ^b	1766.3736	0.121
5	3	*1766.252 ^b	1766.3367	0.085	1768.294	1768.2744	-0.019
5	4	1768.980	1769.0103	0.030	*1770.340 ^b	1770.2382	-0.102
5	5	*1771.287 ^b	1771.4221	0.135	*1772.287 ^b	1772.1568	-0.130
6	1	*1784.943 ^b	1784.9786	0.036		1790.4233	
6	2	1787.051 ^b	1787.0400	-0.011		1791.2904	
6	3	1789.512 ^b	1789.4539	-0.058		1792.4866	
6	4	1791.843	1791.8397	-0.003	*1793.775 ^b	1793.8652	-0.090
6	5	1794.030	1794.0568	0.027	1795.443	1795.3532	-0.090
6	6	*1796.093 ^b	1796.0505	-0.042	1796.921 ^b	1796.8803	-0.041
7	1		1809.6964			1816.9173	
7	2	1811.191 ^b	1811.2162	0.025		1817.2016	
7	3	1813.121	1813.1456	0.024		1817.6746	
7	4	1815.080 ^b	1815.1589	0.079		1818.3518	
7	5		1817.1006			1819.2543	
7	6	1818.914 ^b	1818.9004	-0.014		1820.3709	
7	7		1820.5207			1821.6008	
8	1		1834.9730			1844.3174	
8	2		1836.0185			1844.1236	
8	3	1837.457	1837.4414	-0.015		1843.9132	
8	4		1839.0134			1843.8270	
8	5	1840.601	1840.5976	-0.003		1844.0058	
8	6	*1842.147 ^b	1842.1217	-0.025		1844.5395	
8	7		1843.5454			1845.4106	
8	8		1844.8371			1846.4318	
9	1		1860.7833			1872.6912	
9	2		1861.4293			1872.1019	
9	3		1862.3604			1871.2724	
9	4		1863.4492			1870.4136	
9	5		1864.6034			1869.7701	
9	6		1865.7667			1869.5535	
9	7		1866.9055			1869.8663	
9	8		1867.9941			1870.6298	
9	9		1869.0027			1871.5110	
10	1		1887.1257			1855.7222	
10	2		1887.4401			1901.2291	
10	3		1887.9171			1899.8425	
10	4		1888.5098			1898.2353	
10	5		1889.1802			1896.7171	
10	6		1889.9035			1895.6109	

TABLE III—Continued

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$
		s^{P}_{R}			a^{P}_{R}		
10	7		1890.6649			1895.1606	
10	8		1891.4519			1895.4323	
10	9		1892.2469			1896.2285	
10	10		1893.0182			1897.0065	
		s^{R}_{P}			a^{R}_{P}		
2	0	1586.859	1586.8905	0.031
3	0	1567.990	1567.9820	-0.008
3	1	1561.756	1561.7647	0.009	1562.369	1562.3783	0.009
4	0	1552.147	1552.0983	-0.049
4	1	1543.213	1543.2388	0.026	*1543.976 ^b	1544.0147	0.039
4	2	1537.464	1537.4717	0.008	*1538.288 ^b	1538.3108	0.023
5	0	*1533.861 ^b	1533.7662	-0.095
5	1	1524.948	1524.9773	0.029	*1525.761 ^b	1525.8208	0.060
5	2	1519.527	1519.5267	0.000	1520.747	1520.7207	-0.026
5	3	*1513.054 ^b	1513.0786	0.025	1514.236	1514.2343	-0.001
6	0	1521.264	1521.2243	-0.040
6	1		1506.8824		*1507.809 ^b	1507.7154	-0.094
6	2	*1501.859 ^b	1501.9012	0.042	1503.431	1503.3869	-0.044
6	3	1495.726	1495.7247	-0.001	1497.518	1497.4829	-0.035
6	4	1488.596 ^b	1488.5850	-0.011	1490.191	1490.1889	-0.002
7	0	1502.754	1502.7137	-0.040
7	1	1488.962 ^b	1488.9154	-0.047		1489.7439	
7	2	1484.496	1484.5084	0.012	1486.245 ^b	1486.2209	-0.024
7	3	1478.715	1478.7080	-0.007	1481.083	1481.0309	-0.052
7	4	*1471.889 ^b	1471.8475	-0.041	1474.397	1474.3912	-0.006
7	5	1463.997	1463.9890	-0.008	1466.212	1466.2159	0.004
8	0	1494.241	1494.3012	0.060
8	1	1471.147	1471.0952	-0.052		1472.0249	
8	2	1467.344	1467.2891	-0.054	1469.180	1469.2347	0.055
8	3	1461.969	1461.9553	-0.013		1464.8287	
8	4	1455.495 ^b	1455.4543	-0.041	1458.961	1458.9233	-0.038
8	5		1447.8958		1451.530	1451.4957	-0.034
8	6	1439.310 ^b	1439.2895	-0.020		1442.3400	
9	0	1474.737	1474.7816	0.045
9	1		1453.4751			1454.7163	
9	2	1450.180	1450.2295	0.049		1452.5523	
9	3	1445.414	1445.4154	0.001		1448.9270	
9	4	*1439.310 ^b	1439.3445	-0.035		1443.8018	
9	5	1432.170	1432.1498	-0.020		1437.1169	
9	6	1423.901	1423.8678	-0.033	1428.824	1428.7759	-0.048
9	7		1414.4866			1418.5357	
10	0		1471.6725	
10	1		1436.1282			1438.0228	
10	2		1433.3655			1436.4106	
10	3		1429.0762			1433.5140	
10	4		1423.4811			1429.1507	
10	5		1416.7038			1423.1851	
10	6		1408.7949			1415.5329	

