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# A Simultaneous Analysis of the Microwave, Submillimeterwave, Far Infrared, and Infrared–Microwave Two-Photon Transitions between the Ground and $\nu_2$ Inversion–Rotation Levels of $^{14}NH_3$

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Fourier transform infrared spectra of the inversion–rotation transitions have been measured with 0.010-$cm^{-1}$ resolution between 40 and 300 $cm^{-1}$ in the ground state and $\nu_2$ excited states of $^{14}NH_3$. Submillimeterwave spectra of the inversion and inversion–rotation transitions in the $\nu_2$ state of $^{14}NH_3$, including a few $\Delta k = \pm 3$ "perturbation-allowed" transitions, have been measured with microwave accuracy between 540 and 770 GHz. A simultaneous least-squares analysis of these data, the microwave ground-state transition frequencies, and the $\nu_2$ infrared–microwave two-photon transition frequencies has been carried out. A theory of the $\Delta k = \pm 3n$ interactions in the ground and $\nu_2$ excited states of ammonia (S. P. Belov, L. I. Gershtein, A. F. Krupnov, A. V. Maslovskij, Š. Urban, V. Špirko, and D. Papoušek, *J. Mol. Spectrosc.* **84**, 288–304 (1980)) has been used in the analysis. A set of the ground- and $\nu_2$-state molecular parameters has been obtained which describes the experimental data within the precision of the experiment. The "smoothed" values of transition frequencies can be used for calibration purposes with a precision better than $3 \times 10^{-5}$ $cm^{-1}$ in the submillimeterwave region, better than $10^{-3}$ $cm^{-1}$ in the far-infrared region, and better than $1.5 \times 10^{-3}$ $cm^{-1}$ in the region 700–1200 $cm^{-1}$.

## I. INTRODUCTION

Precise knowledge of the frequencies of transitions between the ground and $\nu_2$ inversion–rotation levels of ammonia is important; e.g., for astrophysical studies of the planetary and interstellar ammonia, in the investigation of optically pumped ammonia lasers, and for calibration purposes in the far- and medium-infrared regions.

In a previous paper (*1*) we measured the high-resolution infrared spectra of $^{14}NH_3$ in the region of the $\nu_2$, $2\nu_2$, and $\nu_4$ bands and analyzed them using a

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modified theory of the Coriolis and $l$-type interactions in ammonia; the theory of the $\Delta k = \pm 3n$ interactions was not introduced in that analysis. In a subsequent paper (*2*), we derived a theory of the $\Delta k = \pm 3n$ interactions, taking into account the large amplitude motion in ammonia, and applied it to the analysis of the submillimeterwave data on the inversion and inversion–rotation transitions in the $\nu_2$ state of $^{14}NH_3$.

In the present paper we extended our measurements to the far-infrared region between 40 and 300 $cm^{-1}$ (Fourier transform spectroscopy of the inversion–rotation transitions in the ground and $\nu_2$ excited states of ammonia). We have also remeasured the spectra in the submillimeterwave region between 540 and 700 GHz (inversion and inversion–rotation transitions in the $\nu_2$ excited state) mostly with microwave accuracy.

We combined the results of our previous measurements (*1*, *2*), the present data, and precise literature data on the ground-state inversion transitions and the $\nu_2$ band frequencies in a simultaneous least-squares analysis of the experimental data of three types: (i) microwave and far-infrared frequencies of transitions between the inversion and inversion–rotation energy levels in the ground state, (ii) frequencies of infrared–microwave two-photon transitions between the ground- and $\nu_2$-state energy levels, and (iii) submillimeterwave and far-infrared frequencies of transitions between the inversion and inversion–rotation levels in the $\nu_2$ state.

In this analysis, the theory of the $\Delta k = \pm 3n$ interactions in ammonia (*2*) has been applied to the ground and excited $\nu_2$ states. The experimental data used in the analysis were found to be internally consistent and extremely precise; ground-state and excited $\nu_2$-state molecular parameters of $^{14}NH_3$ have been obtained which describe these data within the accuracy of the experimental data. The "smoothed" values of the transition frequencies in the far- and medium-infrared regions obtained in this work are believed to be of accuracy sufficient for calibration purposes in the submillimeterwave, far-infrared, and medium-infrared regions.

## II. EXPERIMENTAL DETAILS

The success in solving the problem outlined in Part I of this paper depends on the accuracy and internal consistency of the experimental data used in the analysis. As for the ground-state microwave data, we have used the frequencies of the pure inversion transitions of Poynter and Kakar (*3*) and Sinha and Smith (*4*) together with some frequencies of the inversion–rotation transitions measured by Gordy *et al.* (*5*) and Krupnov *et al.* (*6*).

For the $\nu_2$ band transitions, infrared–microwave (*7*, *8*) and infrared heterodyne measurements (*9*) have been combined with diode laser measurements calibrated as described in our previous paper (*1*).

The ground-state rotational and centrifugal distortion constants can be determined from the combination differences using the $\nu_2$-band frequencies. However, the very precise data on the $\nu_2$ band (*7–9*) are not sufficiently complete to determine precise values of the higher-order centrifugal distortion constants.

The ground-state parameters could be determined from the inversion–rotation transitions which appear in the far-infrared region. The only available data on these transitions are those of Dowling (*10*) which, however, have only been measured with 0.08-$cm^{-1}$ resolution and up to $J = 11$. We have therefore remeasured the far-infrared spectrum of ammonia in the range 35–278 $cm^{-1}$ using a Fourier spectrometer recently built at the University of Oulu (*11*).

We have recorded the apodized Fourier spectra between 35 and 100 $cm^{-1}$ using an 18-$\mu$m thick beamsplitter and between 100 and 278 $cm^{-1}$ using an 8-$\mu$m thick beamsplitter. The total pressure of the sample in the cell for both spectra was 10.5 $\times 10^{-3}$ Pa (1.4 Torr). The sample, in liquid form before vaporization, comprises 25% $NH_3$ and 75% water (used for calibration). The resolution determined as a half-width of the weak lines was 0.014 $cm^{-1}$.

In order to resolve certain fine details, we have measured unapodized spectra in the corresponding spectral regions with 0.010-$cm^{-1}$ resolution using an 18-$\mu$m beamsplitter. The total pressure of the sample in the cell was $8.25 \times 10^{-3}$ Pa (1.1 Torr).

We have been able to assign the ground-state inversion–rotation transitions of $^{14}NH_3$ up to $J = 13$ (Table I). It can be seen that we have resolved almost completely the $K$ structure of these transitions, except for a few transitions which are indicated in Table I.

We have also assigned the lines of the inversion–rotation transitions in the $\nu_2$ excited state of $^{14}NH_3$ up to $J = 11$ (Table II). Many lines in our spectra could be assigned to the ground-state inversion–rotation spectrum of $^{15}NH_3$ occurring at natural abundance in the sample. Their frequencies agreed within the experimental accuracy with the recent Fourier spectra of $^{15}NH_3$ measured by Carlotti *et al.* (*12*), and they are not reported in our paper.

Typical parts of our apodized and unapodized Fourier spectra are shown in Figs. 1–5.

The basic source of information on the inversion and inversion–rotation transitions in the $\nu_2$ excited state of ammonia are our submillimeterwave measurements reported in detail in our previous paper (*2*). In the present paper, we remeasured the spectra in the region 540–700 GHz.

The high-sensitivity submillimeterwave spectrometer RAD (*13, 14*) at the Institute for Applied Physics of the Academy of Sciences USSR in Gorkii has been used with a system employing phase-sensitive frequency stabilization of the backward wave oscillator (*15*). The absolute accuracy of the measurements of frequencies is $\pm 10$ kHz for lines with signal-to-noise ratios higher than 600; for the weakest lines (cf. Table III and Fig. 6) the experimental uncertainty can reach $\pm 0.5$ MHz. However, as we pointed out in our previous paper (*2*), the line centers of ammonia for transitions in the $\nu_2$ excited state exhibit an anomalously large pressure dependence. In the present paper we measured at pressures of 53 Pa (0.4 Torr) of ammonia in the acoustic cell of the submillimeterwave spectrometer. The experimental uncertainty of the line frequencies taking into account this effect is therefore about $\pm 1$ MHz.

The results of measurements together with our previous submillimeterwave data are given in Tables III and V.

## TABLE I

Inversion–Rotation Transition Wavenumbers ($cm^{-1}$) and Intensities ($cm^{-2}$ $atm^{-1}$) of $^{14}NH_3$ in the Ground State[a]

| J | K | s←s C | s←s O | (O-C) x10^5 | I | s←a C | s←a O | (O-C) x10^5 | I |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 0( | 20.673261 | ——— | ——— | 0. | 19.09648 | 19.096481 1)[b] | 0 | 0.14E+00 |
| 1 | 0 | 40.32312 | ——— | ——— | 0.11E+01 | 38.97607) | ——— | ——— | 0. |
| 1 | 1 | 40.53622 | ——— | ——— | 0.42E+00 | 38.97537 | 38.976191(100) | 73 | 0.39E+00 |
| 2 | 0( | 60.32362) | ——— | ——— | 0. | 58.82481 | ——— | ——— | 0.26E+01 |
| 2 | 1 | 60.33954 | 60.340761(200) | 115 | 0.13E+01 | 58.82738 | ——— | ——— | 0.12E+01 |
| 2 | 2 | 60.38778 | 60.387001(200) | -75 | 0.87E+00 | 58.83479 | ——— | ——— | 0.82E+00 |
| 3 | 0 | 80.05603 | ——— | ——— | 0.49E+01 | 78.62216) | ——— | ——— | 0. |
| 3 | 1 | 80.07463 | ——— | ——— | 0.23E+01 | 78.62881 | ——— | ——— | 0.23E+01 |
| 3 | 2 | 80.13094 | ——— | ——— | 0.20E+01 | 78.64532 | ——— | ——— | 0.19E+01 |
| 3 | 3 | 80.22629 | ——— | ——— | 0.25E+01 | 78.67327 | ——— | ——— | 0.24E+01 |
| 4 | 0( | 99.70245) | ——— | ——— | 0. | 98.34779 | ——— | ——— | 0.61E+01 |
| 4 | 1 | 99.72363 | 99.723701(200) | 8 | 0.30E+01 | 98.35491 | ——— | ——— | 0.30E+01 |
| 4 | 2 | 99.78754 | 99.788601(100) | -94 | 0.28E+01 | 98.37407 | ——— | ——— | 0.27E+01 |
| 4 | 3 | 99.89552 | 99.896501(200) | 98 | 0.47E+01 | 98.42871 | ——— | ——— | 0.45E+01 |
| 4 | 4 | 100.05020 | 100.049801(200) | -40 | 0.13E+01 | 98.48937 | ——— | ——— | 0.14E+01 |
| 5 | 0 | 119.24982 | ——— | ——— | 0.64E+01 | 117.98182) | ——— | ——— | 0. |
| 5 | 1 | 119.26938 | ——— | ——— | 0.32E+01 | 117.99417 | 117.99258(200) | -167 | 0.31E+01 |
| 5 | 2 | 119.34050 | 119.339201(100) | -129 | 0.30E+01 | 118.03185 | 118.030481(200) | -65 | 0.39E+01 |
| 5 | 3 | 119.46077 | 119.460501(100) | -27 | 0.56E+01 | 118.09173 | 118.092201(200) | 47 | 0.55E+01 |
| 5 | 4 | 119.63187 | 119.632601(100) | 72 | 0.24E+01 | 118.17594 | 118.174881(100) | -113 | 0.23E+01 |
| 5 | 5 | 119.85807 | 119.858001( 80) | -46 | 0.19E+01 | 118.28144 | 118.281001(100) | -44 | 0.13E+01 |
| 6 | 0( | 138.66995) | ——— | ——— | 0. | 137.50508 | ——— | ——— | 0.54E+01 |
| 6 | 1 | 138.69586 | 138.696801(200) | 100 | 0.27E+01 | 137.52057 | ——— | ——— | 0.27E+01 |
| 6 | 2 | 138.77365 | 138.773201( 80) | -45 | 0.27E+01 | 137.56695 | 137.567201( 80) | 25 | 0.27E+01 |
| 6 | 3 | 138.90487 | 138.907201(100) | 282 | 0.32E+01 | 137.64434 | ——— | ——— | 0.51E+02 |
| 6 | 4 | 139.09188 | 139.090001(200) | -187 | 0.24E+01 | 137.75851 | 137.740781(200) | -80 | 0.24E+01 |
| 6 | 5 | 139.33808 | 139.337401( 80) | -68 | 0.21E+01 | 137.88583 | 137.884681( 80) | -102 | 0.20E+01 |
| 6 | 6 | 139.64843 | 139.647401(200) | -132 | 0.27E+01 | 138.04795 | 138.045801(200) | -215 | 0.27E+01 |
| 7 | 0 | 157.98976 | ——— | ——— | 0.40E+01 | 156.89924) | ——— | ——— | 0. |
| 7 | 1 | 157.98766 | ——— | ——— | 0.20E+01 | 156.91778 | 156.91780(100) | 1 | 0.20E+01 |
| 7 | 2 | 158.07180 | 158.071801( 60) | 0 | 0.20E+01 | 156.97334 | 156.97300( 60) | -33 | 0.20E+01 |
| 7 | 3 | 158.21453 | 158.214301(100) | -22 | 0.41E+01 | 157.06466 | 157.062001(200) | +265 | 0.40E+01 |
| 7 | 4 | 158.41503 | 158.414701(200) | -32 | 0.20E+01 | 157.19430 | 157.195501(200) | 119 | 0.20E+01 |
| 7 | 5 | 158.67982 | 158.678601(200) | -121 | 0.19E+01 | 157.35846 | 157.357901( 80) | -55 | 0.19E+01 |
| 7 | 6 | 159.01282 | 159.011201(200) | -142 | 0.33E+01 | 157.55681 | ——— | ——— | 0.33E+01 |
| 7 | 7 | 159.41992 | 159.418801(100) | -112 | 0.11E+01 | 157.78721 | 157.786801(100) | ——— | 0.11E+01 |
| 8 | 0( | 177.10088) | ——— | ——— | 0. | 176.14708 | ——— | ——— | 0.26E+01 |
| 8 | 1 | 177.13071 | 177.129901(200) | -81 | 0.13E+01 | 176.16853 | ——— | ——— | 0.13E+01 |
| 8 | 2 | 177.22065 | 177.219461(200) | -129 | 0.13E+01 | 176.23286 | 176.232901(100) | 3 | 0.13E+01 |
| 8 | 3 | 177.37022 | 177.368301(100) | -192 | 0.27E+01 | 176.34178 | 176.341501(100) | -28 | 0.27E+01 |
| 8 | 4 | 177.58712 | 177.585401(200) | -171 | 0.14E+01 | 176.48963 | 176.488401(100) | -123 | 0.14E+01 |
| 8 | 5 | 177.86910 | 177.869301(100) | 20 | 0.14E+01 | 176.68139 | ——— | ——— | 0.14E+01 |
| 8 | 6 | 178.22262 | 178.223701(100) | 137 | 0.27E+01 | 176.91444 | ——— | ——— | 0.26E+01 |
| 8 | 7 | 178.65392 | 178.653801(300) | -11 | 0.12E+01 | 177.18731 | ——— | ——— | 0.12E+01 |
| 8 | 8 | 179.17126 | ——— | ——— | 0.83E+00 | 177.49795 | ——— | ——— | 0.81E+00 |
| 9 | 0 | 196.08008 | ——— | ——— | 0.15E+01 | 195.23254) | ——— | ——— | 0. |
| 9 | 1 | 196.11166 | ——— | ——— | 0.74E+00 | 195.25679 | 195.25650(100) | -25 | 0.73E+00 |
| 9 | 2 | 196.20705 | 196.207301( 70) | 24 | 0.75E+00 | 195.32940 | 195.33030( 70) | 89 | 0.74E+00 |
| 9 | 3 | 196.37055 | 196.371301( 70) | 75 | 0.26E+01 | 195.44747 | 195.447601( 70) | 13 | 0.13E+01 |
| 9 | 4 | 196.59491 | 196.595201( 70) | 28 | 0.81E+00 | 195.62008 | 195.621101( 70) | 102 | 0.80E+00 |
| 9 | 5 | 196.89273 | 196.892601(100) | -13 | 0.84E+00 | 195.83798 | 195.837001(200) | -98 | 0.83E+00 |
| 9 | 6 | 197.26531 | 197.266401( 80) | 109 | 0.17E+01 | 196.10380 | 196.106001(200) | 211 | 0.17E+01 |
| 9 | 7 | 197.71858 | 197.718661( 70) | 1 | 0.87E+00 | 196.41899 | 196.417001( 70) | 0 | 0.85E+00 |
| 9 | 8 | 198.26043 | 198.263601( 70) | 17 | 0.80E+00 | 196.77573 | 196.775801( 70) | 4 | 0.78E+00 |
| 9 | 9 | 198.90125 | 198.901301( 70) | 4 | 0.11E+01 | 197.17728 | 197.177901( 70) | 21 | 0.11E+01 |
| 10 | 0( | 214.88481) | ——— | ——— | 0. | 214.14085 | 214.14150(200) | 65 | 0.73E+00 |
| 10 | 1 | 214.91814 | 214.917301( 80) | -84 | 0.37E+00 | 214.16765 | ——— | ——— | 0.37E+00 |
| 10 | 2 | 215.01852 | 215.019301( 80) | 78 | 0.38E+00 | 214.24810 | 214.248201( 80) | 9 | 0.38E+00 |
| 10 | 3 | 215.18216 | 215.181201( 80) | -96 | 0.79E+00 | 214.38719 | 214.387101( 80) | -9 | 0.78E+00 |
| 10 | 4 | 215.42613 | 215.426101(200) | -1 | 0.42E+00 | 214.57038 | ——— | ——— | 0.41E+00 |
| 10 | 5 | 215.73845 | 215.739001( 80) | 50 | 0.44E+00 | 214.81300 | 214.813401( 80) | 40 | 0.44E+00 |
| 10 | 6 | 216.12851 | 216.129201(200) | 58 | 0.95E+00 | 215.10968 | ——— | ——— | 0.94E+00 |
| 10 | 7 | 216.60185 | 216.602001( 90) | 14 | 0.50E+00 | 215.44045 | 215.440501( 90) | ——— | 0.50E+00 |
| 10 | 8 | 217.16598 | 217.165991( 90) | -7 | 0.52E+00 | 215.86459 | 215.865401( 90) | 80 | 0.51E+00 |
| 10 | 9 | 217.83068 | 217.829901( 90) | -97 | 0.97E+00 | 216.32043 | 216.320301( 90) | -13 | 0.96E+00 |
| 10 | 10 | 218.60683 | 218.613201( 70) | 37 | 0.36E+00 | 216.82470 | 216.825701( 70) | 100 | 0.35E+00 |
| 11 | 0 | 233.50381 | ——— | ——— | 0.93E+00 | 232.08321) | ——— | ——— | 0. |
| 11 | 1 | 233.53867 | 233.538501( 60) | -17 | 0.16E+00 | 232.08773 | 232.087801( 60) | 6 | 0.16E+00 |
| 11 | 2 | 233.64364 | 233.643801( 60) | 16 | 0.17E+00 | 232.97545 | 232.975101( 60) | -34 | 0.17E+00 |
| 11 | 3 | 233.82745 | 233.827401( 60) | -5 | 0.36E+00 | 233.11455 | 233.113201( 80) | 65 | 0.35E+00 |
| 11 | 4 | 234.08630 | 234.086801(230) | -56 | 0.19E+00 | 233.32748 | ——— | ——— | 0.19E+00 |
| 11 | 5 | 234.39506 | 234.395301( 60) | 24 | 0.21E+00 | 233.59264 | 233.592901( 60) | 25 | 0.20E+00 |
| 11 | 6 | 234.80101 | 234.800901( 60) | -10 | 0.45E+00 | 233.91786 | 233.918301( 60) | 43 | 0.44E+00 |
| 11 | 7 | 235.29261 | 235.292001(200) | -61 | 0.25E+00 | 234.30351 | 234.303101( 60) | -40 | 0.24E+00 |
| 11 | 8 | 235.87692 | 235.876701( 60) | -22 | 0.27E+00 | 234.74964 | 234.749601( 60) | +4 | 0.27E+00 |
| 11 | 9 | 236.56314 | 236.563001( 60) | -13 | 0.57E+00 | 235.23565 | 235.235901( 60) | +65 | 0.56E+00 |
| 11 | 10 | 237.36325 | 237.362901( 60) | -35 | 0.28E+00 | 235.81974 | 235.818901( 60) | -83 | 0.27E+00 |
| 11 | 11 | 238.29303 | 238.292701( 60) | -33 | 0.21E+00 | 236.43809 | 236.437901( 60) | -58 | 0.21E+00 |
| 12 | 0( | 251.92632) | ——— | ——— | 0. | 251.37330 | 251.373901(100) | 59 | 0.13E+00 |
| 12 | 1 | 251.96259 | 251.962201(200) | -39 | 0.66E-01 | 251.40475 | 251.404401(100) | -34 | 0.66E-01 |
| 12 | 2 | 252.07178 | 252.071501( 50) | -28 | 0.68E-01 | 251.49917 | 251.499101( 80) | -7 | 0.68E-01 |
| 12 | 3 | 252.24390 | 252.243901(100) | -200 | 0.14E+00 | 251.66768 | 251.666701( 80) | -98 | 0.14E+00 |
| 12 | 4 | 252.51412 | ——— | ——— | 0.77E-01 | 251.87847 | 251.878801(100) | -46 | 0.77E-01 |
| 12 | 5 | 252.85198 | 252.851401(100) | -58 | 0.84E-01 | 252.16455 | 252.165101( 80) | 54 | 0.84E-01 |
| 12 | 6 | 253.27245 | 253.272501( 80) | 5 | 0.19E+00 | 252.51598 | 252.515901(200) | -7 | 0.19E+00 |
| 12 | 7 | 253.78061 | ——— | ——— | 0.11E+00 | 252.93360 | 252.934601( 80) | 100 | 0.10E+00 |
| 12 | 8 | 254.38315 | 254.382801( 80) | -34 | 0.12E+00 | 253.41813 | 253.419101( 80) | 96 | 0.12E+00 |
| 12 | 9 | 255.08869 | 255.089601( 80) | 91 | 0.27E+00 | 253.96992 | ——— | ——— | 0.26E+00 |
| 12 | 10 | 255.90839 | 255.908201( 80) | -19 | 0.15E+00 | 254.58852 | 254.58918( 50) | 98 | 0.14E+00 |
| 12 | 11 | 256.85683 | 256.856101( 50) | -71 | 0.19E+00 | 255.27195 | 255.27160( 50) | -34 | 0.14E+00 |
| 12 | 12 | 257.95307 | 257.953601( 50) | 53 | 0.23E+00 | 256.01572 | 256.01620( 50) | 47 | 0.22E+00 |
| 13 | 0 | 270.14232 | 270.142301(100) | -1 | 0.47E-01 | 269.67414) | ——— | ——— | 0. |
| 13 | 1 | 270.17992 | 270.180201( 80) | 28 | 0.24E-01 | 269.70760 | 269.70760( 50) | 0 | 0.24E-01 |
| 13 | 2 | 270.29300 | 270.292601(100) | -39 | 0.25E-01 | 269.80819 | 269.808601( 80) | -138 | 0.24E-01 |
| 13 | 3 | 270.49834 | 270.500201(300) | 186 | 0.52E-01 | 269.96898 | 269.964901( 80) | 391 | 0.52E-01 |
| 13 | 4 | 270.75060 | 270.751701(200) | 109 | 0.28E-01 | 270.21246 | ——— | ——— | 0.28E-01 |
| 13 | 5 | 271.09955 | 271.100201( 80) | 61 | 0.31E-01 | 270.51768 | ——— | ——— | 0.31E-01 |
| 13 | 6 | 271.53329 | 271.533301( 50) | 6 | 0.69E-01 | 270.89290 | 270.892901( 80) | -10 | 0.69E-01 |
| 13 | 7 | 272.05864 | 272.056201( 80) | -260 | 0.40E-01 | 271.33960 | 271.337701( 90) | -195 | 0.39E-01 |
| 13 | 8 | 272.67536 | 272.677201( 80) | 164 | 0.46E-01 | 271.85896 | ——— | ——— | 0.45E-01 |
| 13 | 9 | 273.39819 | 273.399701( 50) | 150 | 0.11E+00 | 272.45207 | 272.452901( 80) | 83 | 0.11E+00 |
| 13 | 10 | 274.23531 | 274.234901( 80) | -43 | 0.61E-01 | 273.11988 | ——— | ——— | 0.61E-01 |
| 13 | 11 | 275.20013 | 275.199801( 80) | -32 | 0.69E-01 | 273.84149 | 273.861801( 80) | 30 | 0.68E-01 |
| 13 | 12 | 276.31011 | 276.307501(200) | -260 | 0.14E+00 | 274.67536 | 274.674401( 80) | -95 | 0.14E+00 |
| 13 | 13 | 277.58629 | 277.568001( 50) | -29 | 0.58E-01 | 275.59590 | 275.596301( 50) | 39 | 0.57E-01 |

