

HIGH AND VERY HIGH RESOLUTION SPECTROSCOPY OF THE VIBRATIONAL-
ROTATIONAL STATES OF NON-RIGID MOLECULES WITH PARTICULAR
EMPHASIS ON AMMONIA

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ABSTRACT

Using the vibration-inversion-rotation Hamiltonian for ammonia [V.Špirko, J.M.R.Stone and D.Papoušek, J.Mol.Spectrosc. 60(1976)159], a modified theory is worked out for the $\Delta k = \pm 3n$ interactions between the inversion-rotation energy levels in the ground and excited state of NH_3 which takes into account the large amplitude inversion motion.

The high sensitivity submillimeter-wave spectrometer RAD has been used to measure the inversion and inversion-rotation transitions in the ν_2 state of $^{14}\text{NH}_3$ in the $18\text{--}37\text{ cm}^{-1}$ region with microwave accuracy. The frequencies of the inversion-rotation transitions in the ground and ν_2 excited states have been measured with the 0.014 cm^{-1} resolution in the $35\text{--}300\text{ cm}^{-1}$ region with a Fourier transform spectrometer. The ν_2 band frequencies have been measured under Doppler limited resolution ($<0.002\text{ cm}^{-1}$) with a diode laser spectrometer and with 0.03 cm^{-1} resolution using a grating spectrometer in the $10\text{ }\mu\text{m}$ region.

By a least squares fit of these data and the data of the infrared-microwave two-photon and infrared heterodyne measurements of the ν_2 band, a set of the molecular constants for the ground and ν_2 state is obtained which reproduces the experimental data within the precision of the experiment.

INTRODUCTION

Large amplitude motions in non-rigid molecules, such as e.g. internal rotation, ring-puckering or molecular inversion are well known phenomena in molecular spectroscopy. Especially microwave spectroscopy gathered a considerable amount of information on the energy barriers hindering these motions by measuring frequencies of transitions between the rotational levels split by tunneling effects.

The vibrational-rotational spectra of non-rigid molecules are rather complicated and they have not yet been studied by the high resolution infrared spectroscopy as the rotational spectra by microwave methods. In this paper we shall give an account on the high and very high resolution study of the vibrational-inversional-rotational spectra of ammonia, NH_3 .

The large amplitude motion in this molecule is the inversion during which a relatively low energy barrier of about 2000 cm^{-1} has to be overcome (ref. 2). There are two symmetrically equivalent configurations of the atomic nuclei separated by this barrier (Fig.1) and as a consequence of this, all the vibration-rotation energy levels of ammonia are split into doublets.

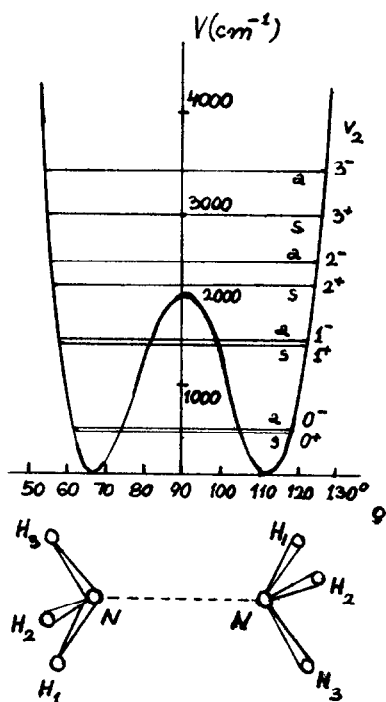


Fig. 1. The double-minimum potential function for NH_3

The theory of this effect as well as the microwave and infrared spectra of ammonia have been already studied by many authors (cf., e.g., ref. 2). The purpose of our work has been to develop a theory allowing for a systematic treatment of the higher order effects in the vibrational-rotational spectra of ammonia which can be observed by the available techniques of high and very high resolution spectroscopy. The results of this theory have been used in a simultaneous least squares analysis of a set of precise transition frequencies which we obtained by measuring the submillimeter-wave, Fourier transform, and the diode laser spectra of $^{14}\text{NH}_3$. Emphasis has been put in this study on a detailed analysis of the $\Delta k = \pm 3n$ higher order interactions between the ground and ν_2 state inversion-rotation levels of $^{14}\text{NH}_3$.