TABLE III—Continued

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{obs}}$
		s^R_P			a^R_P		
10	7		1399.7610			1406.1186	
10	8		1389.5813			1394.7183	
11	0		1420.2757	
11	1		1419.1469			1422.2458 ^c	
11	2		1416.7782			1421.1994 ^c	
11	3		1412.9757			1418.9497	
11	4		1407.8661			1402.0092	
11	5		1401.5382			1395.1671	
11	6		1394.0395			1387.4224	
11	7		1385.3862			1378.8971	
11	8		1375.5727			1369.7325	
11	9		1364.5766			1360.2282	
12	0		1454.1513	
12	1		1402.6499			1454.4490 ^c	
12	2		1400.5891			1400.5114	
12	3		1397.2061			1395.5822	
12	4		1392.5536			1389.4992	
12	5		1386.6760			1382.3974	
12	6		1379.6030			1374.3996	
12	7		1371.3495			1365.5969	
12	8		1361.9180			1356.0518	
12	9		1351.3002			1345.8586	
12	10		1339.4772			1335.2400	
		s^R_Q			a^R_Q		
1	0	1625.487 ^b	1625.4747	-0.013
2	0	1626.133 ^b	1626.1827	0.050
2	1	1621.351	1621.3628	0.012	1621.934	1621.9477	0.014
3	0	1626.340 ^b	1626.4059	0.066
3	1	*1622.623 ^b	1622.6089	-0.014	1623.350	1623.3482	-0.002
3	2	*1616.833 ^b	1616.8789	0.046	1617.668	1617.6804	0.012
4	0	1627.314	1627.4063	0.092
4	1	1624.005	1624.0399	0.035	1624.879 ^b	1624.8401	-0.039
4	2	1618.613	1618.6352	0.022	1619.790	1619.7848	-0.005
4	3	1612.250	1612.2642	0.014	1613.336 ^b	1613.3735	0.038
5	0		1627.9994	
5	1	1625.599 ^b	1625.5392	-0.059	1626.341 ^b	1626.3237	-0.017
5	2	1620.601	1620.6125	0.011	1622.062	1622.0484	-0.013
5	3	1614.511	1614.5273	0.016	1616.273 ^b	1616.2335	-0.039
5	4	1607.502	1607.5166	0.015	1609.045	1609.0653	0.021
6	0	1629.279 ^b	1629.4055	0.127
6	1	1627.009 ^b	1627.0503	0.041	*1627.875 ^b	1627.8269	-0.046
6	2	*1622.623 ^b	1622.7060	0.082	1624.387	1624.3651	-0.022
6	3	1616.980 ^b	1617.0106	0.031	1619.320	1619.2776	-0.043
6	4	*1610.326 ^b	1610.2984	-0.028	1612.801	1612.7827	-0.019
6	5	1602.627	1602.6330	0.006	1604.763	1604.7956	0.033
7	0	*1630.288 ^b	1630.1886	-0.099
7	1	1628.608	1628.5753	-0.032		1629.4513	
7	2	*1624.879 ^b	1624.8396	-0.039	1626.664	1626.7299	0.066
7	3	*1619.603 ^b	1619.6238	0.021	*1622.383 ^b	1622.4393	0.056

TABLE III—Continued

J	K	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{ob}}$	ν_{obs}	ν_{calc}	$\nu_{\text{calc}} - \nu_{\text{ob}}$
		s^R_Q			a^R_Q		
7	4	1613.336 ^b	1613.2894	-0.047	*1616.716 ^b	1616.6968	-0.019
7	5	1605.950	1605.9479	-0.002	*1609.458 ^b	1609.4810	0.023
7	6	*1597.594 ^b	1597.6108	0.017	1600.567	1600.5877	0.021
8	0	1632.5383	...
8	1	...	1630.1519	...	*1631.284 ^b	1631.3391	0.055
8	2	1627.009 ^b	1626.9839	-0.025	1629.279	1629.2511	-0.028
8	3	*1622.383 ^b	1622.2999	-0.083	*1625.599 ^b	1625.7533	0.154
8	4	*1616.378 ^b	1616.4128	-0.035	*1620.709 ^b	1620.8081	0.099
8	5	*1609.458 ^b	1609.4575	0.000	1614.367	1614.3572	-0.010
8	6	1601.469 ^b	1601.4726	0.004	1606.297	1606.3064	0.010
8	7	1592.432	1592.4490	0.017	1596.373 ^b	1596.4147	0.042
9	0	1632.998 ^b	1633.0390	0.040
9	1	*1631.936 ^b	1631.8388	-0.097	...	1633.6804	...
9	2	1629.171 ^b	1629.1603	-0.011	...	1632.1509	...
9	3	...	1625.0123	1629.3931	...
9	4	1619.603 ^b	1619.6169	0.013	...	1625.2257	...
9	5	1613.059	1613.0997	0.041	...	1619.5150	...
9	6	1605.527 ^b	1605.5138	-0.013	*1612.136 ^b	1612.1788	0.043
9	7	1596.840	1596.8688	0.029	1603.130	1603.1443	0.014
9	8	1587.115 ^b	1587.1474	0.032	1592.178 ^b	1592.1907	0.012
10	0	1637.7580	...
10	1	...	1633.7154	1636.7632 ^c	...
10	2	*1631.427 ^b	1631.4369	0.010	...	1635.8058 ^c	...
10	3	...	1627.7859	1633.7053	...
10	4	...	1622.8905	...	*1616.980 ^b	1616.9754	-0.005
10	5	*1616.833 ^b	1616.8416	0.008	*1610.326 ^b	1610.4074	0.081
10	6	...	1609.6895	...	*1602.926 ^b	1603.0025	0.078
10	7	1601.469 ^b	1601.4537	-0.015	*1594.810 ^b	1594.8858	0.076
10	8	1592.178	1592.1325	-0.046	...	1586.2020	...
10	9	*1581.615 ^b	1581.7082	0.093	*1577.276 ^b	1577.2549	-0.021
11	0	...	1636.9352
11	1	...	1635.8893	1687.6396 ^c	...
11	2	...	1633.9242	1633.7968	...
11	3	...	1630.7017	1629.0261	...
11	4	...	1626.2762	1623.1670	...
11	5	...	1620.6945	1616.3566	...
11	6	...	1613.9892	1608.7203	...
11	7	...	1606.1789	1600.3525	...
11	8	...	1597.2703	1591.3194	...
11	9	1587.269	1587.2601	-0.009	...	1581.7197	...
11	10	*1576.198 ^b	1576.1351	-0.063	...	1571.7810	...
		s^R_R			a^R_R		
1	0	1667.349	1667.3303	-0.019
1	1	1661.140	1661.1286	-0.012	1661.685	1661.6937	0.009
2	0	1691.037	1690.9800	-0.057
2	1	1682.187	1682.2070	0.020	1682.925	1682.9176	-0.007
2	2	1676.509	1676.5051	-0.004	1677.263	1677.2771	0.014
3	0	1712.196 ^b	1712.1712	-0.025
3	1	1703.382	1703.4100	0.028	1704.202	1704.1735	-0.028