[a] Our Fourier transform measurements unless stated otherwise; J,K are lower state quantum numbers for transitions with $\Delta J = +1$, $\Delta K = 0$, s←s or s←a; C and O are calculated and observed transition wavenumbers, respectively. I are calculated intensities. Values in parentheses of the observed wavenumbers are estimated experimental uncertainties in units of the last digit quoted. Calculated wavenumbers for transitions from levels with zero spin statistical weights are in parentheses.

[b] Ref. (5).

## TABLE II

Inversion–Rotation Transition Wavenumbers ($cm^{-1}$) and Intensities ($cm^{-2}$ $atm^{-1}$) of $^{14}NH_3$ in the $\nu_2$ State[a]

| J | K | s ← s C | s ← s O | (O-C) x10^5 | I | a ← a C | a ← a O | (O-C) x10^5 | I |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 0( | 55.46537) | ——— | —— | 0. | -15.55227 | -15.552266( 1)[b] | 0 | 0.24E-03 |
| 1 | 0 | 74.86733 | ——— | —— | 0.29E-01 | ( 4.91511) | ——— | —— | 0. |
| 1 | 1 | 79.12238 | ——— | —— | 0.11E-01 | 4.67464 | 4.674681 5)[c] | 4 | 0.42E-04 |
| 2 | 0( | 93.86793) | ——— | —— | 0. | 25.67478 | 25.674771 1)[d] | -1 | 0.40E-02 |
| 2 | 1 | 94.14034 | ——— | —— | 0.24E-01 | 25.44681 | 25.446811 1)[d] | 0 | 0.18E-02 |
| 2 | 2 | 94.90837 | ——— | —— | 0.16E-01 | 24.74330 | 24.743301 1)[d] | 0 | 0.11E-02 |
| 3 | 0 | 112.93139 | 112.93220(100) | 64 | 0.74E-01 | ( 46.68899) | ——— | —— | 0. |
| 3 | 1 | 112.77767 | 112.77790(100) | 22 | 0.36E-01 | 46.46885 | 46.468961(300) | 90 | 0.60E-02 |
| 3 | 2 | 113.53229 | 113.53190(100) | -38 | 0.30E-01 | 45.79994 | 45.801341(300) | 139 | 0.49E-02 |
| 3 | 3 | 114.82141 | 114.82110(100) | -30 | 0.39E-01 | 44.65355 | 44.653401(300) | -14 | 0.59E-02 |
| 4 | 0( | 130.80351) | ——— | —— | 0. | 67.89529 | 67.895001 80) | -29 | 0.22E-01 |
| 4 | 1 | 131.04479 | 131.04450(100) | -28 | 0.41E-01 | 67.68079 | 67.68750(200) | 71 | 0.11E-01 |
| 4 | 2 | 131.78190 | 131.78100(100) | -90 | 0.38E-01 | 67.05869 | 67.05810(200) | -59 | 0.96E-02 |
| 4 | 3 | 133.03513 | 133.03480(100) | -32 | 0.64E-01 | 65.98267 | 65.98300(100) | 33 | 0.15E-01 |
| 4 | 4 | 134.86092 | 134.86100(100) | 48 | 0.21E-01 | 64.41282 | 64.41250(200) | -32 | 0.47E-02 |
| 5 | 0 | 148.73203 | 148.73160( 60) | -42 | 0.77E-01 | ( 89.23704) | ——— | —— | 0. |
| 5 | 1 | 148.96788 | 148.96850(100) | 61 | 0.38E-01 | 89.04191 | ——— | —— | 0.13E-01 |
| 5 | 2 | 149.67810 | 149.67880(100) | 70 | 0.87E-01 | 88.45857 | ——— | —— | 0.13E-01 |
| 5 | 3 | 150.89078 | 150.89040( 80) | -37 | 0.69E-01 | 87.46045 | ——— | —— | 0.23E-01 |
| 5 | 4 | 152.69063 | 152.69020( 80) | -42 | 0.30E-01 | 85.99832 | ——— | —— | 0.92E-02 |
| 5 | 5 | 155.02644 | 155.02470(300) | -174 | 0.20E-01 | 84.01354 | ——— | —— | 0.56E-02 |
| 6 | 0( | 166.93986) | ——— | —— | 0. | 110.64491 | 110.651301 80) | 138 | 0.27E-01 |
| 6 | 1 | 166.96738 | 166.96630(100) | -107 | 0.31E-01 | 110.46872 | ——— | —— | 0.13E-01 |
| 6 | 2 | 167.24812 | 167.24780(150) | -32 | 0.31E-01 | 109.93397 | ——— | —— | 0.13E-01 |
| 6 | 3 | 168.40255 | 168.40310(100) | 54 | 0.60E-01 | 109.01689 | 109.01690( 60) | 1 | 0.25E-01 |
| 6 | 4 | 170.09446 | 170.09470(200) | 23 | 0.28E-01 | 107.67564 | 107.67610(300) | 46 | 0.11E-01 |
| 6 | 5 | 172.36945 | 172.36930( 90) | -14 | 0.25E-01 | 105.84984 | 105.85020( 60) | 36 | 0.91E-02 |
| 6 | 6 | 175.32071 | 175.32860(100) | -10 | 0.33E-01 | 103.45623 | ——— | —— | 0.11E-01 |
| 7 | 0 | 183.65759 | 183.65700(200) | -58 | 0.43E-01 | ( 132.86733) | ——— | —— | 0. |
| 7 | 1 | 183.87621 | 183.87600( 60) | -21 | 0.22E-01 | 131.98011 | ——— | —— | 0.11E-01 |
| 7 | 2 | 184.52387 | 184.52370(200) | -16 | 0.22E-01 | 131.41690 | 131.41520( 80) | -169 | 0.11E-01 |
| 7 | 3 | 185.62829 | 185.62830( 80) | 0 | 0.44E-01 | 130.59260 | 130.59360(100) | 100 | 0.21E-01 |
| 7 | 4 | 187.22718 | 187.22560(200) | -157 | 0.22E-01 | 129.37287 | 129.37120(200) | -166 | 0.10E-01 |
| 7 | 5 | 189.38856 | 189.38700(150) | -50 | 0.21E-01 | 127.71570 | ——— | —— | 0.94E-02 |
| 7 | 6 | 192.19130 | 192.19170( 60) | 40 | 0.38E-01 | 125.59787 | 125.59700( 60) | 83 | 0.16E-01 |
| 7 | 7 | 195.74618 | 195.74670( 60) | 51 | 0.13E-01 | 122.73789 | ——— | —— | 0.50E-02 |
| 8 | 0( | 200.71832) | ——— | —— | 0. | 153.42260 | ——— | —— | 0.15E-01 |
| 8 | 1 | 200.92802 | 200.92680(300) | -122 | 0.13E-01 | 153.26575 | 153.26590( 80) | -324 | 0.76E-02 |
| 8 | 2 | 201.54000 | 201.54110(200) | 109 | 0.14E-01 | 152.81909 | 152.81850( 80) | -59 | 0.76E-02 |
| 8 | 3 | 202.56286 | 202.56350(100) | 63 | 0.28E-01 | 152.10132 | ——— | —— | 0.15E-01 |
| 8 | 4 | 204.08683 | 204.08810(100) | 127 | 0.14E-01 | 151.01775 | 151.01870( 80) | 95 | 0.77E-02 |
| 8 | 5 | 206.12463 | 206.12430( 60) | -34 | 0.13E-01 | 149.53548 | 149.53500( 80) | -48 | 0.75E-02 |
| 8 | 6 | 208.76610 | 208.76340(100) | -270 | 0.29E-01 | 147.58387 | ——— | —— | 0.14E-01 |
| 8 | 7 | 212.11514 | 212.11330(100) | -183 | 0.13E-01 | 145.06582 | ——— | —— | 0.60E-02 |
| 8 | 8 | 216.30694 | ——— | —— | 0.95E-02 | 141.85429 | ——— | —— | 0.39E-02 |
| 9 | 0 | 217.55398 | 217.55940(290) | 341 | 0.14E-01 | ( 174.65107) | ——— | —— | 0. |
| 9 | 1 | 217.75732 | ——— | —— | 0.73E-02 | 174.50911 | ——— | —— | 0.46E-02 |
| 9 | 2 | 218.33222 | 218.33170(200) | -52 | 0.14E-01 | 174.13426 | ——— | —— | 0.47E-02 |
| 9 | 3 | 219.30779 | 219.30500(200) | -278 | 0.16E-01 | 173.50102 | ——— | —— | 0.95E-02 |
| 9 | 4 | 220.71236 | ——— | —— | 0.81E-02 | 172.53999 | 172.53780(100) | -219 | 0.49E-02 |
| 9 | 5 | 222.61988 | 222.62060(100) | 72 | 0.86E-02 | 171.23543 | ——— | —— | 0.50E-02 |
| 9 | 6 | 225.09107 | 225.09160(100) | 52 | 0.18E-01 | 169.51307 | 169.51340( 80) | 32 | 0.99E-02 |
| 9 | 7 | 228.22276 | 228.22370(100) | 94 | 0.92E-02 | 167.28361 | ——— | —— | 0.48E-02 |
| 9 | 8 | 232.14101 | ——— | —— | 0.86E-02 | 164.42996 | ——— | —— | 0.42E-02 |
| 9 | 9 | 237.00827 | 237.00790(100) | -36 | 0.13E-01 | 160.88008 | ——— | —— | 0.56E-02 |
| 10 | 0( | 234.20336) | ——— | —— | 0. | 195.69215 | 195.690701 80) | -144 | 0.48E-02 |
| 10 | 1 | 234.39786 | ——— | —— | 0.36E-02 | 195.55930 | 195.56180( 80) | 250 | 0.24E-02 |
| 10 | 2 | 234.93571 | ——— | —— | 0.37E-02 | 195.23997 | ——— | —— | 0.25E-02 |
| 10 | 3 | 235.80049 | ——— | —— | 0.77E-02 | 194.68991 | 194.69080(300) | 88 | 0.51E-02 |
| 10 | 4 | 237.14168 | ——— | —— | 0.41E-02 | 193.87332 | ——— | —— | 0.27E-02 |
| 10 | 5 | 238.92314 | ——— | —— | 0.42E-02 | 192.74607 | ——— | —— | 0.28E-02 |
| 10 | 6 | 241.21106 | ——— | —— | 0.95E-02 | 191.23201 | ——— | —— | 0.58E-02 |
| 10 | 7 | 244.11883 | ——— | —— | 0.51E-02 | 189.31192 | ——— | —— | 0.30E-02 |
| 10 | 8 | 247.75499 | ——— | —— | 0.54E-02 | 186.81713 | ——— | —— | 0.29E-02 |
| 10 | 9 | 252.27002 | ——— | —— | 0.10E-01 | 183.62922 | ——— | —— | 0.53E-02 |
| 10 | 10 | 257.83665 | ——— | —— | 0.39E-02 | 179.56870 | ——— | —— | 0.18E-02 |
| 11 | 0 | 250.69145 | ——— | —— | 0.31E-02 | ( 216.49115) | ——— | —— | 0. |
| 11 | 1 | 250.88145 | ——— | —— | 0.16E-02 | 216.36197 | ——— | —— | 0.11E-02 |
| 11 | 2 | 251.38443 | ——— | —— | 0.16E-02 | 216.00927 | ——— | —— | 0.12E-02 |
| 11 | 3 | 252.21799 | ——— | —— | 0.34E-02 | 215.46437 | ——— | —— | 0.24E-02 |
| 11 | 4 | 253.40995 | ——— | —— | 0.18E-02 | 214.95840 | ——— | —— | 0.13E-02 |
| 11 | 5 | 255.04831 | ——— | —— | 0.20E-02 | 214.00424 | ——— | —— | 0.14E-02 |
| 11 | 6 | 257.16789 | ——— | —— | 0.44E-02 | 212.73518 | ——— | —— | 0.29E-02 |
| 11 | 7 | 259.84992 | ——— | —— | 0.24E-02 | 211.07817 | ——— | —— | 0.16E-02 |
| 11 | 8 | 263.20134 | ——— | —— | 0.27E-02 | 208.93691 | ——— | —— | 0.16E-02 |
| 11 | 9 | 267.36033 | ——— | —— | 0.58E-02 | 206.18549 | ——— | —— | 0.33E-02 |
| 11 | 10 | 272.50430 | ——— | —— | 0.29E-02 | 202.66074 | ——— | —— | 0.15E-02 |
| 11 | 11 | 278.85978 | ——— | —— | 0.23E-02 | 198.15248 | ——— | —— | 0.11E-02 |
| 12 | 0( | 267.04693) | ——— | —— | 0. | 237.80030 | ——— | —— | 0.95E-03 |
| 12 | 1 | 267.23781 | ——— | —— | 0.62E-03 | 236.86273 | ——— | —— | 0.48E-03 |
| 12 | 2 | 267.71308 | ——— | —— | 0.64E-03 | 236.66117 | ——— | —— | 0.49E-03 |
| 12 | 3 | 268.38484 | ——— | —— | 0.14E-02 | 236.30280 | ——— | —— | 0.10E-02 |
| 12 | 4 | 269.54895 | ——— | —— | 0.73E-03 | 235.74236 | ——— | —— | 0.55E-03 |
| 12 | 5 | 271.05379 | ——— | —— | 0.80E-03 | 234.95481 | ——— | —— | 0.59E-03 |
| 12 | 6 | 272.99879 | ——— | —— | 0.18E-02 | 233.90181 | ——— | —— | 0.13E-02 |
| 12 | 7 | 275.45760 | ——— | —— | 0.10E-02 | 232.51861 | ——— | —— | 0.71E-03 |
| 12 | 8 | 278.52713 | ——— | —— | 0.12E-02 | 230.71942 | ——— | —— | 0.78E-03 |
| 12 | 9 | 282.33306 | ——— | —— | 0.27E-02 | 228.39164 | ——— | —— | 0.17E-02 |
| 12 | 10 | 287.03725 | ——— | —— | 0.15E-02 | 225.38859 | ——— | —— | 0.88E-03 |
| 12 | 11 | 292.84699 | ——— | —— | 0.13E-02 | 221.92037 | ——— | —— | 0.84E-03 |
| 12 | 12 | 300.02694 | ——— | —— | 0.25E-02 | 216.34258 | ——— | —— | 0.12E-02 |
| 13 | 0 | 283.29324 | ——— | —— | 0.44E-03 | ( 237.17998) | ——— | —— | 0. |
| 13 | 1 | 283.44978 | ——— | —— | 0.22E-03 | 236.99212 | ——— | —— | 0.10E-03 |
| 13 | 2 | 283.97483 | ——— | —— | 0.23E-03 | 236.87843 | ——— | —— | 0.18E-03 |
| 13 | 3 | 284.61129 | ——— | —— | 0.49E-03 | 236.65172 | ——— | —— | 0.39E-03 |
| 13 | 4 | 285.58397 | ——— | —— | 0.26E-03 | 236.18173 | ——— | —— | 0.21E-03 |
| 13 | 5 | 286.95973 | ——— | —— | 0.29E-03 | 235.55166 | ——— | —— | 0.23E-03 |
| 13 | 6 | 288.73932 | ——— | —— | 0.66E-03 | 234.70322 | ——— | —— | 0.50E-03 |
| 13 | 7 | 290.97722 | ——— | —— | 0.38E-03 | 233.57972 | ——— | —— | 0.28E-03 |
| 13 | 8 | 293.77251 | ——— | —— | 0.44E-03 | 232.10385 | ——— | —— | 0.32E-03 |
| 13 | 9 | 297.23445 | ——— | —— | 0.10E-02 | 230.18219 | ——— | —— | 0.71E-03 |
| 13 | 10 | 301.50933 | ——— | —— | 0.61E-03 | 247.67850 | ——— | —— | 0.40E-03 |
| 13 | 11 | 306.78510 | ——— | —— | 0.70E-03 | 244.42526 | ——— | —— | 0.43E-03 |
| 13 | 12 | 313.38218 | ——— | —— | 0.15E-02 | 240.20299 | ——— | —— | 0.84E-03 |
| 13 | 13 | 321.36698 | ——— | —— | 0.63E-03 | 234.78985 | ——— | —— | 0.32E-03 |