There are at least three aspects which stimulate this research: (i) The invention of the ammonia laser optically pumped by the TEA CO_2 laser which has potential usefulness in infrared photochemistry including the laser isotope separation processes (refs. 3,4) (ii) the recent discovery of the ν_2 band absorption lines of $^{14}\text{NH}_3$ in the circumstellar clouds in OH/IR supergiants (ref.5) which is a nice example of the steadily increasing importance of the high resolution infrared spectroscopy in astrophysical studies (iii) The possibility of using ammonia lines as precise calibration lines in the far- and medium-infrared regions, for example in the diode laser spectroscopy (ref. 6).

THEORY

Vibration-inversion-rotation Hamiltonian for ammonia

In 1970, Hougen, Bunker, and Johns (ref. 7) developed a new approach to study the large amplitude bending motions in quasilinear molecules in which the bending motion has been removed from the purely vibrational problem and incorporated into the rotational part of the vibrational-rotational Hamiltonian. This has been achieved by allowing the reference configuration of the atomic nuclei to be a suitable function of the large amplitude bending coordinate φ . In 1973, we have shown (ref. 8) how this approach can be extended to molecules with pyramidal inversion. In both cases the resulting Hamiltonian takes formally the same form which is very close to the standard Hamiltonian used in the study of semirigid molecules (cf. ref. 9):

$$H = \frac{1}{2} \mu^{1/4} \sum_{\alpha, \beta = x, y, z, \varphi} (J_{\alpha} - p_{\alpha}) \mu_{\alpha\beta} \mu^{-1/2} (J_{\beta} - p_{\beta}) \mu^{1/4} + \frac{1}{2} \mu^{1/4} \sum_{k=1}^{3N-7} P_k \mu^{-1/2} P_k \mu^{1/4} +$$

$$+ V(Q, Q) . \quad (1)$$

In Eq. (1), J_α ($\alpha = x, y, z$) are the components of the total angular momentum operator with respect to the molecule-fixed axes. The operator J_Q is

$$J_Q = - i\hbar \partial / \partial q \quad (2)$$

where q is the coordinate measuring the inversion motion in ammonia (Fig. 2). The coordinate q measures the angle subtended by the NH bond of the reference configuration and the C_3 symmetry axis in NH_3 ; the reference configuration of the atomic nuclei is defined by the Eckart and Sayvetz conditions such that it follows the large amplitude inversion motion of ammonia. The vibrational displacements of the atomic nuclei are measured with respect to this nonrigid reference configuration and they remain therefore small amplitude motions; ($\nu_1, \nu_{3a}, \nu_{3b}, \nu_{4a}, \nu_{4b}$ vibrations in NH_3); the large amplitude inversion motion has been transferred to the rotational part of the Hamiltonian in Eq. (1) (ν_2 vibration in NH_3).

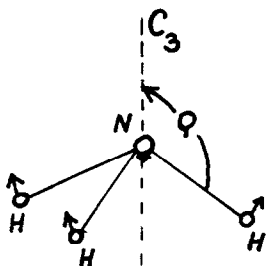


Fig. 2. The ν_2 bending mode in NH_3

The components of the so-called vibrational angular momentum p_α ($\alpha = x, y, z$) and the momentum p_Q are defined as

$$p_\alpha = \sum_{k\ell} \gamma_{k\ell}^\alpha Q_k p_\ell \quad ; \quad \alpha = x, y, z, q . \quad (3)$$

The quantities $\mu_{\alpha\beta}$ ($\alpha, \beta = x, y, z, q$) are the elements of the matrix which is the inverse of the 4×4 matrix the elements of which are

$$I'_{\alpha\beta} = I_{\alpha\beta} - \sum_{klm} \gamma_{km}^{\alpha} \gamma_{lm}^{\beta} Q_k Q_l ; \quad \alpha, \beta = x, y, z, q \quad (4)$$

μ is the determinant of the matrix $[\mu_{\alpha\beta}]$.