TABLE III—Continued

J	K	v_{obs}	v_{calc}	$v_{\text{calc}} - v_{\text{ob}}$	v_{obs}	v_{calc}	$v_{\text{calc}} - v_{\text{ob}}$
		s^{R}_{R}			a^{R}_{R}		
3	2	1698.026	1698.0425	0.016	1699.181	1699.1544	-0.026
3	3	1691.746	1691.7338	-0.012	1692.792	1692.8037	0.012
4	0	1738.843	1738.8193	-0.024
4	1	1724.581	1724.6017	-0.021	1725.378	1725.3430	-0.035
4	2	1719.704	1719.7210	0.017	1721.151 ^b	1721.1125	-0.038
4	3	1713.711	1713.7129	0.002	1715.405	1715.3727	-0.032
4	4	1706.818	1706.8110	-0.007	1708.306	1708.3104	0.004
5	0	1759.503	1759.4664	-0.037
5	1	*1745.743 ^b	1745.7070	-0.036	1746.427	1746.4352	0.008
5	2	1741.417	1741.4172	0.000	1743.050 ^b	1743.0266	-0.023
5	3	1735.817	1735.8132	-0.004	1738.075 ^b	1738.0282	-0.046
5	4	1729.226	1729.2300	0.004	1731.694	1731.6591	-0.035
5	5	1721.728 ^b	1721.7325	0.005	1723.821	1723.8354	0.014
6	0	1789.684	1789.7673	0.083
6	1	1766.751	1766.7102	-0.041	1767.504	1767.5343	0.030
6	2	1763.105	1763.0371	-0.068	1764.804	1764.8741	0.070
6	3	1757.932	1757.9263	-0.006	1760.693	1760.6861	-0.007
6	4	1751.749	1751.7403	-0.009	1755.100	1755.0883	-0.011
6	5	1744.604	1744.5919	-0.012	1748.088	1748.0607	-0.027
6	6	1736.504	1736.4944	-0.010	1739.386	1739.4010	0.015
7	0	1808.848	1808.8894	0.042
7	1	...	1787.6321	1788.7654	...
7	2	1784.507	1784.5343	0.027	...	1786.7464	...
7	3	1779.960	1779.9683	0.008	...	1783.3639	...
7	4	1774.245	1774.2479	0.003	1778.512 ^b	1778.5816	0.070
7	5	1767.504	1767.5096	0.005	1772.334 ^b	1772.3425	0.009
7	6	1759.812	1759.7939	-0.018	1764.538	1764.5541	0.016
7	7	*1751.027 ^b	1751.0942	0.067	1754.986	1754.9777	-0.009
8	0	1843.9000	...
8	1	...	1808.5156	1810.3031	...
8	2	...	1805.9146	1808.8497	...
8	3	1801.872	1801.8967	0.025	...	1806.2194	...
8	4	*1796.635 ^b	1796.6852	-0.050	...	1802.2320	...
8	5	1790.398	1790.4074	0.009	...	1796.7554	...
8	6	1783.150 ^b	1783.1186	-0.031	1789.684 ^b	1789.7093	0.025
8	7	1774.848	1774.8316	-0.017	1781.028	1781.0233	-0.004
8	8	1765.504	1765.5311	0.027	1770.498	1770.4796	-0.018
9	0	...	1860.2487
9	1	*1829.411 ^b	1829.4260	0.015	...	1832.4208 ^c	...
9	2	...	1827.2317	1831.5461 ^c	...
9	3	...	1823.7219	1829.5844	...
9	4	...	1819.0263	1813.0504	...
9	5	...	1813.2375	1806.7373	...
9	6	*1806.393 ^b	1806.4084	0.015	*1799.625 ^b	1799.6484	0.023
9	7	1798.585	1798.5615	-0.024	...	1791.9115	...
9	8	*1789.684 ^b	1789.6986	0.014	...	1783.6744	...
9	9	*1779.727 ^b	1779.8062	0.079	1775.270	1775.2446	-0.026
10	0	1901.7987	...
10	1	...	1850.4577	1902.1571 ^c	...
10	2	...	1848.5829	1848.4033	...
10	3	...	1845.5119	1843.7816	...
10	4	...	1841.3006	1838.1332	...
10	5	...	1835.9979	1831.5969	...
10	6	...	1829.6392	1824.3004	...
10	7	*1822.154	1822.2464	0.092	...	1816.3412	...
10	8	1813.852	1813.8301	-0.022	...	1807.7890	...
10	9	1804.413	1804.3917	-0.022	...	1798.7464	...
10	10	1793.775	1793.9120	0.137	*1789.512 ^b	1789.4456	-0.066

numerically manageable dimension, we have considered the interaction between the ν_2 , $2\nu_2$, $3\nu_2$, ν_4 , and $\nu_2 + \nu_4$ energy levels separately from the interaction between the ν_1 , ν_3 , and $2\nu_4$ levels. The Coriolis ζ coefficients for the interaction between the $\nu_1(A)$ and $\nu_4(E)$ as well as between the $\nu_2(A)$ and $\nu_3(E)$ states are very small and furthermore there is a large difference in energies between these states. This separation of the problem is therefore a very good approximation for the lowest-lying states ν_2 , $2\nu_2$, and ν_4 ; parameters obtained for these states should be considered as the main result of our work.

In our scheme, Coriolis interactions between the ν_2 , $2\nu_2$, $3\nu_2$, ν_4 , and $\nu_2 + \nu_4$ energy levels are described by the operator (4, 5)

$$H_{2,4} = (-i/2)[X_{4a}^{\nu\rho}J_\rho + (1/2)(J_\rho X_{4a}^{\nu\rho})](Q_4^-J_+ - Q_4^+J_-), \quad (18)$$

where $Q_4^\pm = Q_{4a} \pm iQ_{4b}$, $J_\pm = J_x \pm iJ_y$. Besides this, there is a centrifugal distortion operator

$$H_{\text{Cent}} = (1/8)(Y_{4a4a}^{xx} - Y_{4a4a}^{yy})[(Q_4^+)^2J_-^2 + (Q_4^-)^2J_+^2] \quad (19)$$

which connects the $\pm l$ levels in the ν_4 and $\nu_2 + \nu_4$ states. The energy matrix of these interactions is thus the 7×7 matrix given in Table VI. For the nondegenerate vibrational states, the diagonal matrix elements of this matrix are given by Eq. (15). For the inversion-rotational energy levels in the degenerate vibrational states the following expression has been used:

$$\begin{aligned} \left(\frac{E_i}{hc}\right) = & \left(\frac{E_i^0}{hc}\right) + B_iJ(J+1) + (C_i - B_i)k^2 - 2C_i\zeta_4^{(i)}kl_4 - D_J^{(i)}J^2(J+1)^2 \\ & - D_{JK}^{(i)}J(J+1)k^2 - D_K^{(i)}k^4 + \eta_{4J}^{(i)}J(J+1)kl_4 + \eta_{4K}^{(i)}k^3l_4 \\ & + H_{JJJ}^{(i)}J^3(J+1)^3 + H_{JJK}^{(i)}J^2(J+1)^2k^2 + H_{JKK}^{(i)}J(J+1)k^4 + H_{KKK}^{(i)}k^6 \\ & + \tau_{4JJK}^{(i)}J^2(J+1)^2kl_4 + \tau_{4JKK}^{(i)}J(J+1)k^3l_4 + \tau_{4KKK}^{(i)}k^5l_4 + \tau_{4KK}^{*(i)}k^3l_4^3. \end{aligned} \quad (20)$$