[a] Our Fourier transform measurements unless stated otherwise (see Footnote[a] in Table I).
[b] Ref. (17); the a(0,0) energy level of the $\nu_2$ state is higher than the a(1,0) level.
[c] Ref. (18). [d] Ref. (1).

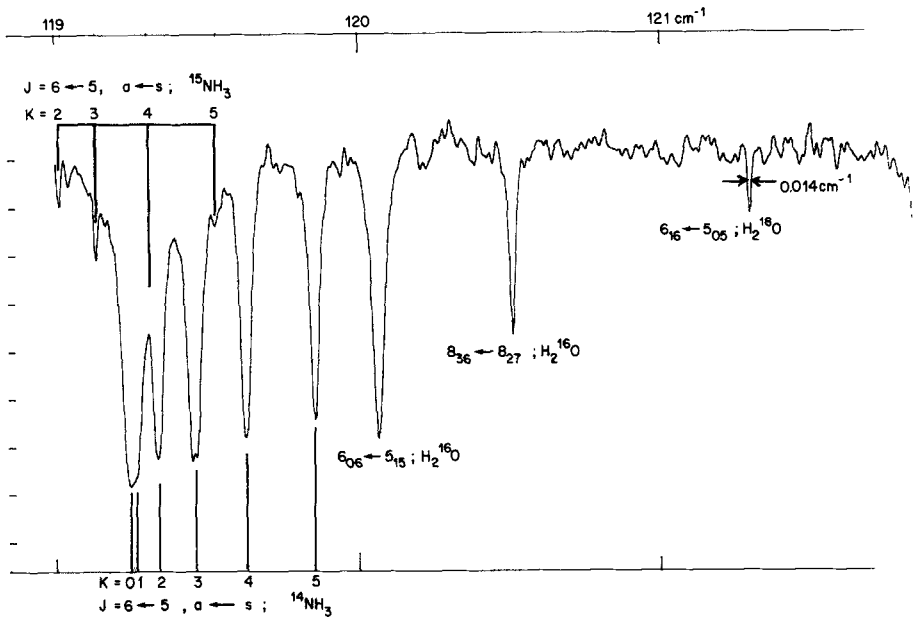


FIG. 1. Partly resolved $K$ structure of the $s(5, K)$ multiplet of the ground-state inversion–rotation transitions of ammonia (apodized spectrum).

## III. THEORETICAL MODEL AND THE SIMULTANEOUS ANALYSIS OF EXPERIMENTAL DATA

We have used the same fourth-order theory of the $\langle J, k | H | J, k \pm 3n \rangle$ interactions in the ground and $\nu_2$ excited states of ammonia as described in the previous paper (*2*). We used the basis of the inversion–rotation wavefunctions

$$|^{(\pm)}\varphi_{i;J,k}\rangle = 2^{-1/2}|\psi_{i;J,k}\rangle[|J, k\rangle \pm |J, -k\rangle], \tag{1}$$

where the inversion wavefunctions $|\psi_{i;J,k}\rangle$ depend on the inversion coordinate $\rho$ (as the dynamic variable) and on the rotational quantum numbers $J$ and $k$ as parameters.

In the basis of wavefunctions defined by Eq. (1), the secular problem for the ground and $\nu_2$ state factorizes into two pairs of matrices for the *para*-$NH_3$ ($E$ states) and four matrices for the *ortho*-$NH_3$ ($A_1, A_2$ states) [see Tables V and VI in Ref. (*2*)]. For reasons which we discussed in our previous paper (*2*), we used, for the diagonal matrix elements of the energy matrix, higher-order approximations compared to the fourth-order theory; in general these elements can be written as

$$\begin{aligned}{}^{(i)}_{(m)}E^0(J, K)/h = {}&{}^{(m)}E^0_i/h + B^{(i)}_m J(J+1) + (C^{(i)}_m - B^{(i)}_m)K^2 - {}^{(i)}D^{(m)}_J J^2(J+1)^2 \\ &- {}^{(i)}D^{(m)}_{JK} J(J+1)K^2 - {}^{(i)}D^{(m)}_K K^4 + \sum_{n=0,1,2,3} {}^{(i)}H^{(m)}_{J_{3-n}K_n}[J(J+1)]^{3-n}K^{2n} \\ &+ \sum_{n=0,1,2,3,4} {}^{(i)}G^{(m)}_{J_{4-n}K_n}[J(J+1)]^{4-n}K^{2n} + \sum_{n=0,1,2,3,4,5} {}^{(i)}L^{(m)}_{J_{5-n}K_n}[J(J+1)]^{5-n}K^{2n}. \end{aligned} \tag{2}$$

In Eq. (2), $i$ indicates the parity of the state with respect to inversion [lower

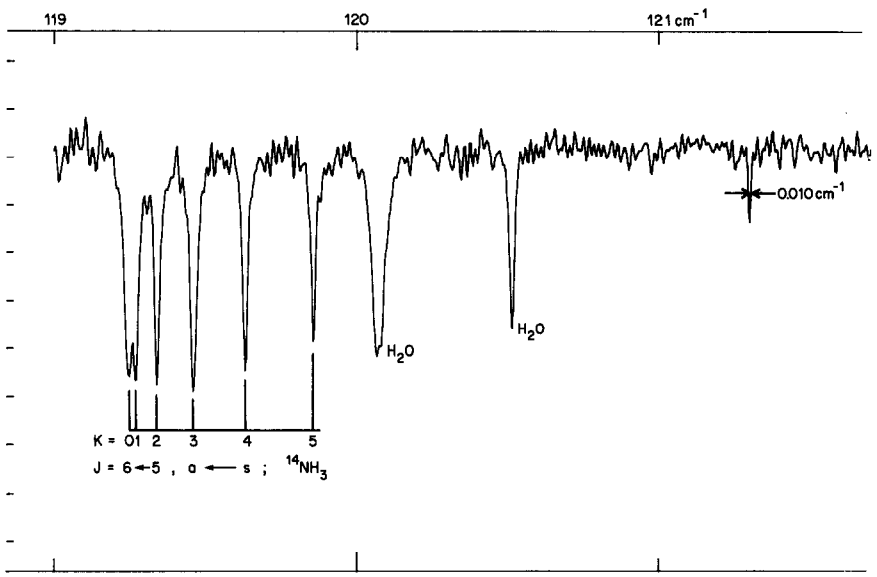


FIG. 2. Resolved $K$ structure of the $s(5, K)$ multiplet of $^{14}NH_3$ (unapodized spectrum).

(denoted by $s$) or upper (denoted by $a$) component of the inversion doublet]; $m = 0$ for the ground state and $m = 1$ for the $\nu_2$ state; a symbol like, for example, ${}^{(i)}G^{(m)}_{J_2K_2}$ means ${}^{(i)}G^{(m)}_{JJKK}$, etc.

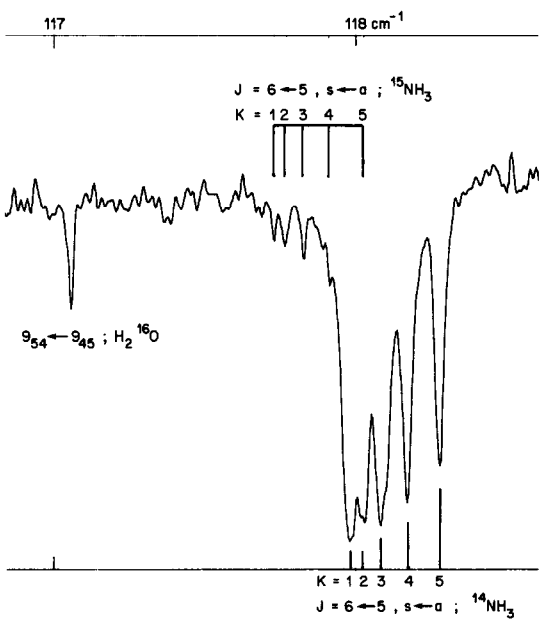


FIG. 3. Partly resolved $K$ structure of the $a(5, K)$ multiplet of the ground-state inversion–rotation transitions of ammonia (apodized spectrum).

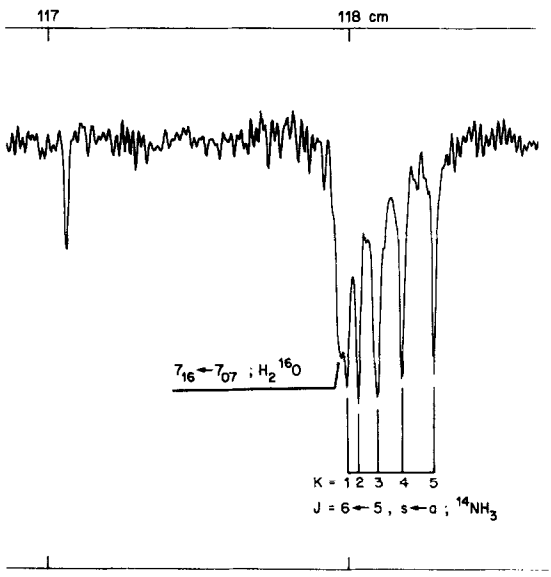


FIG. 4. Resolved $K$ structure of the $a(5, K)$ multiplet of the ground-state inversion–rotation transitions of $^{14}NH_3$ (unapodized spectrum).