The potential energy function V can be expanded for each value of Q as a Taylor series in the normal coordinates Q_k :

$$V = V_0(Q) + \sum_k \kappa_k(Q) Q_k + \frac{1}{2} \sum_k \lambda_k(Q) Q_k^2 + \text{higher order terms} \quad (5)$$

In Eq. (5), $V_0(Q)$ is the double-minimum potential of the reference configuration ($Q_1 = Q_{3a} = Q_{3b} = Q_{4a} = Q_{4b} = 0$). The linear force constants $\kappa_k(Q) = (\partial V / \partial Q_k)_Q$ are not in general zero for all values of Q , since the reference configuration is not the equilibrium configuration for all values of Q .

The close relation between the Hamiltonian in Eq. (1) and the standard vibrational-rotational Hamiltonian for semirigid molecules (ref. 9) is a great advantage because it makes it possible to study all the higher order effects in the spectra of ammonia using a variational or perturbation approach in a way similar to that developed for semirigid molecules. Before discussing this problem in detail let us remind that the coefficients $\mu_{\alpha\beta}$ (and hence also μ) are in Eq. (1) functions of the small amplitude coordinates Q as well as of

q

There are basically two ways how the vibration-inversion-rotation Hamiltonian defined by Eq. (1) can be applied to the experimental data. In the first approach we expand the vibration-inversion-rotation Hamiltonian (1) in the vibrational coordinates Q and we use a suitable perturbation theory to remove the explicit dependence on Q of the individual terms in the expanded Hamiltonian. This gives an effective vibration-inversion-rotation Hamiltonian that contains only functions of q and the operator $\mathcal{D}_q = -i\hbar \partial / \partial q$.

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. We have used this approach to obtain information on the "true" double-minimum potential function of ammonia using harmonic terms for the small amplitude ν_1, ν_3 , and ν_4 vibrations, and a second-order perturbation treatment of the Hamiltonian expanded up to terms of order of magnitude $\kappa^2 T_v$ (ref. 10). An extension of this treatment which takes into account the anharmonicity of the ν_1, ν_3 , and ν_4 vibrations is now studied by Dr. Špirko (ref. 11); it should yield a complete

anharmonic potential function for ammonia including a double-minimum potential function with a high degree of isotopic invariancy.

Although this treatment is valuable for obtaining information on the potential function, it is not suitable for fitting experimental data with an accuracy comparable to that of the high-resolution infrared spectroscopy (ref. 2). An alternative approach which lends itself to a quantitative description of the experimental data with the accuracy of the experiment is discussed in the following section.

A modified theory of the $\Delta k = \pm 3n$ interactions

We have recently developed an approach to the analysis of the vibrational-rotational spectra of ammonia in which we do not obtain information on the potential function, but effective molecular parameters such as rotational constants, band origins, and interaction parameters are obtained by a least squares fit (ref. 12). We shall demonstrate this approach on the example of the modified theory of the higher-order interactions between the J, k and $J, k \pm 3n$ rotational levels in the ν_2 state of NH_3 .

The effect of the $\Delta k = \pm 3n$ interactions in the ground state inversion spectra of ammonia is well known to microwave spectroscopists (ref. 1). In all the previous theoretical treatments of this effect (refs. 13-15), the inversion motion has been neglected. This seems to be a good approximation for the ground state of NH_3 because the ground-state inversion splitting is small compared to the rotational spacings. However, in the ν_2 excited state, the inversion splitting ($\approx 30 \text{ cm}^{-1}$) is of the order of magnitude of the rotational spacings and the inversion motion has to be properly taken into account (ref. 16).

In developing the fourth-order theory of the $\langle J, k | H | J, k \pm 3n \rangle$ interactions in the ν_2 excited state of ammonia, we use the notation H_{mn} for the various terms in the expansion of the Hamiltonian in Eq. (1). Here the first subscript is the degree in the vibrational operators (Q and P) and the second subscript is the degree in the components of the total angular momentum J (cf. ref. 17).