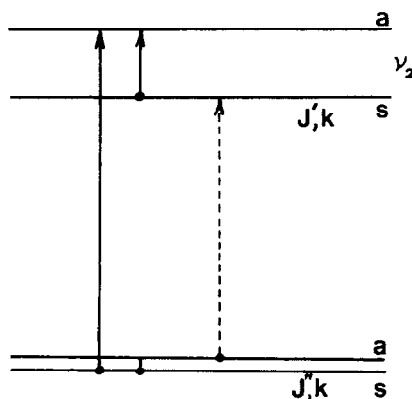


FIG. 3. Energy-level diagram illustrating the calculation of the ν_2 transition frequency (dashed line) from the known ν_2 frequency for a transition starting from a level with opposite parity and from the known pure inversion transitions in the ground and excited ν_2 states (see Table I).

TABLE IV

Submillimeter Wave Inversion and Rotation-Inversion Transitions of $^{14}\text{NH}_3$ in the ν_2 State (MHz)

Pure Inversion Transition Frequencies					
J	K	$\nu_{\text{inv.}}$	J	K	$\nu_{\text{inv.}}$
1	1	1066 650.8 ^a	7	1	810 918.7
			7	2	828 521.9
2	1	1045 318.7	7	3	858 394.2
2	2	1067 676.8 ^a	7	4	902 459.2
			7	5	961 885.4
3	1	1014 084.0	7	6	1039 360.8
3	2	1035 816.2			
3	3	1073 050.7	8	1	747 286.8
			8	2	763 583.3
4	1	973 826.5	8	3	791 531.4
4	2	994 747.8	8	4	831 969.3
4	3	1030 531.2	8	5	887 018.8
			8	6	958 827.9
5	1	925 657.4	8	7	1050 521.5
5	2	945 604.8			
5	3	979 650.0	9	3	721 263.7
5	4	1029 374.5	9	4	759 001.2
			9	5	809 481.9
6	2	889 710.9	9	6	875 368.8
6	3	921 940.3	9	7	959 569.0
6	4	968 810.0	9	8	1065 868.2
6	5	1032 323.0			

Rotation-Inversion Transition Frequencies	
$(J', K') - (J, K)$	$\nu_{\text{inv.-rot.}}$
$a(0,0) - s(1,0)^{a,b}$	466 245.1
$s(2,1) - a(1,1)^c$	140 143.5
$s(3,2) - a(2,2)^a$	741 788.1
$s(3,1) - a(2,1)^a$	762 852.3
$s(3,0) - a(2,0)^a$	769 710.2
$a(3,3) - a(2,0)^d$	772 594.9
$s(3,0) - s(3,3)^d$	1070 166.6

^a Value obtained by extrapolating to zero pressure.^b Ref. (29).^c Ref. (30).^d Forbidden (or perturbation-allowed) transition.

The precision of our ν_2 data would require the additional introduction of operators that connect levels with $\Delta k = \pm 3$ in the ground and ν_2 excited state. A detailed study of this interaction using submillimeter wave data on the inversion and inversion-rotation transitions in the ν_2 excited state will be published in a separate paper. Therefore in the present paper we have not included in our fit transitions from the ground-state levels with $k'' = 3$ or 0 to those ν_2 excited states that are perturbed by this interaction (cf. Table I).

VI. SPECTROSCOPIC PARAMETERS OF $^{14}\text{NH}_3$

In Tables VII to XII, spectroscopic parameters of $^{14}\text{NH}_3$ are presented that have been obtained by a damped least-squares fit (33) to the experimental data

TABLE V
Ground-State Molecular Parameters of $^{14}\text{NH}_3$ (in cm^{-1})

	s	a
B_{O}	9.9466529 ± 0.0000004	9.9416356 ± 0.0000004
D_{J}^{O}	$(8.4721 \pm 0.0002) \times 10^{-4}$	$(8.3184 \pm 0.0002) \times 10^{-4}$
D_{JK}^{O}	$(-15.6907 \pm 0.0007) \times 10^{-4}$	$(-15.2647 \pm 0.0007) \times 10^{-4}$
$H_{\text{JJJ}}^{\text{O}}$	$(2.298 \pm 0.001) \times 10^{-7}$	$(2.071 \pm 0.001) \times 10^{-7}$
$H_{\text{JJK}}^{\text{O}}$	$(-8.554 \pm 0.006) \times 10^{-7}$	$(-7.604 \pm 0.006) \times 10^{-7}$
$H_{\text{JKK}}^{\text{O}}$	$(11.49 \pm 0.02) \times 10^{-7}$	$(10.15 \pm 0.02) \times 10^{-7}$
$[(a)_{\text{C}_{\text{O}}} - (a)_{\text{B}_{\text{O}}}] - [(s)_{\text{C}_{\text{O}}} - (s)_{\text{B}_{\text{O}}}]$		$(6.9989 \pm 0.0001) \times 10^{-3}$
$[(a)_{\text{D}_{\text{K}}}^{\text{O}} - (s)_{\text{D}_{\text{K}}}^{\text{O}}]$		$(2.9512 \pm 0.0002) \times 10^{-5}$
$[(a)_{\text{H}_{\text{KKK}}}^{\text{O}} - (s)_{\text{H}_{\text{KKK}}}^{\text{O}}]$		$(6.3031 \pm 0.0008) \times 10^{-8}$