The operators which describe the $\Delta k = \pm 3n$ interactions in the ground state and $\nu_2$ excited state are defined as follows:

$$H_1' = H_2(\rho)[(J_+^3 + J_-^3)J_z + J_z(J_+^3 + J_-^3)], \tag{3a}$$

$$H_2' = H_3(\rho)(J_+^3 - J_-^3), \tag{3b}$$

$$H_3' = [H_1(\rho) + H_4(\rho) + H_5(\rho)](J_+^6 + J_-^6), \tag{3c}$$

$$H_4' = H(\rho)(J_+^{12} + J_-^{12}), \tag{3d}$$

where the operators $H_1(\rho)$–$H_5(\rho)$ have been explicitly defined in our previous paper (*2*) and $J_\pm = J_x \pm iJ_y$. Note that the $H_3(\rho)$ operator is antisymmetric in the basis of the inversion wavefunctions and thus $H_2'$ is Hermitian (*2*); $H_2'$ is invariant with respect to the time reversal [cf. definition of $H_3(\rho)$ in Ref. (*2*)]. The operator $H_4'$ is beyond the approximation in which the theory of the $\Delta k = \pm 3n$ interactions was discussed in Ref. (*2*); we have found by the numerical analysis of the experimental data that the matrix element of this operator diagonal in $K$ should be introduced.

There are the following matrix elements of the operators in Eq. (3) in the basis of wavefunctions $|\varphi_{(\substack{s\\a});J,k}\rangle = |\psi_{(\substack{s\\a});J,k}\rangle \cdot |J, k\rangle$:

$$\langle \varphi_{(\substack{s\\a});J,k} | H_1' | \varphi_{(\substack{a\\s});k\pm 3} \rangle = \hbar^4 \langle \psi_{(\substack{s\\a});J,k} | H_2(\rho) | \psi_{(\substack{a\\s});J,k\pm 3} \rangle \times (2k \pm 3) \prod_{i=0}^{i=2} [J(J+1) - (k \pm i)(k \pm i \pm 1)]^{1/2}, \tag{4}$$

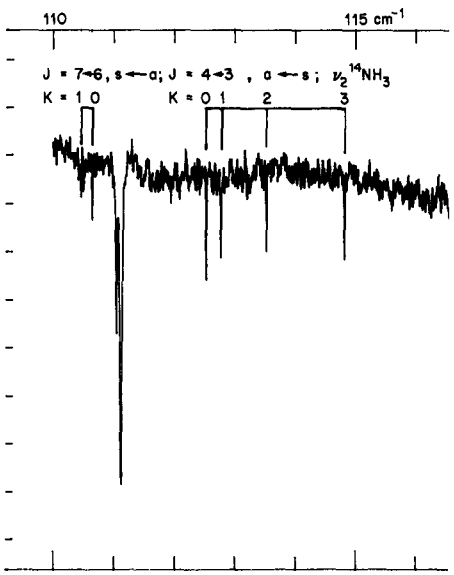


FIG. 5. Resolved $K$ structure of the $s(3, K)$ multiplet of the inversion–rotation transitions in the $\nu_2$ excited state of $^{14}NH_3$ (apodized spectrum).

$$\langle \varphi_{(a^s);J,k} | H_2' | \varphi_{(s^a);J,k\pm3} \rangle = \pm\hbar^3 \langle \psi_{(a^s);J,k} | H_3(\rho) | \psi_{(s^a);J,k\pm3} \rangle \times \prod_{i=0}^{i=2} [J(J+1) - (k \pm i)(k \pm i \pm 1)]^{1/2}. \quad (5)$$

From the matrix elements of the operators $H_3'$ and $H_4'$ [Eqs. (3c) and (3d)], we have considered only those which contribute to the main diagonal of the interaction matrix:

$$\langle \varphi_{(a^s);J,-3} | H_3' | \varphi_{(a^s);J,+3} \rangle = \hbar^6 \langle \psi_{(a^s);J,-3} | H_1(\rho) + H_4(\rho) + H_5(\rho) | \psi_{(a^s);J,+3} \rangle [(J+3)!/(J-3)!], \quad (6)$$

$$\langle \varphi_{(a^s);J,-6} | H_4' | \varphi_{(a^s);J,+6} \rangle = \hbar^{12} \langle \psi_{(a^s);J,-6} | H(\rho) | \psi_{(a^s);J,+6} \rangle \times [(J+6)!/(J-6)!]. \quad (7)$$

Let us denote

$$h^{-3}c(2\pi)^4\alpha = \langle \psi_{(s^a);J,k} | H_2(\rho) | \psi_{(a^s);J,k\pm3} \rangle = \langle \psi_{(a^s);J,k\pm3} | H_2(\rho) | \psi_{(s^a);J,k} \rangle, \quad (8)$$

$$h^{-2}c(2\pi)^3\beta = -\langle \psi_{(a^s);J,k} | H_3(\rho) | \psi_{(s^a);J,k\pm3} \rangle = +\langle \psi_{(s^a);J,k\pm3} | H_3(\rho) | \psi_{(a^s);J,k} \rangle, \quad (9)$$

$$h^{-5}c(2\pi)^6\eta_3^{(a^s)} = \langle \psi_{(a^s);J,-3} | H_1(\rho) + H_4(\rho) + H_5(\rho) | \psi_{(a^s);J,3} \rangle, \quad (10)$$

$$h^{-11}c(2\pi)^{12}\eta_6^{(a^s)} = \langle \psi_{(a^s);J,-6} | H(\rho) | \psi_{(a^s);J,6} \rangle, \quad (11)$$

where $\alpha$, $\beta$, and $\eta$ are in $cm^{-1}$.

We have found that the experimental data used in the present paper do not allow for a separate determination of $\eta_t^{(s)}$ and $\eta_t^{(a)}$ $(t = 3, 6)$; only $\eta_t = (\eta_t^{(s)} + \eta_t^{(a)})/2$ can be determined. On the other hand, we found that the dependence of $\eta_t$ on the rotational quantum numbers should be taken into account because of the

TABLE III

Inversion Transition Wavenumbers ($cm^{-1}$) and Intensities ($cm^{-2}$ $atm^{-1}$) of $^{14}NH_3$ in the $\nu_2$ State[a]

| J | K | C | O | (O-C) x10^5 | I | J | K | C | C | (O-C) x10^5 | I |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 0( | 35.688111 | ------ | --- | 0. | 9 | 8 | 35.55352 | 35.55354( 3) | 1 | 0.12E-02 |
| 1 | 0( | 35.329541 | ------ | --- | 0. | 9 | 9 | 39.99987 | ------ | --- | 0.50E-02 |
| 1 | 1 | 35.57964 | 35.57964( 1) | 0 | 0.27E-02 | 10 | 0( | 20.348771 | ------ | --- | 0. |
| 2 | 0( | 34.622681 | ------ | --- | 0. | 10 | 1 | 20.51572 | 20.515570( 10) | -1 | 0.76E-06 |
| 2 | 1 | 34.86810 | 34.868081( 3) | -1 | 0.12E-02 | 10 | 2 | 20.96742 | 20.967391( 5) | -3 | 0.33E-05 |
| 2 | 2 | 35.61387 | 35.613861( 1) | 0 | 0.53E-02 | 10 | 3 | 21.74793 | 21.747991( 5) | 5 | 0.17E-04 |
| 3 | 0( | 33.59004) | ------ | --- | 0. | 10 | 4 | 22.85480 | ------ | --- | 0.19E-04 |
| 3 | 1 | 33.82624 | 33.826201( 7) | -3 | 0.89E-03 | 10 | 5 | 24.28304 | ------ | --- | 0.40E-04 |
| 3 | 2 | 34.55112 | 34.551131( 5) | 1 | 0.26E-02 | 10 | 6 | 25.97885 | 26.37885( 3) | 1 | 0.16E-03 |
| 3 | 3 | 35.79306 | 35.793121( 3) | 5 | 0.14E-01 | 10 | 7 | 28.93145 | 28.931461( 6) | 1 | 0.16E-03 |
| 4 | 0( | 32.252521 | ------ | --- | 0. | 10 | 8 | 32.15759 | 32.157591( 5) | 0 | 0.34E-03 |
| 4 | 1 | 32.48538 | 32.485336( 3) | -2 | 0.29E-03 | 10 | 9 | 36.20832 | 36.208551(167) | 22 | 0.14E-02 |
| 4 | 2 | 33.18123 | 33.181211( 7) | -1 | 0.13E-02 | 10 | 10 | 41.27756 | ------ | --- | 0.16E-02 |
| 4 | 3 | 34.37480 | 34.374821( 6) | 1 | 0.67E-02 | 11 | 0( | 18.16258) | ------ | --- | 0. |
| 4 | 4 | 36.11141 | 36.111651(167) | 23 | 0.74E-02 | 11 | 1 | 18.32285 | ------ | --- | 0.20E-06 |
| 5 | 0( | 30.65570) | ------ | --- | 0. | 11 | 2 | 18.72032 | 18.720221( 3) | -9 | 0.88E-06 |
| 5 | 1 | 30.87663 | 30.876611( 6) | -1 | 0.13E-03 | 11 | 3 | 19.36264 | 19.362691( 5) | 6 | 0.46E-05 |
| 5 | 2 | 31.54198 | 31.541981( 6) | 0 | 0.59E-03 | 11 | 4 | 20.41337 | 20.413351( 5) | -1 | 0.51E-05 |
| 5 | 3 | 32.67766 | 32.677611( 7) | -5 | 0.31E-02 | 11 | 5 | 21.78603 | 21.786001( 5) | -2 | 0.10E-04 |
| 5 | 4 | 34.33628 | 34.336241( 7) | -4 | 0.34E-02 | 11 | 6 | 23.57961 | 23.579611( 6) | 0 | 0.42E-04 |
| 5 | 5 | 36.57833 | 36.578671(100) | 33 | 0.71E-02 | 11 | 7 | 25.87546 | 25.875481( 5) | 2 | 0.43E-04 |
| 6 | 0( | 28.83928) | ------ | --- | 0. | 11 | 8 | 28.78027 | 28.780271( 6) | 0 | 0.89E-04 |
| 6 | 1 | 29.04934 | ------ | --- | 0.57E-04 | 11 | 9 | 32.43248 | 32.432491( 3) | 0 | 0.38E-03 |
| 6 | 2 | 29.67795 | 29.677950( 6) | 1 | 0.25E-03 | 11 | 10 | 37.01038 | 37.011271(334) | 88 | 0.42E-03 |
| 6 | 3 | 30.75267 | 30.752621( 33) | -5 | 0.13E-02 | 11 | 11 | 42.74215 | ------ | --- | 0.97E-03 |
| 6 | 4 | 32.31602 | 32.316021( 7) | 0 | 0.15E-02 | 12 | 0( | 16.03772) | ------ | --- | 0. |
| 6 | 5 | 34.43457 | 34.434591( 6) | 1 | 0.30E-02 | 12 | 1 | 16.19867 | ------ | --- | 0.48E-07 |
| 6 | 6 | 37.19513 | ------ | --- | 0.62E-01 | 12 | 2 | 16.55685 | ------ | --- | 0.21E-06 |
| 7 | 0( | 26.850671 | ------ | --- | 0. | 12 | 3 | 17.15097 | 17.19146( 33) | 48 | 0.11E-05 |
| 7 | 1 | 27.04931 | 27.049331( 3) | 2 | 0.22E-04 | 12 | 4 | 18.03823 | 18.038331( 5) | 9 | 0.12E-05 |
| 7 | 2 | 27.63660 | 27.636521( 27) | -8 | 0.99E-04 | 12 | 5 | 19.25823 | ------ | --- | 0.25E-05 |
| 7 | 3 | 28.63299 | 28.632951( 6) | -4 | 0.52E-03 | 12 | 6 | 20.85311 | 20.853101( 5) | -1 | 0.10E-04 |
| 7 | 4 | 30.10280 | 30.102801( 6) | 0 | 0.57E-03 | 12 | 7 | 22.89628 | 22.896301( 5) | 2 | 0.10E-04 |
| 7 | 5 | 32.08504 | 32.085041( 5) | 0 | 0.12E-02 | 12 | 8 | 25.48416 | 25.484171( 3) | 0 | 0.21E-04 |
| 7 | 6 | 34.66935 | 34.669341( 5) | 0 | 0.48E-02 | 12 | 9 | 28.74235 | 28.742311( 6) | -4 | 0.90E-04 |
| 7 | 7 | 37.96668 | ------ | --- | 0.49E-02 | 12 | 10 | 32.83318 | 32.832711(134) | -46 | 0.10E-03 |
| 8 | 0( | 24.73559) | ------ | --- | 0. | 12 | 11 | 37.96516 | ------ | --- | 0.23E-03 |
| 8 | 1 | 24.92679 | 24.926801( 3) | 1 | 0.80E-05 | 12 | 12 | 44.40482 | ------ | --- | 0.11E-02 |
| 8 | 2 | 25.47037 | 25.470401( 3) | 3 | 0.35E-04 | 13 | 0( | 14.00889) | ------ | --- | 0. |
| 8 | 3 | 26.40270 | 26.402651( 33) | -5 | 0.18E-03 | 13 | 1 | 14.17841 | ------ | --- | 0.24E-07 |
| 8 | 4 | 27.75151 | 27.751511( 3) | 0 | 0.20E-03 | 13 | 2 | 14.49498 | ------ | --- | 0.46E-07 |
| 8 | 5 | 29.58776 | 29.587761( 6) | 0 | 0.42E-03 | 13 | 3 | 14.85186 | ------ | --- | 0.24E-06 |
| 8 | 6 | 31.98308 | 31.983081( 6) | -2 | 0.17E-02 | 13 | 4 | 15.76796 | ------ | --- | 0.26E-06 |
| 8 | 7 | 35.04162 | 35.041631( 73) | 0 | 0.17E-02 | 13 | 5 | 16.84076 | ------ | --- | 0.54E-06 |
| 8 | 8 | 38.89913 | ------ | --- | 0.36E-02 | 13 | 6 | 18.24387 | 18.243811( 5) | -5 | 0.22E-05 |
| 9 | 0( | 22.556141 | ------ | --- | 0. | 13 | 7 | 20.04271 | 20.042711( 5) | 0 | 0.22E-05 |
| 9 | 1 | 22.73249 | 22.732481( 5) | 0 | 0.26E-05 | 13 | 8 | 22.32355 | 22.323581( 5) | 3 | 0.45E-05 |
| 9 | 2 | 23.23054 | 23.230551( 5) | 1 | 0.11E-04 | 13 | 9 | 25.15906 | 25.159021( 3) | -3 | 0.19E-04 |
| 9 | 3 | 24.05884 | 24.058771( 6) | -7 | 0.60E-04 | 13 | 10 | 28.81548 | 28.815271(167) | -20 | 0.21E-04 |
| 9 | 4 | 25.31757 | 25.317551( 33) | -2 | 0.66E-04 | 13 | 11 | 33.36146 | 33.361471( 7) | 1 | 0.49E-04 |
| 9 | 5 | 27.00140 | 27.001411( 3) | 0 | 0.14E-03 | 13 | 12 | 39.07915 | ------ | --- | 0.24E-03 |
| 9 | 6 | 29.14915 | 29.149161( 6) | 0 | 0.55E-03 | 13 | 13 | 46.27802 | ------ | --- | 0.30E-03 |
| 9 | 7 | 32.00770 | 32.007781( 33) | 7 | 0.56E-03 | | | | | | |

[a] Our submillimeterwave measurements of the $\Delta J = 0$, $\Delta K = 0$ transitions with the spectrometer RAD [see also Refs. (*1*, *2*)]; cf. footnote a of Table I for the labeling of columns and meaning of parentheses in the calculated and observed wavenumbers. In measurements where transition wavenumbers were determined by interpolating between the calibration lines, the experimental uncertainties are higher than $10^{-4}$ $cm^{-1}$ [cf. Ref. (*2*)].

parametric dependence of $\eta_t$ on the rotational quantum numbers $J$, $K$. A simple perturbation treatment shows that the $J$, $K$ dependence of $\eta_t$ must have the form

$$\eta_3 = \eta_3^0 + \eta_3^J J(J+1) + \eta_3^K K^2 + \eta_3^{JJ} J^2(J+1)^2 + \eta_3^{KK} K^4 + \eta_3^{JK} J(J+1)K^2 + \text{higher-order terms} \quad (12)$$

and

$$\eta_6 = \eta_6^0 + \eta_6^J J(J+1) + \eta_6^K K^2 + \text{higher-order terms.} \quad (13)$$

The numerical treatment of our problem was based on the following procedure: (i) Using a second-order perturbation theory, we have diagonalized the interaction matrices for the *ortho-* and *para-* states of ammonia to obtain analytical expressions for the energy levels $E_k$ as functions of the molecular parameters $\Phi_k$ ($k = 1, 2, \ldots, r$):

$$E_j = f_j(\Phi_1, \Phi_2, \ldots, \Phi_r). \quad (14)$$

(ii) From these expressions, analytical expressions have been obtained for the elements of the Jacobian matrix

$$\partial E_j / \partial \Phi_k = J_{j,k}^{(E)}(\Phi_1, \Phi_2, \ldots, \Phi_r). \quad (15)$$

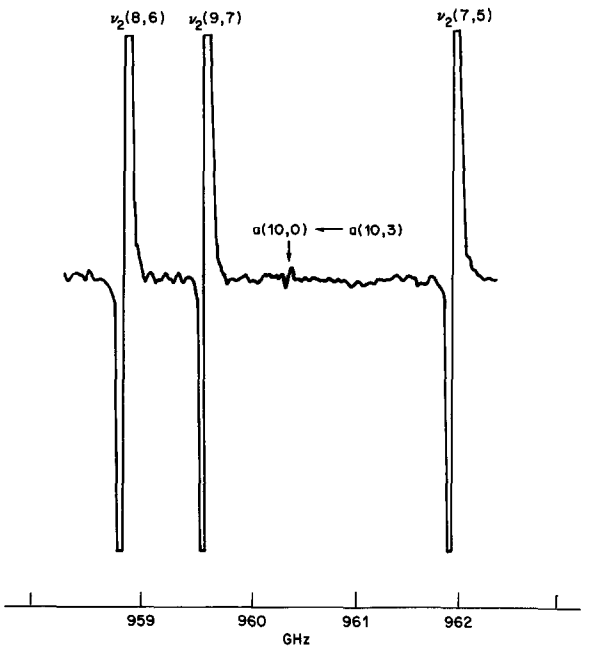


FIG. 6. Part of the submillimeterwave spectrum of ammonia at 960 GHz illustrating the sensitivity of the spectrometer RAD (see the calculated intensities of the spectrum lines in Tables II and V). $\nu_2(J, K)$ denote the lines of the $a(J, K) \leftarrow s(J, K)$ inversion transitions in the $\nu_2$ excited state; $a(10, 0) \leftarrow a(10, 3)$ denotes the line of the ground-state perturbation-allowed transition.