Using the harmonic vibrational energy H_{20} ,

$$H_{20} = \frac{1}{2} \sum_{k=1,3a,3b,4a,4b} [d_k(q)q_k^2 + p_k^2] \quad (6)$$

as the unperturbed Hamiltonian, we find the perturbation terms required in the fourth-order theory of the $\langle J, k | H | J, k \pm 3n \rangle$ interactions to be

$$H_{02} = \frac{1}{2} \sum_{\alpha} \mu_{\alpha\alpha}^0 J_{\alpha}^2, \quad (7)$$

$$H_{12} = \frac{1}{2} \sum_k \sum_{\alpha\beta} x_k^{\alpha\beta} Q_k J_{\alpha} J_{\beta} + \frac{1}{2} \sum_k \sum_{\alpha} (J_{\alpha} x_k^{\alpha\alpha}) Q_k J_{\alpha}, \quad (8)$$

$$H_{22} = \frac{1}{2} \sum_k \sum_{\alpha\beta} y_{k\ell}^{\alpha\beta} Q_k Q_{\ell} J_{\alpha} J_{\beta} + \frac{1}{2} \sum_k \sum_{\alpha} (J_{\alpha} y_{k\ell}^{\alpha\alpha}) Q_k Q_{\ell} J_{\alpha}, \quad (9)$$

$$H_{21} = -\frac{1}{2} \sum_{\alpha} (\mu_{\alpha\alpha}^0 (J_{\alpha} p_{\alpha} + p_{\alpha} J_{\alpha}) - \frac{1}{2} (J_{\alpha} \mu_{\alpha\alpha}^0) p_{\alpha}), \quad (10)$$

$$H_{30} = \frac{1}{6} \sum_{\ell mn} k_{\ell mn} Q_{\ell} Q_m Q_n. \quad (11)$$

In Eqs. (7) - (10), the sum is over x, y, z and the inversion coordinate q , and

$$x_k^{\alpha\beta} [\equiv (\partial \mu_{\alpha\beta} / \partial Q_k)_0] = -a_k^{\alpha\beta} (\mu_{\alpha\alpha}^0 \mu_{\beta\beta}^0), \quad (12a)$$

$$y_{k\ell}^{\alpha\beta} [\equiv \frac{1}{2} (\partial^2 \mu_{\alpha\beta} / \partial Q_k \partial Q_{\ell})_0] = \frac{3}{8} \sum_{\epsilon=x,y,z,q} (a_k^{\alpha\epsilon} a_{\ell}^{\beta\epsilon} + a_{\ell}^{\alpha\epsilon} a_k^{\beta\epsilon}) (\mu_{\alpha\alpha}^0 \mu_{\beta\beta}^0 \mu_{\epsilon\epsilon}^0), \quad (12b)$$

where

$$a_k^{\alpha\beta} = (\partial I_{\alpha\beta} / \partial Q_k)_0 \quad (12c)$$

are the derivatives of the instantaneous inertia tensor $I_{\alpha\beta}$ evaluated at the reference configuration.

After a perturbation diagonalization of the vibrational operators (Q, P) we find the following inversional-rotational operators to describe to fourth order of approximation the interaction between the rotational levels J, k and $J, k \pm 3n$ in the ground state and ν_2 excited state of ammonia:

$$H'_1 = H_2(q) [(J_+^3 + J_-^3) J_z + J_z (J_+^3 + J_-^3)], \quad (13a)$$

$$H'_2 = H_3(q) (J_+^3 - J_-^3), \quad (13b)$$

$$H'_3 = [H_1(q) + H_4(q) + H_5(q)] (J_+^6 + J_-^6), \quad (13c)$$

$$H'_4 = H(q) (J_+^{12} + J_-^{12}) \quad (13d)$$

where the operators $H_1(q) - H_5(q)$ have been explicitly defined in ref. (16) and $J_{\pm} = J_x \pm iJ_y$.