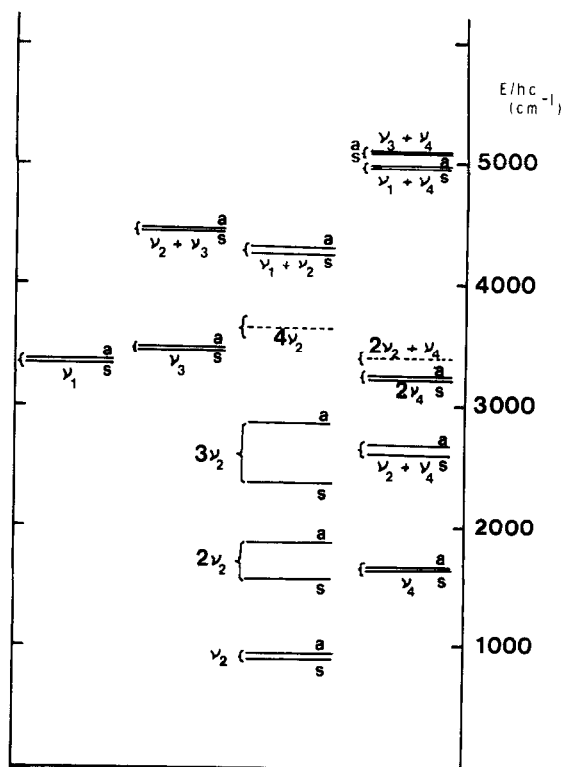


FIG. 4. The lowest vibration and inversion energy levels in NH_3 .

TABLE VI

Energy Matrix of the Coriolis and l -Type Interaction Between the ν_2 , $2\nu_2$, ν_4 , $\nu_2 + \nu_4$, and $3\nu_2$ States of NH_3^a

$ \nu_2^{\pm}, \nu_4^{\ell_4}; J, k\rangle$	$3\nu_2^{\pm}$	$+\ell$ $(\nu_2 + \nu_4)^{\mp}$	$-\ell$ $(\nu_2 + \nu_4)^{\mp}$
$ 3^{\pm}, 0^0; J, k\rangle$	$E_{3\nu_2}(J, k, \ell_4=0)^{\pm}$	$\langle 3^{\pm} \alpha 1^{\mp} \rangle f(J, k+1)$	$-\langle 3^{\pm} \alpha 1^{\mp} \rangle f(J, k-1)$
$ 1^{\mp}, 1^{+1}; J, k+1\rangle$		$E_{\nu_2+\nu_4}(J, k+1, \ell_4=1)^{\mp}$	$\langle 1^{\mp} \beta 1^{\mp} \rangle g(J, k)$
$ 1^{\mp}, 1^{-1}; J, k-1\rangle$			$E_{\nu_2+\nu_4}(J, k-1, \ell_4=-1)^{\mp}$
$ 2^{\pm}, 0^0; J, k\rangle$			
$ 0^{\mp}, 1^{+1}; J, k+1\rangle$	Hermitian		
$ 0^{\mp}, 1^{-1}; J, k-1\rangle$			
$ 1^{\pm}, 0^0; J, k\rangle$			

$2\nu_2^{\pm}$	$+\ell$ ν_4^{\mp}	$-\ell$ ν_4^{\mp}	ν_2^{\pm}
0	$\langle 3^{\pm} \alpha 0^{\mp} \rangle f(J, k+1)$	$-\langle 3^{\pm} \alpha 0^{\mp} \rangle f(J, k-1)$	0
$\langle 1^{\mp} \alpha 2^{\pm} \rangle f(J, k+1)$	0	0	0
$-\langle 1^{\mp} \alpha 2^{\pm} \rangle f(J, k-1)$	0	0	0
$E_{2\nu_2}(J, k, \ell_4=0)^{\pm}$	$\langle 2^{\pm} \alpha 0^{\mp} \rangle f(J, k+1)$	$-\langle 2^{\pm} \alpha 0^{\mp} \rangle f(J, k-1)$	0
	$E_{\nu_4}(J, k+1, \ell_4=+1)^{\mp}$	$\langle 0^{\mp} \beta 0^{\mp} \rangle g(J, k)$	$\langle 0^{\mp} \alpha 1^{\pm} \rangle f(J, k+1)$
		$E_{\nu_4}(J, k-1, \ell_4=-1)^{\mp}$	$-\langle 0^{\mp} \alpha 1^{\pm} \rangle f(J, k-1)$
			$E_{\nu_2}(J, k, \ell_4=0)^{\pm}$

^a $\alpha(\text{cm}^{-1}) = h^{3/2}[2(2\pi)^{5/2}c]^{-1}[X_{aa}^x \partial/\partial \rho + \frac{1}{2}(\partial X_{aa}^x/\partial \rho)]\lambda_4(\rho)^{-1/4}$, where the first operator $\partial/\partial \rho$ operates outside the square brackets while the second one operates only within the brackets; $\beta(\text{cm}^{-1}) = h^2[8(2\pi)^3c]^{-1}(Y_{aa}^{xx} - Y_{aa}^{yy})\lambda_4(\rho)^{-1/2}$; $f(J, k \pm 1) = +[J(J+1) - k(k \pm 1)]^{1/2}$; $g(J, k) = f(J, k+1) \times f(J, k-1)$; $\langle 3^{\pm} | \alpha | 1^{\mp} \rangle$ means $\langle \nu_2 = 3^{\pm} | \alpha | \nu_2 = 1^{\mp} \rangle$, etc.; and $E_n(J, k, \ell_4)^{\pm} = E_i/\hbar c$, where E_i is defined in Eq. (20).

on the ν_2 , $2\nu_2$, and ν_4 bands given in Tables I to III and on the data on the $\nu_2 + \nu_4$ and $3\nu_2$ bands (11). Because the fitted parameters are in general correlated, considerable care had to be taken to use suitable damping factors during the first cycles of iteration in order to reach the convergence region where the damping

TABLE VII

Independent Linear Combinations of the Parameters of the ν_2 Band of $^{14}\text{NH}_3$ (in cm^{-1})