(iii) For a given frequency $\nu_{pq}$ of the transition between the energy levels $E_p$ and $E_q$, the Jacobian matrix was obtained simply as

$$\partial\nu_{pq}/\partial\Phi_k(J^{(E)}_{p,k} - J^{(E)}_{q,k})/h. \tag{16}$$

(iv) The minimum of the function

$$F(\Phi) = \sum_{p,q} w_{pq}[\nu^{(\text{calc})}_{pq} - \nu^{(\text{exp})}_{pq}]^2 \tag{17}$$

has been found by using the method of damped least-squares (*19*). In Eq. (17), summation extends over all the experimental data; $w_{pq}$ are their statistical weights.

It is convenient to introduce the following vectors of molecular parameters which can, in principle, be determined from the experimental data used in our work:

$$X^{(J)}_m = B^{(s)}_m, {}^{(s)}D^{(m)}_J, {}^{(s)}H^{(m)}_{JJJ}, \ldots, {}^{(s)}L^{(m)}_{JJJJJ}, \tag{18}$$

$$X^{(JK)}_m = {}^{(s)}D^{(m)}_{JK}, {}^{(s)}H^{m}_{JJK}, {}^{(s)}H^{(m)}_{JKK}, \ldots, {}^{(s)}L^{(m)}_{JKKKK}, \tag{19}$$

$$X^{(K)}_m = C^{(s)}_m - B^{(s)}_m, {}^{(s)}D^{(m)}_K, {}^{(s)}H^{(m)}_{KKK}, \ldots, {}^{(s)}L^{(m)}_{KKKKK}, \tag{20}$$

$$\Delta X_m = \Delta E_m, \Delta B_m, \Delta(C_m - B_m), \Delta D^{(m)}_J, \Delta D^{m}_{JK}, \Delta D^{(m)}_K, \Delta H^{(m)}_{JJJ}, \ldots, \Delta L^{(m)}_{KKKKK}; \tag{21}$$

in the last equation, the general term $\Delta X^{(m)}_j$ is defined as

$$\Delta X^{(m)}_j = {}^{(a)}X^{(m)}_j - {}^{(s)}X^{(m)}_j, \tag{22}$$

where ${}^{(i)}X^{(m)}_j$ stands for any one of the elements on the right-hand side of Eq. (21).

## TABLE IV

Transition Wavenumbers ($cm^{-1}$) and Intensities ($cm^{-2}$ $atm^{-1}$) in the $\nu_2$ Band of $^{14}NH_3$[a]

| J | K | aP(J,K) C | aP(J,K) O | (O-C) x10$^5$ | I | aP(J,K) C | aP(J,K) O | | (O-C) x10$^5$ | I |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0( | 911.76038) | ——— | ——— | 0. | 948.23206 | 948.23280(200)[b] | | 74 | 0.28E+01 |
| 2 | 0 | 892.15666 | ——— | ——— | 0.45E+01 | ( 928.24988) | ——— | | ——— | 0. |
| 2 | 1 | 891.88102 | ——— | ——— | 0.17E+01 | 928.23205 | ——— | | ——— | 0.17E+01 |
| 3 | 0( | 872.84138) | ——— | ——— | 0. | 908.19818 | ——— | | ——— | 0.50E+01 |
| 3 | 1 | 872.56715 | ——— | ——— | 0.23E+01 | 908.17691 | ——— | | ——— | 0.23E+01 |
| 3 | 2 | 871.73682 | ——— | ——— | 0.15E+01 | 908.11235 | ——— | | ——— | 0.15E+01 |
| 4 | 0 | 853.81793 | ——— | ——— | 0.45E+01 | ( 888.10672) | ——— | | ——— | 0. |
| 4 | 1 | 853.54827 | ——— | ——— | 0.21E+01 | 888.07968 | 888.07790( 50)[c] | | -157 | 0.21E+01 |
| 4 | 2 | 852.72481 | ——— | ——— | 0.18E+01 | 887.99887 | 887.99800( 50)[c] | | -107 | 0.18E+01 |
| 4 | 3 | 851.32699 | ——— | ——— | 0.23E+01 | 887.87685 | 887.87683( 30)[d] | | -1 | 0.23E+01 |
| 5 | 0( | 835.09327) | ——— | ——— | 0. | 868.00178 | ——— | | ——— | 0.34E+01 |
| 5 | 1 | 834.82392 | ——— | ——— | 0.17E+01 | 867.98001 | ——— | | ——— | 0.16E+01 |
| 5 | 2 | 834.01228 | ——— | ——— | 0.15E+01 | 867.87102 | ——— | | ——— | 0.15E+01 |
| 5 | 3 | 832.63488 | ——— | ——— | 0.25E+01 | 867.71968 | ——— | | ——— | 0.25E+01 |
| 5 | 4 | 830.69313 | ——— | ——— | 0.80E+00 | 867.52817 | ——— | | ——— | 0.80E+00 |
| 6 | 0 | 816.68117 | ——— | ——— | 0.22E+01 | ( 847.91496) | ——— | | ——— | 0. |
| 6 | 1 | 816.38644 | ——— | ——— | 0.11E+01 | 847.87654 | ——— | | ——— | 0.11E+01 |
| 6 | 2 | 815.59122 | ——— | ——— | 0.11E+01 | 847.76313 | ——— | | ——— | 0.11E+01 |
| 6 | 3 | 814.24158 | ——— | ——— | 0.20E+01 | 847.57829 | ——— | | ——— | 0.20E+01 |
| 6 | 4 | 812.30113 | ——— | ——— | 0.82E+00 | 847.33772 | ——— | | ——— | 0.82E+00 |
| 6 | 5 | 809.71476 | ——— | ——— | 0.93E+00 | 847.05137 | ——— | | ——— | 0.93E+00 |
| 7 | 0( | 798.48201) | ——— | ——— | 0. | 827.67812 | ——— | | ——— | 0.13E+01 |
| 7 | 1 | 798.22265 | ——— | ——— | 0.66E+00 | 827.83375 | ——— | | ——— | 0.65E+00 |
| 7 | 2 | 797.44684 | ——— | ——— | 0.63E+00 | 827.78287 | ——— | | ——— | 0.64E+00 |
| 7 | 3 | 796.13435 | ——— | ——— | 0.13E+01 | 827.68801 | ——— | | ——— | 0.12E+01 |
| 7 | 4 | 794.24416 | ——— | ——— | 0.98E+00 | 827.20125 | ——— | | ——— | 0.98E+00 |
| 7 | 5 | 791.72682 | ——— | ——— | 0.90E+00 | 826.85537 | ——— | | ——— | 0.90E+00 |
| 7 | 6 | 788.51038 | ——— | ——— | 0.65E+00 | 826.47021 | ——— | | ——— | 0.65E+00 |
| 8 | 0 | 780.56828 | ——— | ——— | 0.69E+00 | ( 807.92263) | ——— | | ——— | 0. |
| 8 | 1 | 780.31481 | ——— | ——— | 0.33E+00 | 807.87225 | ——— | | ——— | 0.34E+00 |
| 8 | 2 | 779.56434 | ——— | ——— | 0.33E+00 | 807.72283 | ——— | | ——— | 0.34E+00 |
| 8 | 3 | 778.29038 | ——— | ——— | 0.69E+00 | 807.47225 | ——— | | ——— | 0.69E+00 |
| 8 | 4 | 776.46186 | ——— | ——— | 0.34E+00 | 807.14433 | ——— | | ——— | 0.34E+00 |
| 8 | 5 | 774.02536 | ——— | ——— | 0.32E+00 | 806.73781 | ——— | | ——— | 0.32E+00 |
| 8 | 6 | 770.91381 | ——— | ——— | 0.96E+00 | 806.27428 | ——— | | ——— | 0.96E+00 |
| 8 | 7 | 767.03745 | ——— | ——— | 0.19E+00 | 805.77908 | ——— | | ——— | 0.19E+00 |
| 9 | 0( | 762.88910) | ——— | ——— | 0. | 788.07878 | ——— | | ——— | 0.32E+00 |
| 9 | 1 | 762.64165 | ——— | ——— | 0.16E+00 | 788.02849 | ——— | | ——— | 0.16E+00 |
| 9 | 2 | 761.91903 | ——— | ——— | 0.17E+00 | 787.87554 | ——— | | ——— | 0.16E+00 |
| 9 | 3 | 760.69462 | ——— | ——— | 0.34E+00 | 787.57689 | ——— | | ——— | 0.33E+00 |
| 9 | 4 | 758.93008 | ——— | ——— | 0.17E+00 | 787.19941 | ——— | | ——— | 0.17E+00 |
| 9 | 5 | 756.58442 | ——— | ——— | 0.17E+00 | 786.73258 | ——— | | ——— | 0.17E+00 |
| 9 | 6 | 753.59083 | ——— | ——— | 0.33E+00 | 786.19067 | ——— | | ——— | 0.33E+00 |
| 9 | 7 | 749.86384 | ——— | ——— | 0.13E+00 | 785.59632 | ——— | | ——— | 0.13E+00 |
| 9 | 8 | 745.29234 | ——— | ——— | 0.10E+00 | 784.98060 | ——— | | ——— | 0.10E+00 |
| 10 | 0 | 745.42138 | ——— | ——— | 0.14E+00 | ( 768.37488) | ——— | | ——— | 0. |
| 10 | 1 | 745.17958 | ——— | ——— | 0.69E-01 | 768.31202 | ——— | | ——— | 0.68E-01 |
| 10 | 2 | 744.48756 | ——— | ——— | 0.71E-01 | 768.12964 | ——— | | ——— | 0.70E-01 |
| 10 | 3 | 743.30766 | ——— | ——— | 0.15E+00 | 767.81002 | ——— | | ——— | 0.14E+00 |
| 10 | 4 | 741.62224 | ——— | ——— | 0.76E-01 | 767.39683 | ——— | | ——— | 0.75E-01 |
| 10 | 5 | 739.37525 | ——— | ——— | 0.79E-01 | 766.87108 | ——— | | ——— | 0.78E-01 |
| 10 | 6 | 736.50924 | ——— | ——— | 0.16E+00 | 766.25274 | ——— | | ——— | 0.16E+00 |
| 10 | 7 | 732.94356 | ——— | ——— | 0.80E-01 | 765.56119 | ——— | | ——— | 0.80E-01 |
| 10 | 8 | 728.57447 | ——— | ——— | 0.73E-01 | 764.82355 | ——— | | ——— | 0.74E-01 |
| 10 | 9 | 723.27039 | ——— | ——— | 0.10E+00 | 764.02767 | ——— | | ——— | 0.10E+00 |
| 11 | 0( | 728.14114) | ——— | ——— | 0. | 748.83631 | ——— | | ——— | 0.52E-01 |
| 11 | 1 | 727.90389 | ——— | ——— | 0.27E-01 | 748.76924 | ——— | | ——— | 0.26E-01 |
| 11 | 2 | 727.24537 | ——— | ——— | 0.27E-01 | 748.57171 | ——— | | ——— | 0.27E-01 |
| 11 | 3 | 726.12888 | ——— | ——— | 0.57E-01 | 748.22825 | ——— | | ——— | 0.56E-01 |
| 11 | 4 | 724.51070 | ——— | ——— | 0.30E-01 | 747.76402 | ——— | | ——— | 0.29E-01 |
| 11 | 5 | 722.38802 | ——— | ——— | 0.32E-01 | 747.18213 | ——— | | ——— | 0.31E-01 |
| 11 | 6 | 719.63730 | ——— | ——— | 0.68E-01 | 746.49063 | ——— | | ——— | 0.67E-01 |
| 11 | 7 | 716.24294 | ——— | ——— | 0.36E-01 | 745.70586 | ——— | | ——— | 0.35E-01 |
| 11 | 8 | 712.08748 | ——— | ——— | 0.36E-01 | 744.85089 | ——— | | ——— | 0.36E-01 |
| 11 | 9 | 707.04707 | ——— | ——— | 0.68E-01 | 743.95823 | ——— | | ——— | 0.69E-01 |
| 11 | 10 | 700.96596 | ——— | ——— | 0.25E-01 | 743.07349 | ——— | | ——— | 0.25E-01 |
| 12 | 0 | 711.02485 | ——— | ——— | 0.18E-01 | ( 729.46811) | ——— | | ——— | 0. |
| 12 | 1 | 710.78987 | ——— | ——— | 0.92E-02 | 729.41402 | ——— | | ——— | 0.91E-02 |
| 12 | 2 | 710.10884 | ——— | ——— | 0.95E-02 | 729.20564 | ——— | | ——— | 0.93E-02 |
| 12 | 3 | 709.00072 | ——— | ——— | 0.20E-01 | 728.81481 | ——— | | ——— | 0.20E-01 |
| 12 | 4 | 707.56818 | ——— | ——— | 0.11E-01 | 728.32498 | ——— | | ——— | 0.10E-01 |
| 12 | 5 | 705.53314 | ——— | ——— | 0.11E-01 | 727.69052 | ——— | | ——— | 0.11E-01 |
| 12 | 6 | 702.94223 | ——— | ——— | 0.25E-01 | 726.93050 | ——— | | ——— | 0.25E-01 |
| 12 | 7 | 699.72517 | ——— | ——— | 0.14E-01 | 726.05826 | ——— | | ——— | 0.14E-01 |
| 12 | 8 | 695.79116 | ——— | ——— | 0.15E-01 | 725.09283 | ——— | | ——— | 0.15E-01 |
| 12 | 9 | 691.02431 | ——— | ——— | 0.31E-01 | 724.06144 | ——— | | ——— | 0.31E-01 |
| 12 | 10 | 685.27890 | ——— | ——— | 0.15E-01 | 723.00282 | ——— | | ——— | 0.15E-01 |
| 12 | 11 | 678.37215 | ——— | ——— | 0.11E-01 | 721.97141 | ——— | | ——— | 0.11E-01 |
| 13 | 0( | 694.05094) | ——— | ——— | 0. | 710.34300 | ——— | | ——— | 0.96E-02 |
| 13 | 1 | 693.81340 | ——— | ——— | 0.29E-02 | 710.29660 | ——— | | ——— | 0.29E-02 |
| 13 | 2 | 693.23313 | ——— | ——— | 0.30E-02 | 710.05330 | ——— | | ——— | 0.29E-02 |
| 13 | 3 | 692.23528 | ——— | ——— | 0.63E-02 | 709.64102 | ——— | | ——— | 0.62E-02 |
| 13 | 4 | 690.76918 | ——— | ——— | 0.34E-02 | 709.09970 | ——— | | ——— | 0.33E-02 |
| 13 | 5 | 688.84278 | ——— | ——— | 0.37E-02 | 708.41710 | ——— | | ——— | 0.36E-02 |
| 13 | 6 | 686.39323 | ——— | ——— | 0.82E-02 | 707.59415 | ——— | | ——— | 0.81E-02 |
| 13 | 7 | 683.35583 | ——— | ——— | 0.46E-02 | 706.64149 | ——— | | ——— | 0.45E-02 |
| 13 | 8 | 679.64686 | ——— | ——— | 0.51E-02 | 705.57431 | ——— | | ——— | 0.51E-02 |
| 13 | 9 | 675.15625 | ——— | ——— | 0.12E-01 | 704.43472 | ——— | | ——— | 0.11E-01 |
| 13 | 10 | 669.77516 | ——— | ——— | 0.62E-02 | 703.19488 | ——— | | ——— | 0.62E-02 |
| 13 | 11 | 663.26707 | ——— | ——— | 0.61E-02 | 701.95998 | ——— | | ——— | 0.62E-02 |
| 13 | 12 | 655.48243 | ——— | ——— | 0.95E-02 | 700.77537 | ——— | | ——— | 0.98E-02 |
| 14 | 0 | 677.20095 | ——— | ——— | 0.17E-02 | ( 691.42371) | ——— | | ——— | 0. |
| 14 | 1 | 676.94941 | ——— | ——— | 0.84E-03 | 691.34360 | ——— | | ——— | 0.82E-03 |
| 14 | 2 | 676.42147 | ——— | ——— | 0.87E-03 | 691.13794 | ——— | | ——— | 0.84E-03 |
| 14 | 3 | 675.44469 | ——— | ——— | 0.18E-02 | 690.65913 | ——— | | ——— | 0.18E-02 |
| 14 | 4 | 674.09146 | ——— | ——— | 0.99E-03 | 690.10827 | ——— | | ——— | 0.96E-03 |
| 14 | 5 | 672.27231 | ——— | ——— | 0.21E-02 | 689.37890 | ——— | | ——— | 0.11E-02 |
| 14 | 6 | 669.96272 | ——— | ——— | 0.24E-02 | 688.49982 | ——— | | ——— | 0.24E-02 |
| 14 | 7 | 667.10369 | ——— | ——— | 0.14E-02 | 687.47377 | ——— | | ——— | 0.14E-02 |
| 14 | 8 | 663.61837 | ——— | ——— | 0.16E-02 | 686.31675 | ——— | | ——— | 0.16E-02 |
| 14 | 9 | 659.40817 | ——— | ——— | 0.37E-02 | 685.03924 | ——— | | ——— | 0.36E-02 |
| 14 | 10 | 654.34796 | ——— | ——— | 0.21E-02 | 683.67273 | ——— | | ——— | 0.21E-02 |
| 14 | 11 | 648.28023 | ——— | ——— | 0.23E-02 | 682.25257 | ——— | | ——— | 0.24E-02 |
| 14 | 12 | 641.00783 | ——— | ——— | 0.48E-02 | 680.83261 | ——— | | ——— | 0.49E-02 |
| 14 | 13 | 632.28507 | ——— | ——— | 0.19E-02 | 679.48949 | ——— | | ——— | 0.20E-02 |