So far the treatment is the same as that described at the end

of the previous section. In the following we shall deviate from this approach. We shall use the basis of the inversion-rotation wave functions

$$|\varphi_{(s)}^{(a)}; J, k\rangle = |\psi_{(s)}^{(a)}; J, k\rangle |J, k\rangle \quad (14)$$

where the inversion wave functions $|\psi_{(s)}^{(a)}; J, k\rangle$ depend on the inversion coordinate Q (as the dynamic variable) and on the rotational quantum numbers J and k (as parameters) (cf. ref. 8). $|J, k\rangle$ are the symmetric top rotational wave functions; s and a labels denote the parity of the inversion function with respect to inversion. In these basis functions, the energy matrix of the $\Delta k = \pm 3n$ interactions has been constructed. For example, there are the following matrix elements of the operators H'_1 and H'_2 in the basis defined by Eq. (14):

$$\begin{aligned} \langle \varphi_{(s)}^{(a)}; J, k | H'_1 | \varphi_{(s)}^{(a)}; J, k \pm 3 \rangle &= \pi^4 \langle \psi_{(s)}^{(a)}; J, k | H_2(Q) | \psi_{(s)}^{(a)}; J, k \pm 3 \rangle \cdot \\ &\cdot (2k \pm 3) \prod_{i=0}^{i=2} [J(J+1) - (k \pm i)(k \pm i \pm 1)]^{1/2} \end{aligned} \quad (15a)$$

$$\begin{aligned} \langle \varphi_{(s)}^{(a)}; J, k | H'_2 | \varphi_{(s)}^{(a)}; J, k \pm 3 \rangle &= \pm \pi^3 \langle \psi_{(s)}^{(a)}; J, k | H_3(Q) | \psi_{(s)}^{(a)}; J, k \pm 3 \rangle \cdot \\ &\prod_{i=0}^{i=2} [J(J+1) - (k \pm i)(k \pm i \pm 1)]^{1/2} . \end{aligned} \quad (15b)$$

The important difference between this approach and that described in the previous section is that now we assume the inversion wave functions $|\psi_{(s)}^{(a)}; J, k\rangle$ to be known; the Q -independent matrix elements such as e.g. $\langle \psi_{(s)}^{(a)}; J, k | H_2(Q) | \psi_{(s)}^{(a)}; J, k \pm 3 \rangle$ are effective spectroscopical parameters the values of which are determined by a least squares fit of the experimental data.

EXPERIMENTAL

The energy level diagram of the ground state and ν_2 excited state inversion-rotation levels of $^{14}\text{NH}_3$ is given in Fig. 3. Arrows in this diagram indicate all types of transitions between the inversion-rotation energy levels which have been included into a simultaneous least squares fit of the molecular parameters as described in the previous section. These transitions are purely inversion transitions in the ground and ν_2 excited states, rotation-inversion transitions in the ground and ν_2 states, and the ν_2 band transitions.

Except for the ground state inversion spectra which appear in the microwave region and have been already measured very accurately (refs. 18,19), we have either remeasured or measured for the first

time all other types of transitions in a joint work of several laboratories using four different techniques of high and very high resolution spectroscopy (note in the diagram in Fig. 3 that we have measured also certain $\Delta k = \pm 3$ perturbation allowed transitions in the ν_2 state). The high sensitivity submillimeter-wave spectrometer RAD (ref. 20) at the Institute for Applied Physics of the Academy of Sciences USSR has been used to measure the spectra in the $18 - 37 \text{ cm}^{-1}$ region with 10^{-5} cm^{-1} resolution (Fig. 4).