ν_0 (s + a) *	968.12224 ± 0.00006	ν_0 (a + s) *	931.64155 ± 0.00007
^aB	10.21521 ± 0.00007	^sB	10.50682 ± 0.00003
$(^a\text{C} - ^a\text{B}) - (^s\text{C}^0 - ^s\text{B}^0)$	-0.33864 ± 0.00007	$(^s\text{C} - ^s\text{B}) - (^a\text{C}^0 - ^a\text{B}^0)$	-0.65066 ± 0.00003
$^s\text{D}_J^0 - ^a\text{D}_J$	$(0.855 \pm 0.001)10^{-4}$	$^a\text{D}_J^0 - ^s\text{D}_J$	$(-2.325 \pm 0.002)10^{-4}$
$^s\text{D}_{\text{JK}}^0 - ^a\text{D}_{\text{JK}}$	$(-1.875 \pm 0.002)10^{-4}$	$^a\text{D}_{\text{JK}}^0 - ^s\text{D}_{\text{JK}}$	$(7.396 \pm 0.004)10^{-4}$
$^s\text{D}_K^0 - ^a\text{D}_K$	$(1.095 \pm 0.001)10^{-4}$	$^a\text{D}_K^0 - ^s\text{D}_K$	$(-5.500 \pm 0.002)10^{-4}$
$^a\text{H}_{\text{JJJ}} - ^s\text{H}_{\text{JJJ}}^0$	$(-1.950 \pm 0.004)10^{-7}$	$^s\text{H}_{\text{JJJ}} - ^a\text{H}_{\text{JJJ}}^0$	$(-0.58 \pm 0.02)10^{-7}$
$^a\text{H}_{\text{JJK}} - ^s\text{H}_{\text{JJK}}^0$	$(6.50 \pm 0.02)10^{-7}$	$^s\text{H}_{\text{JJK}} - ^a\text{H}_{\text{JJK}}^0$	$(0.54 \pm 0.04)10^{-7}$
$^a\text{H}_{\text{JKK}} - ^s\text{H}_{\text{JKK}}^0$	$(-7.59 \pm 0.02)10^{-7}$	$^s\text{H}_{\text{JKK}} - ^a\text{H}_{\text{JKK}}^0$	$(-1.41 \pm 0.06)10^{-7}$
$^a\text{H}_{\text{KKK}} - ^s\text{H}_{\text{KKK}}^0$	$(3.14 \pm 0.01)10^{-7}$	$^s\text{H}_{\text{KKK}} - ^a\text{H}_{\text{KKK}}^0$	$(1.46 \pm 0.03)10^{-7}$

Inversion splitting in the $J = k = 0$ ν_2 state: 35.68728 ± 0.00020 * The band origin ν_0 is defined as $\nu_0 = (E_p^0 - E_p^0)/hc$ [Eq. (16)].

factor could be put equal to zero. Calculations have been done with the CDC Cyber 172 computer using double-precision arithmetic (120 bits).

Because in the investigated system of interacting levels not k but $k - l_4$ is a good quantum number, the standard assignment of the transition frequencies to the ν_2 , $2\nu_2$, ν_4 , etc., bands is only approximate. This is especially true for the $s2\nu_2$, av_4 levels because of the level crossing in this system. The only objective criterion on which such assignments can be based is to consider the coefficients of mixing of the wavefunctions in the system of interacting levels,

$$\psi_i = \sum_k c_{ik} \psi_{ik}^0, \quad (21)$$

TABLE VIII

Independent Linear Combinations of the Parameters of the $2\nu_2$ Band of $^{14}\text{NH}_3$ (in cm^{-1})

ν_0 (s + a) *	1882.1751 ± 0.0001	ν_0 (a + s) *	1596.6753 ± 0.0020
^aB	9.73747 ± 0.00009	^sB	10.5676 ± 0.0002
$(^a\text{C} - ^a\text{B}) - (^s\text{C} - ^s\text{B})$	0.15203 ± 0.00008	$(^s\text{C} - ^s\text{B}) - (^a\text{C} - ^a\text{B})$	-0.9284 ± 0.0002
$^s\text{D}_J^0 - ^a\text{D}_J$	$(3.860 \pm 0.006)10^{-4}$	$^a\text{D}_J^0 - ^s\text{D}_J$	$(3.23 \pm 0.04)10^{-4}$
$^s\text{D}_{\text{JK}}^0 - ^a\text{D}_{\text{JK}}$	$(-10.225 \pm 0.010)10^{-4}$	$^a\text{D}_{\text{JK}}^0 - ^s\text{D}_{\text{JK}}$	$(-6.56 \pm 0.007)10^{-4}$
$^s\text{D}_K^0 - ^a\text{D}_K$	$(6.057 \pm 0.007)10^{-4}$	$^a\text{D}_K^0 - ^s\text{D}_K$	$(4.94 \pm 0.06)10^{-4}$
$^a\text{H}_{\text{JJJ}} - ^s\text{H}_{\text{JJJ}}^0$	$(-0.478 \pm 0.005)10^{-6}$	$^s\text{H}_{\text{JJJ}} - ^a\text{H}_{\text{JJJ}}^0$	$(-0.227 \pm 0.030)10^{-6}$
$^a\text{H}_{\text{JJK}} - ^s\text{H}_{\text{JJK}}^0$	$(1.868 \pm 0.020)10^{-6}$	$^s\text{H}_{\text{JJK}} - ^a\text{H}_{\text{JJK}}^0$	$(3.22 \pm 0.08)10^{-6}$
$^a\text{H}_{\text{JKK}} - ^s\text{H}_{\text{JKK}}^0$	$(-4.179 \pm 0.040)10^{-6}$	$^s\text{H}_{\text{JKK}} - ^a\text{H}_{\text{JKK}}^0$	$(-14.67 \pm 0.20)10^{-6}$
$^a\text{H}_{\text{KKK}} - ^s\text{H}_{\text{KKK}}^0$	$(4.596 \pm 0.030)10^{-6}$	$^s\text{H}_{\text{KKK}} - ^a\text{H}_{\text{KKK}}^0$	$(13.87 \pm 0.10)10^{-6}$

Inversion splitting in the $J = k = 0$ $2\nu_2$ state: 284.7064 ± 0.0020 * The band origin ν_0 is defined as $\nu_0 = (E_p^0 - E_p^0)/hc$ [Eq. (16)].