[a] C and O are calculated and observed transition wavenumbers, I are calculated intensities. Values in parentheses of the observed wavenumbers are estimated experimental uncertainties in units of the last digit quoted; aX(J,K) and aX(J,K) with X = P,Q,R denote transitions from the lower (a) or upper (a) component of the ground state inversion doublets. Calculated wavenumbers for transitions from levels with zero spin statistical weights are in parentheses. [b] Ref.(24). [c] Ref.(8). [d] Ref.(9). [e] Ref.(7). [f] Ref.(25). [g] Ref.(1).

TABLE IV—*Continued*

| J | K | sQ(J,K) C | sQ(J,K) O | (O-C) x10^5 | I | sQ(J,K) C | sQ(J,K) O | (O-C) x10^5 | I |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 0( | 931.64043) | ——— | —— | 0. | ( 968.12195) | ——— | —— | 0. |
| 1 | 0( | 931.89642) | ——— | —— | 0. | ( 968.00932) | ——— | —— | 0. |
| 1 | 1 | 931.62778 | 931.62776( 20)a | -1 | 0.22E+01 | 967.99778 | 967.99774( 10)a | -3 | 0.22E+01 |
| 2 | 0( | 932.40131) | ——— | —— | 0. | ( 967.76768) | ——— | —— | 0. |
| 2 | 1 | 932.13619 | 932.13618( 20)a | -9 | 0.10E+01 | 967.77479 | ——— | —— | 0.10E+01 |
| 2 | 2 | 931.83328 | 931.83342( 20)a | 14 | 0.43E+01 | 967.73894 | 967.73859( 10)a | 14 | 0.42E+01 |
| 3 | 0( | 933.13884) | ——— | —— | 0. | ( 967.44480) | ——— | —— | 0. |
| 3 | 1 | 932.88125 | ——— | —— | 0.53E+00 | 967.44916 | ——— | —— | 0.53E+00 |
| 3 | 2 | 932.89408 | 932.89402( 20)a | -5 | 0.22E+01 | 967.40886 | ——— | —— | 0.22E+01 |
| 3 | 3 | 930.75706 | ——— | —— | 0.11E+02 | 967.34634 | 967.34632( 20)a | -1 | 0.11E+02 |
| 4 | 0( | 934.09697) | ——— | —— | 0. | ( 967.04826) | ——— | —— | 0. |
| 4 | 1 | 933.84256 | 933.84190( 50)c | -66 | 0.28E+00 | 967.03891 | ——— | —— | 0.28E+00 |
| 4 | 2 | 933.07587 | 933.07620(100)a | 33 | 0.12E+01 | 966.98184 | ——— | —— | 0.12E+01 |
| 4 | 3 | 931.77359 | ——— | —— | 0.98E+01 | 966.90920 | ——— | —— | 0.98E+01 |
| 4 | 4 | 929.89813 | 929.89820( 50)c | 6 | 0.58E+01 | 966.81475 | ——— | —— | 0.58E+01 |
| 5 | 0( | 935.24108) | ——— | —— | 0. | ( 966.55269) | ——— | —— | 0. |
| 5 | 1 | 934.99408 | ——— | —— | 0.14E+00 | 966.53244 | ——— | —— | 0.14E+00 |
| 5 | 2 | 934.25258 | 934.25240( 50)c | 20 | 0.60E+00 | 966.47378 | ——— | —— | 0.39E+00 |
| 5 | 3 | 932.99233 | 932.99243( 15)a | 8 | 0.29E+01 | 966.38901 | ——— | —— | 0.29E+01 |
| 5 | 4 | 931.17737 | 931.17735( 30)a | -2 | 0.30E+01 | 966.26928 | 966.26931( 10)a | 2 | 0.29E+01 |
| 5 | 5 | 928.75449 | 928.75430( 50)c | -19 | 0.54E+01 | 966.15116 | 966.15100( 10)a | -15 | 0.54E+01 |
| 6 | 0( | 936.54191) | ——— | —— | 0. | ( 965.99128) | ——— | —— | 0. |
| 6 | 1 | 936.30498 | ——— | —— | 0.68E-01 | 965.98779 | ——— | —— | 0.67E-01 |
| 6 | 2 | 935.59177 | ——— | —— | 0.29E+00 | 965.89924 | ——— | —— | 0.28E+00 |
| 6 | 3 | 934.37969 | ——— | —— | 0.14E+01 | 965.79140 | ——— | —— | 0.14E+01 |
| 6 | 4 | 932.63573 | 932.63589( 10)c | 15 | 0.14E+01 | 965.65206 | ——— | —— | 0.14E+01 |
| 6 | 5 | 930.30663 | 930.30653( 20)a | -9 | 0.28E+01 | 965.49948 | ——— | —— | 0.28E+01 |
| 6 | 6 | 927.32303 | 927.32328( 10)c | 24 | 0.90E+01 | 965.35393 | ——— | —— | 0.90E+01 |
| 7 | 0( | 937.97126) | ——— | —— | 0. | ( 965.37870) | ——— | —— | 0. |
| 7 | 1 | 937.74072 | ——— | —— | 0.30E-01 | 965.38178 | ——— | —— | 0.30E-01 |
| 7 | 2 | 937.05956 | ——— | —— | 0.13E+00 | 965.27294 | ——— | —— | 0.13E+00 |
| 7 | 3 | 935.90193 | ——— | —— | 0.63E+00 | 965.13790 | 965.13730(100)a | -59 | 0.62E+00 |
| 7 | 4 | 934.23583 | 934.23580( 50)c | -2 | 0.63E+00 | 964.97969 | ——— | —— | 0.62E+00 |
| 7 | 5 | 932.01123 | ——— | —— | 0.12E+01 | 964.79825 | 964.79006( 10)a | -18 | 0.11E+01 |
| 7 | 6 | 929.16174 | 929.16160( 50)c | -13 | 0.40E+01 | 964.59579 | 964.59340(100)a | -38 | 0.40E+01 |
| 7 | 7 | 925.59961 | ——— | —— | 0.34E+01 | 964.42405 | 964.42410( 20) | 5 | 0.34E+01 |
| 8 | 0( | 939.48628) | ——— | —— | 0. | ( 964.72955) | ——— | —— | 0. |
| 8 | 1 | 939.26424 | ——— | —— | 0.13E-01 | 964.69915 | ——— | —— | 0.12E-01 |
| 8 | 2 | 938.61804 | ——— | —— | 0.53E-01 | 964.61009 | ——— | —— | 0.52E-01 |
| 8 | 3 | 937.51597 | ——— | —— | 0.26E+00 | 964.46755 | ——— | —— | 0.26E+00 |
| 8 | 4 | 935.93753 | ——— | —— | 0.26E+00 | 964.26870 | ——— | —— | 0.26E+00 |
| 8 | 5 | 933.82614 | 933.82600( 40)a | -13 | 0.48E+00 | 964.04128 | ——— | —— | 0.47E+00 |
| 8 | 6 | 931.12203 | 931.12190( 20)a | -13 | 0.17E+01 | 963.79823 | ——— | —— | 0.16E+01 |
| 8 | 7 | 927.74281 | 927.74196( 30)a | -5 | 0.14E+01 | 963.55838 | 963.55820(100)a | -18 | 0.14E+01 |
| 8 | 8 | 923.57902 | ——— | —— | 0.24E+01 | 963.34279 | 963.34268( 10)a | -10 | 0.24E+01 |
| 9 | 0( | 941.05128) | ——— | —— | 0. | ( 964.03752) | ——— | —— | 0. |
| 9 | 1 | 940.83718 | ——— | —— | 0.49E-02 | 964.02372 | ——— | —— | 0.47E-02 |
| 9 | 2 | 940.22849 | ——— | —— | 0.20E-01 | 963.92318 | ——— | —— | 0.20E-01 |
| 9 | 3 | 939.19865 | ——— | —— | 0.10E+00 | 963.73705 | ——— | —— | 0.98E-01 |
| 9 | 4 | 937.69933 | 937.69890( 50)c | -43 | 0.10E+00 | 963.53473 | ——— | —— | 0.98E-01 |
| 9 | 5 | 935.70766 | ——— | —— | 0.18E+00 | 963.26939 | ——— | —— | 0.18E+00 |
| 9 | 6 | 933.15748 | 933.15710(100)a | -37 | 0.64E+00 | 962.97370 | 962.97368( 20)a | -1 | 0.63E+00 |
| 9 | 7 | 929.97048 | 929.97110( 50)a | 61 | 0.54E+00 | 962.66984 | ——— | —— | 0.54E+00 |
| 9 | 8 | 926.04574 | 926.04584( 20)a | 7 | 0.92E+00 | 962.38842 | ——— | —— | 0.91E+00 |
| 9 | 9 | 921.25908 | ——— | —— | 0.31E+01 | 962.17131 | ——— | —— | 0.31E+01 |
| 10 | 0( | 942.62859) | ——— | —— | 0. | ( 963.37472) | ——— | —— | 0. |
| 10 | 1 | 942.42117 | ——— | —— | 0.17E-02 | 963.33775 | ——— | —— | 0.17E-02 |
| 10 | 2 | 941.85235 | ——— | —— | 0.72E-02 | 963.23132 | ——— | —— | 0.71E-02 |
| 10 | 3 | 940.86752 | ——— | —— | 0.35E-01 | 963.03897 | ——— | —— | 0.35E-01 |
| 10 | 4 | 939.47981 | ——— | —— | 0.35E-01 | 962.79162 | ——— | —— | 0.35E-01 |
| 10 | 5 | 937.61208 | 937.61190( 50)c | -18 | 0.65E-01 | 962.48936 | ——— | —— | 0.63E-01 |
| 10 | 6 | 935.22146 | 935.22160( 50)c | 13 | 0.22E+00 | 962.14466 | ——— | —— | 0.22E+00 |
| 10 | 7 | 932.22487 | ——— | —— | 0.14E+00 | 961.77625 | ——— | —— | 0.14E+00 |
| 10 | 8 | 928.55790 | 928.55810( 50)c | 20 | 0.32E+00 | 961.41104 | ——— | —— | 0.32E+00 |
| 10 | 9 | 924.07034 | ——— | —— | 0.11E+01 | 961.08607 | ——— | —— | 0.11E+01 |
| 10 | 10 | 918.62058 | 918.62090( 40)c | 31 | 0.94E+00 | 960.85230 | 960.85232( 20)a | 2 | 0.94E+00 |
| 11 | 0( | 944.38280) | ——— | —— | 0. | ( 962.69124) | ——— | —— | 0. |
| 11 | 1 | 943.97890 | ——— | —— | 0.56E-03 | 962.65139 | ——— | —— | 0.55E-03 |
| 11 | 2 | 943.45277 | ——— | —— | 0.24E-02 | 962.54000 | ——— | —— | 0.23E-02 |
| 11 | 3 | 942.56672 | ——— | —— | 0.12E-01 | 962.28081 | ——— | —— | 0.11E-01 |
| 11 | 4 | 941.23902 | ——— | —— | 0.12E-01 | 962.05098 | ——— | —— | 0.11E-01 |
| 11 | 5 | 939.49713 | ——— | —— | 0.22E-01 | 961.71423 | ——— | —— | 0.21E-01 |
| 11 | 6 | 937.26876 | ——— | —— | 0.73E-01 | 961.32285 | ——— | —— | 0.71E-01 |
| 11 | 7 | 934.48631 | ——— | —— | 0.62E-01 | 960.89324 | ——— | —— | 0.61E-01 |
| 11 | 8 | 931.06220 | ——— | —— | 0.10E+00 | 960.44829 | ——— | —— | 0.10E+00 |
| 11 | 9 | 926.88461 | ——— | —— | 0.35E+00 | 960.01993 | 960.01990( 20)a | -3 | 0.35E+00 |
| 11 | 10 | 921.81237 | 921.81200( 60)c | -16 | 0.30E+00 | 959.63253 | ——— | —— | 0.30E+00 |
| 11 | 11 | 915.66735 | ——— | —— | 0.53E+00 | 959.40733 | ——— | —— | 0.53E+00 |
| 12 | 0( | 945.67859) | ——— | —— | 0. | ( 962.01498) | ——— | —— | 0. |
| 12 | 1 | 945.47469 | ——— | —— | 0.17E-03 | 961.97266 | ——— | —— | 0.16E-03 |
| 12 | 2 | 944.99563 | ——— | —— | 0.71E-03 | 961.86176 | ——— | —— | 0.69E-03 |
| 12 | 3 | 944.11773 | ——— | —— | 0.35E-02 | 961.67016 | ——— | —— | 0.34E-02 |
| 12 | 4 | 942.91994 | ——— | —— | 0.35E-02 | 961.42153 | ——— | —— | 0.34E-02 |
| 12 | 5 | 941.32342 | ——— | —— | 0.63E-02 | 960.95300 | ——— | —— | 0.61E-02 |
| 12 | 6 | 939.23703 | ——— | —— | 0.22E-01 | 960.51879 | ——— | —— | 0.21E-01 |
| 12 | 7 | 936.67880 | ——— | —— | 0.19E-01 | 960.03272 | ——— | —— | 0.18E-01 |
| 12 | 8 | 933.50828 | ——— | —— | 0.31E-01 | 959.51390 | ——— | —— | 0.31E-01 |
| 12 | 9 | 929.64229 | ——— | —— | 0.11E+00 | 958.98929 | ——— | —— | 0.10E+00 |
| 12 | 10 | 924.95002 | 924.94990(100)f | -11 | 0.90E-01 | 958.49473 | ——— | —— | 0.89E-01 |
| 12 | 11 | 919.26678 | ——— | —— | 0.18E+00 | 958.08984 | ——— | —— | 0.18E+00 |
| 12 | 12 | 912.38627 | ——— | —— | 0.56E+00 | 957.83931 | ——— | —— | 0.56E+00 |
| 13 | 0( | 947.08895) | ——— | —— | 0. | ( 961.93219) | ——— | —— | 0. |
| 13 | 1 | 946.87279 | ——— | —— | 0.47E-04 | 961.90774 | ——— | —— | 0.43E-04 |
| 13 | 2 | 946.49115 | ——— | —— | 0.20E-03 | 961.80948 | ——— | —— | 0.19E-03 |
| 13 | 3 | 945.72825 | ——— | —— | 0.96E-03 | 960.83489 | ——— | —— | 0.93E-03 |
| 13 | 4 | 944.54977 | ——— | —— | 0.96E-03 | 960.61802 | ——— | —— | 0.93E-03 |
| 13 | 5 | 943.05582 | ——— | —— | 0.17E-02 | 960.21266 | ——— | —— | 0.17E-02 |
| 13 | 6 | 941.24816 | ——— | —— | 0.60E-02 | 959.73943 | ——— | —— | 0.59E-02 |
| 13 | 7 | 938.77072 | ——— | —— | 0.51E-02 | 959.28281 | ——— | —— | 0.50E-02 |
| 13 | 8 | 935.85017 | ——— | —— | 0.86E-02 | 958.81728 | ——— | —— | 0.84E-02 |
| 13 | 9 | 932.29225 | ——— | —— | 0.29E-01 | 958.40542 | ——— | —— | 0.28E-01 |
| 13 | 10 | 927.97643 | ——— | —— | 0.25E-01 | 957.99875 | ——— | —— | 0.24E-01 |
| 13 | 11 | 922.75260 | ——— | —— | 0.43E-01 | 957.64141 | ——— | —— | 0.42E-01 |
| 13 | 12 | 916.42882 | ——— | —— | 0.15E+00 | 957.39789 | ——— | —— | 0.15E+00 |
| 13 | 13 | 908.76737 | ——— | —— | 0.14E+00 | 957.25139 | 957.25089( 70)b | -50 | 0.14E+00 |

In Eqs. (18)–(22), $m = 0$ for the ground state and $m = 1$ for the $\nu_2$ state; the upper indices $s$ and $a$ denote respectively the lower and upper component of the inversion doublet; $\Delta E_m$ in Eq. (21) is defined as $\Delta E_m = E_m^{(a)} - E_m^{(s)}$, i.e., as the inversion splitting for $J = K = 0$ in the ground state ($m = 0$) and in the upper state ($m = 1$).