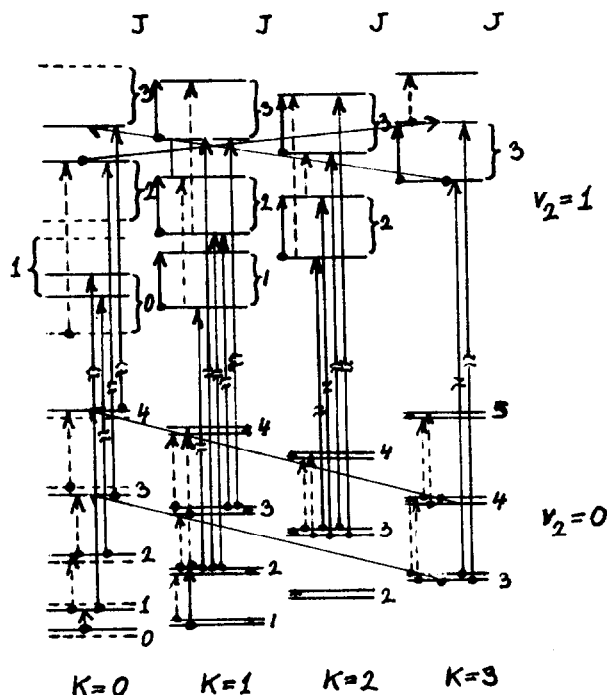


Fig. 3. Energy level scheme of the ground state and ν_2 excited state inversion-rotation levels of ammonia

The far-infrared spectra of ammonia have been measured with 0.010 cm^{-1} resolution with a Fourier spectrometer which was built at the University of Oulu in Finland (ref. 21)(Fig. 5). The infrared spectra have been measured under Doppler limited resolution ($< 0.002 \text{ cm}^{-1}$) with a diode laser spectrometer (Fig. 6) and with 0.03 cm^{-1} resolution with a grating spectrometer at the Ohio State University in Columbus.

In this way, we arrived at a unique set of extremely precise and internally consistent transition frequencies which were combined

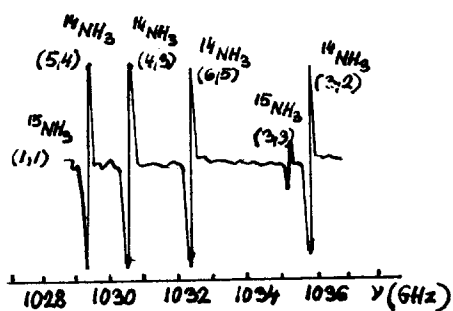


Fig. 4. Part of the submillimeter-wave spectrum of $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ in the 33 cm^{-1} region ($\approx 1000\text{ GHz}$). The spectrum lines correspond to the pure inversion transitions in the ν_2 -excited state.

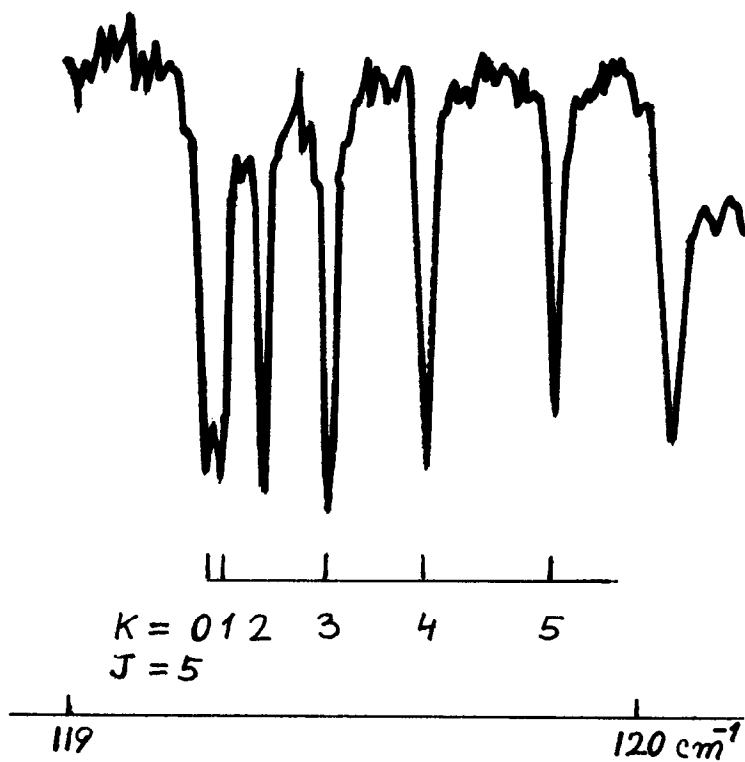


Fig. 5. Lines of the inversion-rotation transitions in the ground state of $^{14}\text{NH}_3$ [$a \leftarrow s$, ($J = 5, K$) multiplet]