TABLE IX

Independent Linear Combinations of the Parameters of the ν_4 Band of $^{14}\text{NH}_3$ (in cm^{-1})^a

	$s \leftrightarrow s, n = s$	$a \leftrightarrow a, n = a$
$\nu_0 - (n_{\text{C}}^{\text{O}} - n_{\text{B}}^{\text{O}}) + \frac{1}{4}(n_{\text{K}} + n_{\text{KK}}^*) - \frac{2n_{\text{KKK}}}{3}$	1629.99072 ± 0.00021	1630.3391 ± 0.0008
$n_{\text{C}} - n_{\text{B}} - n_{\text{C}}n_{\text{K}} + n_{\text{K}} + n_{\text{KK}}^* - \frac{4}{3}n_{\text{KKK}}$	-2.43295 ± 0.00005	-2.41663 ± 0.00017
$n_{\text{C}} - n_{\text{B}} - (n_{\text{C}}^{\text{O}} - n_{\text{B}}^{\text{O}}) - \frac{5n_{\text{KKK}}}{2} + \frac{3}{2}(n_{\text{K}} + n_{\text{KK}}^*)$	-0.160203 ± 0.000035	-0.15235 ± 0.00008
n_{B}	10.040597 ± 0.000027	10.02747 ± 0.00006
$n_{\text{D}_J^{\text{O}}} - n_{\text{D}_J}$	$(-2.235 \pm 0.006)10^{-4}$	$(-0.871 \pm 0.019)10^{-4}$
$n_{\text{D}_{\text{JK}}^{\text{O}}} - n_{\text{D}_{\text{JK}}}$	$(5.503 \pm 0.014)10^{-4}$	$(1.393 \pm 0.044)10^{-4}$
$n_{\text{D}_K^{\text{O}}} - n_{\text{D}_K} + \frac{5n_{\text{KKK}}}{2}$	$(-2.706 \pm 0.011)10^{-4}$	$(2.580 \pm 0.041)10^{-4}$
$n_{\text{H}_{\text{JJJ}}^{\text{O}}} - n_{\text{H}_{\text{JJJ}}}$	$(1.2014 \pm 0.0040)10^{-6}$	$(0.2486 \pm 0.0018)10^{-5}$
$n_{\text{H}_{\text{JJK}}^{\text{O}}} - n_{\text{H}_{\text{JJK}}}$	$(-3.689 \pm 0.015)10^{-6}$	$(-1.167 \pm 0.007)10^{-5}$
$n_{\text{H}_{\text{JKK}}^{\text{O}}} - n_{\text{H}_{\text{JKK}}}$	$(3.096 \pm 0.025)10^{-6}$	$(2.545 \pm 0.012)10^{-5}$
$n_{\text{H}_{\text{KKK}}^{\text{O}}} - n_{\text{H}_{\text{KKK}}}$	$(-0.557 \pm 0.013)10^{-6}$	$(-1.753 \pm 0.006)10^{-5}$
n_{H_J}	$(-0.967 \pm 0.038)10^{-4}$	$(5.08 \pm 0.17)10^{-4}$
$n_{\text{T}_{\text{JJK}}}$	$(1.1278 \pm 0.0042)10^{-5}$	$(0.2702 \pm 0.0025)10^{-4}$
$n_{\text{T}_{\text{JKK}}}$	$(-2.708 \pm 0.006)10^{-5}$	$(-1.3090 \pm 0.0028)10^{-4}$
$n_{\text{D}_K^{\text{O}}} + \frac{5n_{\text{KKK}}}{6} - \frac{1}{4}(n_{\text{K}} + n_{\text{KK}}^*)$	$(1.0438 \pm 0.0011)10^{-3}$	$(1.0501 \pm 0.0038)10^{-3}$
$n_{\text{H}_{\text{KKK}}^{\text{O}}} + \frac{1n_{\text{KKK}}}{6}$	$(2.3124 \pm 0.0030)10^{-6}$	$(1.6732 \pm 0.0015)10^{-5}$
$n_{\text{K}} - n_{\text{K}}(\nu_2 + \nu_4) + n_{\text{KK}}^* - n_{\text{KK}}^*(\nu_2 + \nu_4)$	$(-4.7168 \pm 0.0046)10^{-3}$	$(1.905 \pm 0.016)10^{-3}$
$n_{\text{T}_{\text{KKK}}} - n_{\text{T}_{\text{KKK}}}(\nu_2 + \nu_4)$	0^b	0^b
Inversion splitting in the $J = k = 0 \nu_4$ state: 1.1488 ± 0.0010		

^a The band origin ν_0 is defined as $\nu_0 = (E_{\text{P}}^0 - E_{\text{P}}^{\text{P}})/hc$ [Eq. (20)].^b Constrained value.

where ψ_{ik}^0 are the unperturbed wavefunctions. Our assignments in Tables I to III are essentially based on the principle of the maximum contribution of the unperturbed wavefunction ψ_{ik}^0 to the perturbed state. This is illustrated by Table XIII which, however, also shows that in some cases this principle may not work.

TABLE X

Off-Diagonal Matrix Elements of the Coriolis and l -Type Interaction^a

$\langle 3^- \alpha 1^+ \rangle$	6.6934 ± 0.0018	$\langle 3^+ \alpha 1^- \rangle$	-1.484 ± 0.021
$\langle 3^- \alpha 0^+ \rangle$	0.504 ± 0.011	$\langle 3^+ \alpha 0^- \rangle$	-5.9031 ± 0.0010
$\langle 2^- \alpha 1^+ \rangle$	5.2619 ± 0.0032	$\langle 2^+ \alpha 1^- \rangle$	11.3684 ± 0.0040
$\langle 2^- \alpha 0^+ \rangle$	-2.194 ± 0.006	$\langle 2^+ \alpha 0^- \rangle$	-1.2827 ± 0.0025
$\langle 1^- \alpha 0^+ \rangle$	10.338 ± 0.031	$\langle 1^+ \alpha 0^- \rangle$	11.461 ± 0.009
$\langle 1^+ \beta 1^+ \rangle$	-0.244 ± 0.029	$\langle 1^- \beta 1^- \rangle$	0.00466 ± 0.00041
$\langle 0^+ \beta 0^+ \rangle$	-0.00291 ± 0.00011	$\langle 0^- \beta 0^- \rangle$	-0.00701 ± 0.00021

^a Matrix elements are defined in Table VI.