We introduce also the vector of the $\Delta k = \pm 3n$ interaction parameters [see

TABLE IV—*Continued*

| J | K | C | aR(J,K) O | (O-C) x10$^5$ | I | C | aR(J,K) O | (O-C) x10$^5$ | I |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 0 | 951.77627 | ——— | —— | 0.32E+01 | ( 987.89921) | ——— | —— | 0. |
| 1 | 0( | 972.14107) | ——— | —— | 0. | 1007.54712 | ——— | —— | 0.60E+01 |
| 1 | 1 | 971.88206 | 971.88204( 10)[b] | -1 | 0.23E+01 | 1007.54832 | ——— | —— | 0.23E+01 |
| 2 | 0 | 992.69878 | ——— | —— | 0.76E+01 | (1027.05298) | ——— | —— | 0. |
| 2 | 1 | 992.45030 | ——— | —— | 0.34E+01 | 1027.04703 | 1027.046700( 50)[c] | -33 | 0.34E+01 |
| 2 | 2 | 991.69053 | ——— | —— | 0.23E+01 | 1027.03299 | 1027.033300( 50)[c] | 55 | 0.22E+01 |
| 3 | 0( | 1013.41788) | ——— | —— | 0. | 1046.48532 | 1046.485040( 60)[g] | 8 | 0.77E+01 |
| 3 | 1 | 1013.17554 | ——— | —— | 0.37E+01 | 1046.48059 | 1046.480900( 50)[g] | 21 | 0.37E+01 |
| 3 | 2 | 1012.44514 | ——— | —— | 0.31E+01 | 1046.38683 | 1046.388100( 40)[g] | 6 | 0.31E+01 |
| 3 | 3 | 1011.20366 | 1011.20350( 10)[f] | -16 | 0.40E+01 | 1046.37468 | 1046.374500( 30)[g] | -18 | 0.40E+01 |
| 4 | 0 | 1034.24478 | ——— | —— | 0.48E+01 | (1065.59923) | ——— | —— | 0. |
| 4 | 1 | 1034.02273 | ——— | —— | 0.33E+01 | 1065.59432 | 1065.594400( 30)[c] | 7 | 0.33E+01 |
| 4 | 2 | 1033.31979 | ——— | —— | 0.31E+01 | 1065.58172 | 1065.582400( 30)[c] | 67 | 0.30E+01 |
| 4 | 3 | 1032.13106 | ——— | —— | 0.31E+01 | 1065.56552 | 1065.565500( 50)[c] | -2 | 0.50E+01 |
| 4 | 4 | 1030.42237 | ——— | —— | 0.16E+01 | 1065.56385 | 1065.563600( 50)[g] | -25 | 0.16E+01 |
| 5 | 0( | 1055.13982) | ——— | —— | 0. | 1084.62982 | 1084.629000( 60)[g] | 56 | 0.31E+01 |
| 5 | 1 | 1054.91262 | ——— | —— | 0.26E+01 | 1084.62370 | 1084.624400( 60)[g] | 70 | 0.25E+01 |
| 5 | 2 | 1054.25275 | ——— | —— | 0.25E+01 | 1084.60981 | 1084.610200( 50)[g] | 38 | 0.24E+01 |
| 5 | 3 | 1053.13045 | ——— | —— | 0.46E+01 | 1084.59313 | 1084.593960( 20)[g] | -6 | 0.43E+01 |
| 5 | 4 | 1051.51198 | ——— | —— | 0.19E+01 | 1084.58363 | 1084.583710( 10)[g] | 8 | 0.19E+01 |
| 5 | 5 | 1049.34637 | ——— | —— | 0.12E+01 | 1084.59927 | 1084.599240( 10)[g] | -2 | 0.12E+01 |
| 6 | 0 | 1076.03311 | ——— | —— | 0.35E+01 | (1103.49186) | ——— | —— | 0. |
| 6 | 1 | 1075.82304 | ——— | —— | 0.17E+01 | 1103.48583 | 1103.486400( 80)[g] | 57 | 0.17E+01 |
| 6 | 2 | 1075.20329 | 1075.20240(200)[c] | -88 | 0.17E+01 | 1103.46982 | 1103.470400( 70)[g] | 58 | 0.17E+01 |
| 6 | 3 | 1074.14924 | ——— | —— | 0.32E+01 | 1103.44128 | 1103.443300( 60)[g] | 22 | 0.33E+01 |
| 6 | 4 | 1072.62739 | ——— | —— | 0.16E+01 | 1103.43050 | 1103.431100( 60)[g] | 59 | 0.15E+01 |
| 6 | 5 | 1070.59104 | 1070.59090( 50)[c] | -13 | 0.13E+01 | 1103.43439 | 1103.434200( 50)[g] | -15 | 0.13E+01 |
| 6 | 6 | 1067.97435 | ——— | —— | 0.17E+01 | 1103.47992 | 1103.480200( 80)[g] | 66 | 0.17E+01 |
| 7 | 0( | 1096.88920) | ——— | —— | 0. | 1122.18562 | 1122.189300(100)[g] | 18 | 0.21E+01 |
| 7 | 1 | 1096.69014 | ——— | —— | 0.11E+01 | 1122.17868 | 1122.179300(100)[g] | -58 | 0.10E+01 |
| 7 | 2 | 1096.11306 | 1096.11320( 50)[c] | 13 | 0.11E+01 | 1122.16021 | 1122.160300( 60)[g] | 9 | 0.10E+01 |
| 7 | 3 | 1095.12950 | ——— | —— | 0.21E+01 | 1122.13320 | 1122.133200( 70)[g] | 0 | 0.21E+01 |
| 7 | 4 | 1093.71150 | 1093.71190( 50) | 40 | 0.10E+01 | 1122.10486 | 1122.104200( 50)[g] | 13 | 0.10E+01 |
| 7 | 5 | 1091.81197 | ——— | —— | 0.99E+00 | 1122.09371 | 1122.093700( 70)[g] | -1 | 0.97E+00 |
| 7 | 6 | 1089.36996 | ——— | —— | 0.17E+01 | 1122.11774 | 1122.118100( 70)[g] | 56 | 0.17E+01 |
| 7 | 7 | 1086.30417 | ——— | —— | 0.58E+00 | 1122.20355 | 1122.204300(100)[g] | 74 | 0.57E+00 |
| 8 | 0 | 1117.64846 | ——— | —— | 0.11E+01 | (1140.70828) | ——— | —— | 0. |
| 8 | 1 | 1117.49777 | ——— | —— | 0.57E+00 | 1140.70038 | ——— | —— | 0.55E+00 |
| 8 | 2 | 1116.92750 | ——— | —— | 0.58E+00 | 1140.67973 | ——— | —— | 0.56E+00 |
| 8 | 3 | 1116.01995 | ——— | —— | 0.12E+01 | 1140.62771 | ——— | —— | 0.11E+01 |
| 8 | 4 | 1114.70678 | ——— | —— | 0.60E+00 | 1140.60402 | ——— | —— | 0.58E+00 |
| 8 | 5 | 1112.94938 | ——— | —— | 0.60E+00 | 1140.57926 | ——— | —— | 0.59E+00 |
| 8 | 6 | 1110.68898 | ——— | —— | 0.12E+01 | 1140.57925 | ——— | —— | 0.11E+01 |
| 8 | 7 | 1107.84945 | ——— | —— | 0.52E+00 | 1140.63210 | ——— | —— | 0.51E+00 |
| 8 | 8 | 1104.33244 | ——— | —— | 0.36E+00 | 1140.77854 | ——— | —— | 0.36E+00 |
| 9 | 0( | 1138.25845) | ——— | —— | 0. | 1159.05736 | ——— | —— | 0.93E+00 |
| 9 | 1 | 1138.07878 | ——— | —— | 0.28E+00 | 1159.04855 | ——— | —— | 0.27E+00 |
| 9 | 2 | 1137.59329 | ——— | —— | 0.28E+00 | 1159.02686 | ——— | —— | 0.27E+00 |
| 9 | 3 | 1136.75851 | ——— | —— | 0.58E+00 | 1158.98599 | ——— | —— | 0.57E+00 |
| 9 | 4 | 1135.53690 | ——— | —— | 0.30E+00 | 1158.92951 | ——— | —— | 0.30E+00 |
| 9 | 5 | 1133.94459 | ——— | —— | 0.32E+00 | 1158.88786 | ——— | —— | 0.31E+00 |
| 9 | 6 | 1131.86970 | ——— | —— | 0.95E+00 | 1158.89362 | ——— | —— | 0.94E+00 |
| 9 | 7 | 1129.26179 | ——— | —— | 0.33E+00 | 1158.88490 | ——— | —— | 0.32E+00 |
| 9 | 8 | 1126.02915 | ——— | —— | 0.30E+00 | 1158.97391 | ——— | —— | 0.29E+00 |
| 9 | 9 | 1122.05503 | 1122.05550( 70)[g] | 47 | 0.43E+00 | 1159.17992 | ——— | —— | 0.42E+00 |
| 10 | 0 | 1158.66951 | ——— | —— | 0.24E+00 | (1177.22945) | ——— | —— | 0. |
| 10 | 1 | 1158.49619 | ——— | —— | 0.12E+00 | 1177.21989 | ——— | —— | 0.12E+00 |
| 10 | 2 | 1158.05978 | ——— | —— | 0.12E+00 | 1177.19961 | ——— | —— | 0.12E+00 |
| 10 | 3 | 1157.30536 | ——— | —— | 0.26E+00 | 1177.11193 | ——— | —— | 0.25E+00 |
| 10 | 4 | 1156.20812 | ——— | —— | 0.14E+00 | 1177.07850 | ——— | —— | 0.13E+00 |
| 10 | 5 | 1154.74120 | ——— | —— | 0.15E+00 | 1177.02165 | ——— | —— | 0.14E+00 |
| 10 | 6 | 1152.85292 | ——— | —— | 0.31E+00 | 1176.97888 | ——— | —— | 0.30E+00 |
| 10 | 7 | 1150.47823 | ——— | —— | 0.17E+00 | 1176.96363 | ——— | —— | 0.16E+00 |
| 10 | 8 | 1147.53261 | ——— | —— | 0.17E+00 | 1177.00845 | ——— | —— | 0.17E+00 |
| 10 | 9 | 1143.90788 | ——— | —— | 0.32E+00 | 1177.14777 | ——— | —— | 0.32E+00 |
| 10 | 10 | 1139.46603 | ——— | —— | 0.12E+00 | 1177.43139 | ——— | —— | 0.12E+00 |
| 11 | 0( | 1178.83576) | ——— | —— | 0. | 1195.22011 | ——— | —— | 0.92E-01 |
| 11 | 1 | 1178.64372 | ——— | —— | 0.48E-01 | 1195.21883 | ——— | —— | 0.47E-01 |
| 11 | 2 | 1178.28036 | ——— | —— | 0.50E-01 | 1195.19612 | ——— | —— | 0.48E-01 |
| 11 | 3 | 1177.59373 | ——— | —— | 0.10E+00 | 1195.13615 | ——— | —— | 0.10E+00 |
| 11 | 4 | 1176.61078 | ——— | —— | 0.56E-01 | 1195.04753 | ——— | —— | 0.54E-01 |
| 11 | 5 | 1175.28741 | ——— | —— | 0.60E-01 | 1194.97671 | ——— | —— | 0.58E-01 |
| 11 | 6 | 1173.58354 | ——— | —— | 0.13E+00 | 1194.91114 | ——— | —— | 0.13E+00 |
| 11 | 7 | 1171.43994 | ——— | —— | 0.73E-01 | 1194.86770 | ——— | —— | 0.71E-01 |
| 11 | 8 | 1168.77938 | ——— | —— | 0.79E-01 | 1194.86936 | ——— | —— | 0.77E-01 |
| 11 | 9 | 1165.50259 | ——— | —— | 0.17E+00 | 1194.94778 | ——— | —— | 0.16E+00 |
| 11 | 10 | 1161.48329 | ——— | —— | 0.61E-01 | 1195.14845 | ——— | —— | 0.59E-01 |
| 11 | 11 | 1156.56197 | ——— | —— | 0.62E-01 | 1195.52697 | ——— | —— | 0.61E-01 |
| 12 | 0 | 1198.71660 | ——— | —— | 0.34E-01 | (1213.02617) | ——— | —— | 0. |
| 12 | 1 | 1198.53408 | ——— | —— | 0.17E-01 | 1213.01385 | ——— | —— | 0.17E-01 |
| 12 | 2 | 1198.21364 | ——— | —— | 0.18E-01 | 1213.01791 | ——— | —— | 0.17E-01 |
| 12 | 3 | 1197.61071 | ——— | —— | 0.38E-01 | 1212.98402 | ——— | —— | 0.37E-01 |
| 12 | 4 | 1196.72053 | ——— | —— | 0.20E-01 | 1212.83185 | ——— | —— | 0.20E-01 |
| 12 | 5 | 1195.53644 | ——— | —— | 0.22E-01 | 1212.74856 | ——— | —— | 0.22E-01 |
| 12 | 6 | 1194.01194 | ——— | —— | 0.50E-01 | 1212.66447 | ——— | —— | 0.48E-01 |
| 12 | 7 | 1192.09365 | ——— | —— | 0.28E-01 | 1212.59483 | ——— | —— | 0.27E-01 |
| 12 | 8 | 1189.71186 | ——— | —— | 0.32E-01 | 1212.59686 | ——— | —— | 0.31E-01 |
| 12 | 9 | 1186.77629 | ——— | —— | 0.71E-01 | 1212.57999 | ——— | —— | 0.69E-01 |
| 12 | 10 | 1183.17179 | ——— | —— | 0.30E-01 | 1212.74880 | ——— | —— | 0.29E-01 |
| 12 | 11 | 1178.75231 | ——— | —— | 0.39E-01 | 1212.97887 | ——— | —— | 0.38E-01 |
| 12 | 12 | 1173.53367 | ——— | —— | 0.61E-01 | 1213.14104 | ——— | —— | 0.60E-01 |
| 13 | 0( | 1218.27783) | ——— | —— | 0. | 1230.60899 | ——— | —— | 0.11E-01 |
| 13 | 1 | 1218.04332 | ——— | —— | 0.57E-02 | 1230.62611 | ——— | —— | 0.55E-02 |
| 13 | 2 | 1217.62436 | ——— | —— | 0.59E-02 | 1230.60930 | ——— | —— | 0.57E-02 |
| 13 | 3 | 1217.27184 | ——— | —— | 0.13E-01 | 1230.53621 | ——— | —— | 0.12E-01 |
| 13 | 4 | 1216.49945 | ——— | —— | 0.68E-02 | 1230.42883 | ——— | —— | 0.65E-02 |
| 13 | 5 | 1215.44823 | ——— | —— | 0.79E-02 | 1230.33165 | ——— | —— | 0.72E-02 |
| 13 | 6 | 1214.09524 | ——— | —— | 0.17E-01 | 1230.23128 | ——— | —— | 0.16E-01 |
| 13 | 7 | 1212.39315 | ——— | —— | 0.96E-02 | 1230.11232 | ——— | —— | 0.93E-02 |
| 13 | 8 | 1210.27957 | ——— | —— | 0.11E-01 | 1230.06624 | ——— | —— | 0.11E-01 |
| 13 | 9 | 1207.67350 | ——— | —— | 0.26E-01 | 1230.04081 | ——— | —— | 0.25E-01 |
| 13 | 10 | 1204.47091 | ——— | —— | 0.19E-01 | 1230.09261 | ——— | —— | 0.19E-01 |
| 13 | 11 | 1200.53931 | ——— | —— | 0.17E-01 | 1230.26346 | ——— | —— | 0.16E-01 |
| 13 | 12 | 1195.71098 | ——— | —— | 0.35E-01 | 1230.62812 | ——— | —— | 0.34E-01 |
| 13 | 13 | 1189.77443 | ——— | —— | 0.19E-01 | 1231.24034 | ——— | —— | 0.18E-01 |

Eqs. (8)–(13)]

$$X_m^{(3n)} = \alpha_m, \beta_m, \eta_3^{(m)}, \eta_6^{(m)}. \tag{23}$$

We can now write in a symbolic form the following equations which specify the molecular parameters which can be determined from the individual types of experimental data:

$$\nu_{\text{inv}}^{(m)}(\Delta v_2 = 0;\ \Delta J = 0,\ \Delta K = 0,\ s \leftrightarrow a) = f(\Delta X_m, X_m^{(3n)}; X_m^{(JK)}, X_m^{(K)}) \quad (m = 0, 1), \tag{24}$$

$$\nu_{\text{inv-rot}}^{(m)}(\Delta v_2 = 0;\ \Delta J = \pm 1,\ \Delta K = 0;\ s \leftrightarrow a) = f(\Delta X_m, X_m^{(J)}, X_m^{(JK)}; X_m^{(3n)}, X_m^{(K)}) \quad (m = 0,1), \tag{25}$$

$$\nu_2(\Delta v_2 = 1; \Delta J = 0, \Delta K = 0; s \leftrightarrow a) = f(X_1^{(J)} - X_0^{(J)}, X_1^{(JK)} + X_0^{(JK)}, X_1^{(K)} - X_0^{(K)}, E_1^s - E_0^s; X_1^{(3n)}, X_0^{(3n)}, X_0^{(JK)}, X_0^{(K)}, X_1^{(JK)}, X_1^{(K)}), \tag{26}$$

$$\nu_{\text{rot}}^{(m)}\left[\Delta v_2 = 0;\ \Delta J = 0,\ \Delta K = \pm 3;\ \left(\frac{s}{a}\right) \leftrightarrow \left(\frac{s}{a}\right)\right] = f(X_m^{(3n)}, X_m^{(JK)}, X_m^{(K)}; \Delta X_m) \quad (m = 0, 1), \tag{27}$$

$$\nu_{\text{rot}}^{(1)}\left[\Delta v_2 = 0;\ \Delta J = \pm 1,\ \Delta K = \pm 3;\ \left(\frac{s}{a}\right) \leftrightarrow \left(\frac{s}{a}\right)\right] = f(X_1^{(3n)}, X_1^{(J)}, X_1^{(JK)}, X_1^{(K)}; \Delta X_1). \tag{28}$$

TABLE V

Wavenumbers ($cm^{-1}$) and Intensities ($cm^{-2}\ atm^{-1}$) of Perturbation-Allowed Transitions $\Delta K = \pm 3$ in $^{14}NH_3$[a]

| Transition | $\nu_{calc}$ | $\nu_{obs}$ | $\nu_{obs}-\nu_{calc}$ | I($cm^{-2}atm^{-1}$) |
|---|---|---|---|---|
| | | Ground State Transitions | | |
| s(3,0)←s(3,3) | 33.37620 | - | - | $1.1\times10^{-7}$ |
| s(4,0)←s(4,3) | 33.20594 | - | - | $3.8\times10^{-7}$ |
| s(5,0)←s(5,3) | 33.12502 | - | - | $3.5\times10^{-7}$ |
| s(6,0)←s(6,3) | 32.91007 | 32.9090(20) | -0.0011 | $1.1\times10^{-6}$ |
| s(7,0)←s(7,3) | 32.77081 | 32.7703(10) | 0.0004 | $1.4\times10^{-6}$ |
| s(8,0)←s(8,3) | 32.51604 | 32.5169(20) | 0.0009 | $1.2\times10^{-6}$ |
| s(9,0)←s(9,3) | 32.32134 | -[b] | - | $9.5\times10^{-7}$ |
| a(10,0)←a(10,3) | 32.03079 | 32.0324(20) | 0.0016 | $5.9\times10^{-7}$ |
| | | $\nu_2$ State Transitions | | |
| s(3,0)←s(3,3) | 35.69689 | 35.69692(3) | 0.00003 | $3.5\times10^{-4}$ |
| a(4,0)←a(4,3) | 33.40704 | - | - | $1.7\times10^{-9}$ |
| s(5,0)←s(5,3) | 35.31966 | - | - | $3.1\times10^{-6}$ |
| a(6,0)←a(6,3) | 33.16092 | - | - | $5.8\times10^{-9}$ |
| s(7,0)←s(7,3) | 34.79394 | - | - | $8.9\times10^{-7}$ |
| a(3,3)←a(2,0) | 25.77095 | 25.77099(3) | 0.00004 | $9.9\times10^{-5}$ |
| | | $\Delta K = \pm 3$ Transitions in the $\nu_2$ Band[c] | | |
| $^{s}(-3)Q(3,3)$ | 967.25016 | 967.2502(10) | 0.0000 | $2.6\times10^{-1}$ |
| $^{a}(-3)Q(4,3)$ | 999.55543 | - | - | $2.0\times10^{-6}$ |
| $^{s}(-3)Q(5,3)$ | 969.02201 | 969.0210(30) | -0.001 | $2.5\times10^{-3}$ |
| $^{a}(-3)Q(6,3)$ | 998.29327 | - | - | $6.6\times10^{-6}$ |
| $^{s}(-3)Q(7,3)$ | 971.29885 | - | - | $7.4\times10^{-4}$ |

[a] Ground state and $\nu_2$ state transitions wavenumbers taken from our measurements; $\Delta K = \pm 3$ transitions in the $\nu_2$ band see ref. (16); values in parentheses of $\nu_{obs}$ are estimated experimental uncertainties in units of the last digit quoted.

[b] Blended by $H_2O$ absorption.

[c] $^{(s/a)}(-3)Q(J,K)$ means a $\nu_2$ transition from the ground state J,K level with $\Delta J = 0$, $\Delta K = -3$, $(s/a) \leftrightarrow (s/a)$.

TABLE VI

Ground-State and $\nu_2$-Excited State Molecular Parameters of $^{14}NH_3$ ($cm^{-1}$)[a]

| Parameter | Ground-State Value | $\nu_2$-State Value | Parameter | Ground-State Value | $\nu_2$-State Value |
|---|---|---|---|---|---|
| $\Delta E_o$ | 0.7934084(24) | 35.688107(17) | $^{(s)}E_o$ | 0 | 932.43384(13)[c] |
| $\Delta B$ | -5.05353(19)$10^{-3}$ | -0.1801512(41) | $^{(s)}B$ | 9.9466429(59) | 10.0701789(82) |
| $\Delta(C-B)$ | 7.05281(30)$10^{-3}$ | 0.2516660(76) | $^{(s)}C - {}^{(s)}B$ | -3.718280(24) | -3.981008(18) |
| $\Delta D_J$ | -1.67879(49)$10^{-5}$ | -0.43378(15)$10^{-3}$ | $^{(s)}D_J$ | 0.84953(46)$10^{-3}$ | 1.13076(57)$10^{-3}$ |
| $\Delta D_{JK}$ | 4.6327(13)$10^{-5}$ | 1.18809(41)$10^{-3}$ | $^{(s)}D_{JK}$ | -1.5783(16)$10^{-3}$ | -2.4226(15)$10^{-3}$ |
| $\Delta D_K$ | -3.17515(97)$10^{-5}$ | -0.80621(37)$10^{-3}$ | $^{(s)}D_K$ | 1.0107(18)$10^{-3}$ | 1.6172(19)$10^{-3}$ |
| $\Delta H_{JJJ}$ | -0.38725(51)$10^{-7}$ | -0.6094(18)$10^{-6}$ | $^{(s)}H_{JJJ}$ | 0.2578(42)$10^{-6}$ | 0.5577(92)$10^{-6}$ |
| $\Delta H_{JJK}$ | 1.5834(19)$10^{-7}$ | 2.4355(73)$10^{-6}$ | $^{(s)}H_{JJK}$ | -0.906(16)$10^{-6}$ | -2.221(37)$10^{-6}$ |
| $\Delta H_{JKK}$ | -2.1493(23)$10^{-7}$ | -3.205(11)$10^{-6}$ | $^{(s)}H_{JKK}$ | 1.078(25)$10^{-6}$ | 2.904(67)$10^{-6}$ |
| $\Delta H_{KKK}$ | 0.9665(12)$10^{-7}$ | 1.3877(66)$10^{-6}$ | $^{(s)}H_{KKK}$ | -0.200x$10^{-6}$ [b] | -1.010(34)$10^{-6}$ |
| $\Delta G_{JJJJ}$ | 0.6320(23)$10^{-10}$ | 0.4321(69)$10^{-9}$ | $^{(s)}G_{JJJJ}$ | -0.116(10)$10^{-9}$ | -0.246(40)$10^{-9}$ |
| $\Delta G_{JJJK}$ | -3.434(11)$10^{-10}$ | -2.192(39)$10^{-9}$ | $^{(s)}G_{JJJK}$ | 0.565(50)$10^{-9}$ | 1.33(26)$10^{-9}$ |
| $\Delta G_{JJKK}$ | 7.008(19)$10^{-10}$ | 4.056(90)$10^{-9}$ | $^{(s)}G_{JJKK}$ | -1.069(88)$10^{-9}$ | -2.59(70)$10^{-9}$ |
| $\Delta G_{JKKK}$ | -6.314(18)$10^{-10}$ | -3.23(11)$10^{-9}$ | $^{(s)}G_{JKKK}$ | 0.929(87)$10^{-9}$ | 2.15(72)$10^{-9}$ |
| $\Delta G_{KKKK}$ | 2.1129(70)$10^{-10}$ | 0.920(57)$10^{-9}$ | $^{(s)}G_{KKKK}$ | -0.0333x$10^{-9}$ [b] | -0.35(26)$10^{-9}$ |
| $\Delta L_{JJJJJ}$ | -0.5489(38)$10^{-13}$ | 0[b] | $\eta_3^o$ | 4.2958(64)$10^{-9}$ | 3.54(62)$10^{-9}$ |
| $\Delta L_{JJJJK}$ | 3.777(22)$10^{-13}$ | 0[b] | $\eta_3^J$ | -5.571(75)$10^{-12}$ | -2.3(11)$10^{-11}$ |
| $\Delta L_{JJJKK}$ | -10.516(54)$10^{-13}$ | 0[b] | $\eta_3^{JJ}$ | 2.89(22)$10^{-15}$ | 6.1(49)$10^{-14}$ |
| $\Delta L_{JJKKK}$ | 14.496(75)$10^{-13}$ | 0[b] | $\eta_6$ | -3.26(72)$10^{-20}$ | 0[b] |
| $\Delta L_{JKKKK}$ | -9.846(51)$10^{-13}$ | 0[b] | $\omega$ | 8.01(27)$10^{-5}$ | 12.810(36)$10^{-5}$ |
| $\Delta L_{KKKKK}$ | 2.639(15)$10^{-13}$ | 0[b] | | | |

[a] Values in parantheses are standard deviations of the parameters, given in units of the last digit quoted. [b] Constrained value. [c] Band origin for the s→a transition is 968.12195(13), for the a→s transition 931.64043(13) $cm^{-1}$.

It is obvious from Eqs. (24) that the same vector of molecular parameters may occur in different equations [for example, $\Delta X_m$ in Eqs. (24), (25), and (27)]. This illustrates the importance of a simultaneous least-squares fit to all the experimental data. Besides this, individual experimental data provide, in general, information of different quality for the determination of molecular parameters, either because of differences in their experimental accuracy or because individual parameters are more or less sensitive to these data. This is automatically taken into account during the iterational procedure described above [cf. Eqs. (14)–(17)], either in the process of formation of the whole Jacobian matrix, or by statistical weights assigned to individual experimental data.

If a symbol of molecular parameter is written before the semicolon in the right-hand sides of Eqs. (24)–(28), the corresponding experimental data provide "strong" information on this parameter; if it is written behind the semicolon, only "weak" information is obtained on the parameter. For example, the "perturbation-allowed" transitions [Eqs. (27)–(28)] provide "strong" information on the parameters $X_m^{(K)}$ [Eq. (20)] while only "weak" information is involved in the experimental data on the transitions obeying the usual selection rules [cf. also Ref. (*2*)].

Calculations have been done with the CDC Cyber 172 computer using double-precision arithmetic (120 bits). Excepting the ground-state inversion frequencies, the statistical weights assigned to the experimental data were $w_{pq} = \delta_{pq}^{-2}$, where $\delta_{pq}$ is the estimated uncertainty of the measurement (Tables I–V). The ground-state inversion frequencies were weighted as having $\delta = 0.05$ MHz although they have been mostly measured with better accuracy (*3*, *4*). This was because our theoretical

model does not describe the hyperfine splittings of the rotational levels of ammonia. A value of the speed of light of $c = 299\,792.458$ km sec$^{-1}$ was used in converting the wavenumber units into frequency units.

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 factor could be put equal to zero.

## IV. RESULTS AND DISCUSSION

The values of the transition frequencies, calculated from the converged set of molecular parameters in Table VI are compared with the experimental data in Tables I–V. In the last column of Tables I–V, the calculated intensities of the corresponding spectral lines are given. The intensities were calculated for $T = 300$ K by standard methods (*20*) using Boltzmann factors and taking into account spatial degeneracy and spin statistical weights. The intensities of the "perturbation-allowed" transitions (Table V) were calculated from the coefficients of the mixing of the corresponding wavefunctions. The $J, K$ dependence of the transition moments for the inversion–rotation and inversion transitions in the ground and $\nu_2$ state of $^{14}NH_3$ has been taken from the paper of Shimoda *et al.* (*21*). The transition moments obtained by Špirko (*22*) have been used for the inversion–rotation transitions in the $\nu_2$ band.

It is obvious from Tables I–V that we arrived at a quantitative description of the experimental data. The "smoothed" values of the transition frequencies are believed to be so accurate that $^{14}NH_3$ could now be used for calibration purposes in the far-infrared region and especially in the 10-$\mu$m region in diode laser spectroscopy. We believe that the precision of our calculated $\nu_2$-band wavenumbers in Table IV is better than 0.0015 cm$^{-1}$ for transitions to the upper state $J' < 10$.

The standard deviation of the calculated ground-state inversion frequencies was 0.16 MHz. These microwave inversion frequencies have been described with an agreement slightly worse than 0.05 MHz assigned to these data in our theoretical treatment (Part III). The accuracy of our description of the ground-state microwave inversion frequencies is certainly sufficient for the purpose of the present work. Our fit in this respect represents the best description of these data based on a "physical" approach.

Molecular parameters obtained in our work (Table VI) can be considered to be the most precise parameters for the ground and $\nu_2$ states of $^{14}NH_3$ published so far. In this respect one must mention the recently published impressive work of Shimoda *et al.* (*21*) on the infrared laser Stark spectroscopy of the $\nu_2$ band of ammonia. These authors did not publish the "field-free" transition frequencies in their paper but only the values of molecular parameters. There is an excellent agreement between both papers as for the values of the $\nu_2$ band origin and the $\nu_2$ state parameters $\Delta X_1$ [Eq. (21)]. However, there are differences between the values of other parameters beyond the quoted standard deviations. The reason for this seems to lie in the way in which Shimoda *et al.* (*21*) analyzed their excellent experimental

data. These authors have limited their considerations of the $\Delta k = \pm 3$ interactions to few rotational levels instead of considering sufficiently large interaction matrices. An extension of our simultaneous analysis to their data is possible, although not simple, and it should confirm our preliminary conclusions.

One of the ultimate goals in studying the vibrational–rotational states of ammonia is the determination of the energy levels of ammonia. The calculated intensities of the "perturbation-allowed" transitions in Table V indicate why it is so difficult to observe their lines in the ground and $\nu_2$ states [except those in the $\nu_2$ state which have enhanced intensities due to a close coincidence between the (3, 3) and (3, 0) levels, cf. Ref. (*2*)].

Although we have been able to assign certain extremely weak lines in the submillimeterwave spectra to the "perturbation-allowed" transitions in the ground state of ammonia (cf. Fig. 6 and Table V), they are of the same type as the previously detected transitions (*2*, *16*) and the determination of a sufficiently complete set of spectroscopically "forbidden" parameters for ammonia has not yet been possible. The solution of this problem seems to be more promising by studying the perturbation-allowed transitions in the infrared $2\nu_4$ band of ammonia (*23*).

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