TABLE XI

Independent Linear Combinations of the Parameters of the $3\nu_2$ Band of $^{14}\text{NH}_3$ (in cm^{-1})

ν_0 (s + a) *	2895.6063 ± 0.0012	ν_0 (a + s) *	2383.3804 ± 0.0026
a_B	8.91779 ± 0.00026	s_B	9.42827 ± 0.00031
$(a_C - a_B) - (s_C^O - s_B^O)$	1.10027 ± 0.00018	$(s_C - s_B) - (a_C^O - a_B^O)$	0.47510 ± 0.00028
$s_{D_J}^O - a_{D_J}$	$(1.179 \pm 0.042) 10^{-3}$	$a_{D_J}^O - s_{D_J}$	$(0.963 \pm 0.019) 10^{-3}$
$s_{D_{JK}}^O - a_{D_{JK}}$	$(-3.165 \pm 0.058) 10^{-3}$	$a_{D_{JK}}^O - s_{D_{JK}}$	$(-2.528 \pm 0.043) 10^{-3}$
$s_{D_K}^O - a_{D_K}$	$(1.994 \pm 0.038) 10^{-3}$	$a_{D_K}^O - s_{D_K}$	$(1.661 \pm 0.038) 10^{-3}$
$a_{H_{JJJ}} - s_{H_{JJJ}}^O$	$(-1.573 \pm 0.049) 10^{-5}$	$s_{H_{JJJ}} - a_{H_{JJJ}}^O$	$(-0.769 \pm 0.026) 10^{-6}$
$a_{H_{JJK}} - s_{H_{JJK}}^O$	$(4.618 \pm 0.059) 10^{-5}$	$s_{H_{JJK}} - a_{H_{JJK}}^O$	$(2.269 \pm 0.061) 10^{-6}$
$a_{H_{JKK}} - s_{H_{JKK}}^O$	$(-4.096 \pm 0.058) 10^{-5}$	$s_{H_{JKK}} - a_{H_{JKK}}^O$	$(-2.222 \pm 0.038) 10^{-6}$
$a_{H_{KKK}} - s_{H_{KKK}}^O$	$(1.039 \pm 0.029) 10^{-5}$	$s_{H_{KKK}} - a_{H_{KKK}}^O$	$(0.737 \pm 0.032) 10^{-6}$
Inversion splitting in the $J = k = 0$ $3\nu_2$ state: 511.4325 ± 0.0040			

* The band origin ν_0 is defined as $\nu_0 = (E_i^0 - E_f^0)/hc$ [Eq. (16)].

For example, the 1855.468 cm^{-1} and 1901.229 cm^{-1} transitions should both be assigned as $a^PR(10,2)$, $\nu_4(-l)$. To avoid this, we assign the 1901.229 cm^{-1} transition as $a^PR(10,2)$, $\nu_4(-l)$ because it has a larger contribution from the $|0^-, 1^{-1}; 11, 1\rangle$ state than the 1855.468 cm^{-1} transition. The latter is then assigned as $aR(10,2)$, $2\nu_2$ because its second-largest contribution is from the $|2^+, 0^0; 11, 2\rangle$ state. The few such cases that occurred in our data are indicated in Tables II and III by special labels.

TABLE XII

Independent Linear Combinations of the Parameters of the $\nu_2 + \nu_4$ Band of $^{14}\text{NH}_3$ (in cm^{-1})^a

	$s \leftrightarrow s, n = s$	$a \leftrightarrow a, n = a$
$\nu_0 - (n_C^O - n_B^O) + \frac{1}{4}n_{\eta_K}$	2544.2587 ± 0.0012	2588.9592 ± 0.0017
$n_C - n_B - n_C^n \xi_4 + n_{\eta_K}$	-3.0029 ± 0.0006	-2.4137 ± 0.0008
$n_C - n_B - (n_C^O - n_B^O) + \frac{3}{2}n_{\eta_K}$	-0.6471 ± 0.0006	-0.1187 ± 0.0006
n_B	10.38786 ± 0.00021	9.97176 ± 0.00046
$n_{D_J}^O - n_{D_J}$	$(5.302 \pm 0.011) 10^{-4}$	$(-1.759 \pm 0.009) 10^{-4}$
$n_{D_{JK}}^O - n_{D_{JK}}$	$(-4.539 \pm 0.007) 10^{-4}$	$(11.711 \pm 0.047) 10^{-4}$
$n_{D_K}^O - n_{D_K}$	$(-3.314 \pm 0.021) 10^{-4}$	$(-15.881 \pm 0.051) 10^{-4}$
n_{η_J}	$(2.369 \pm 0.005) 10^{-3}$	$(-6.503 \pm 0.009) 10^{-3}$
Inversion splitting in $J = k = 0$ $\nu_2 + \nu_4$ state: 45.4993 ± 0.0030		

^a The band origin is defined as $\nu_0 = (E_i^0 - E_f^0)/hc$ [Eq. (20)]; sextic parameters have been neglected.

TABLE XIII
Example of the Assignments Based on the Values of $(c_{ik}^2 / \sum_k c_{ik}^2) \times 100$ for $J = 11, k - l_4 = 2$

Calc. freq. (cm^{-1})	Assignment	$ v_2^+, v_4^{l_4}, j, k\rangle$									
		$ 3^+, 0^0; 11, 2\rangle$	$ 1^-, 1^{+1}; 11, 3\rangle$	$ 1^-, 1^{-1}; 11, 1\rangle$	$ 2^+, 0^0; 11, 2\rangle$	$ 0^-, 1^{+1}; 11, 3\rangle$	$ 0^-, 1^{-1}; 11, 1\rangle$	$ 1^+, 0^0; 11, 2\rangle$	$ 1^+, 0^0; 11, 1\rangle$	$ 1^+, 0^0; 11, 2\rangle$	$ 1^+, 0^0; 11, 1\rangle$
1158.060	$aR(10, 2), v_2$	0.0	0.0	0.0	0.0	3.3	3.3	0.0	0.0	93.4	0.0
1848.403	$a^R(10, 2), v_4(+k)$	0.2	0.8	0.8	42.5	51.9	2.6	1.3	1.3	1.3	1.3
1855.468	$aR(10, 2), 2v_2$	0.0	0.7	0.7	38.1	13.7	40.6	0.2	0.2	0.2	0.2
1901.229	$a^P(10, 2), v_4(-k)$	1.7	0.4	0.4	15.8	24.1	52.6	5.2	5.2	5.2	5.2
2557.356	$aR(10, 2), 3v_2$	97.4	0.3	0.3	0.1	0.9	1.0	0.0	0.0	0.0	0.0
2797.258	$a^R(10, 2), v_2+v_4(+k)$	0.1	73.9	25.8	0.2	0.0	0.0	0.0	0.0	0.0	0.0
2838.523	$a^P(10, 2), v_2+v_4(-k)$	0.6	23.9	72.1	3.3	0.0	0.0	0.0	0.0	0.0	0.0

It should be emphasized that such assignments are only formal if there is strong mixing of the upper-state wavefunctions. Strictly speaking, we should give the same label to a series of lines originating from the same ground inversion-rotational level J'' , k'' and terminating on upper-state levels with the same J' , $k' - l_4$ quantum numbers.

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