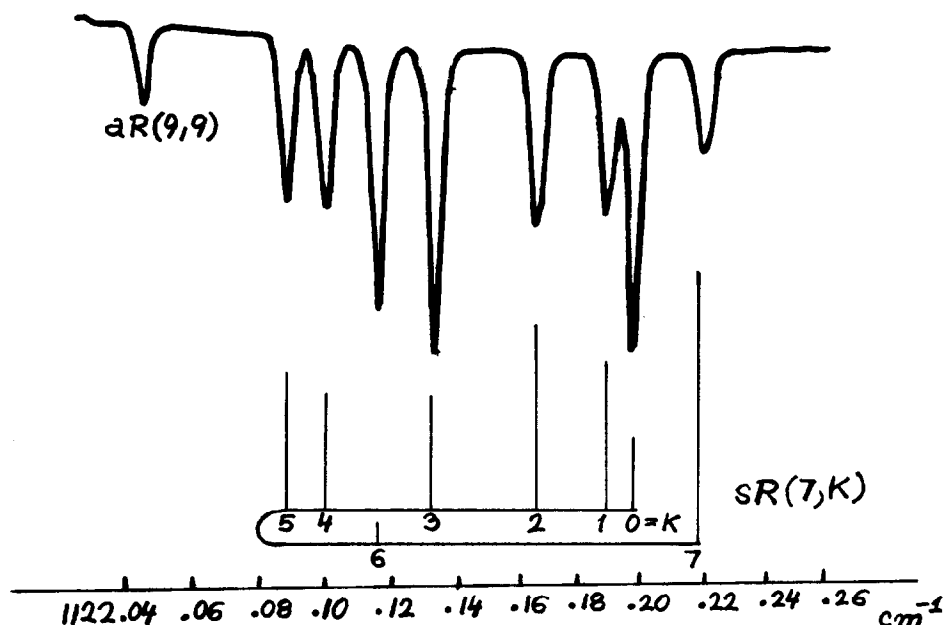


Fig. 6. Resolution of the $sR(7,K)$ multiplet in the ν_2 band of $^{14}\text{NH}_3$ with the diode laser spectrometer.

with the ground-state microwave data on the pure inversion frequencies (refs. 18,19), infrared-microwave two-photon (refs. 22,23) and infrared heterodyne measurements (ref. 24) of the ν_2 band transitions

RESULTS

In a simultaneous least squares analysis (damped least squares, iterative solution to the "inverse" secular problem) of these experimental data, a set of 74 converged values of molecular parameters was obtained including the ground and ν_2 state inversion splittings, band origins, rotational constants, centrifugal distortion constants up to the octic terms and parameters of the $\Delta k = \pm 3n$ interactions.

For example, the ground and upper state ($J = K = 0$) inversion splittings were found to be $\Delta_i = 0.7934084(24)$ and $35.688107(17)$ cm^{-1} , respectively; the band origin of the ν_2 transitions of the $a \leftarrow s$ type is $968.12195(13)$ cm^{-1} and $931.64043(14)$ cm^{-1} for the $s \leftarrow a$ transition; the ground state rotational for the lower (s) component of the inversion doublet is $^{(s)}B_0 = 9.9466429(59)$ cm^{-1} and $^{(s)}B_1 = 10.0701789(82)$ cm^{-1} for the ν_2 state^x (for a complete list

^x Values in parantheses are standard deviations of the parameters, given in units of the last digit quoted.

of these parameters see ref. 25). These parameters reproduce 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 $3 \times 10^{-5} \text{ cm}^{-1}$ in the submillimeter-wave region, better than 10^{-3} cm^{-1} in the far-infrared region, and better than $1.5 \times 10^{-3} \text{ cm}^{-1}$ in the region $700 - 1200 \text{ cm}^{-1}$.

CONCLUSIONS

We believe that the approach to the analysis of the vibrational-rotational spectra of ammonia described here is rather general and could be applied to other types of large amplitude motions in non-rigid molecules. This holds, of course, for quasilinear molecules for which this approach was originally developed (ref. 7) but for example also for molecules with more complicated motions as was discussed recently (ref. 26).

As for the ammonia problem, one of the ultimate goals of this study is the determination of the complete anharmonic potential function for ammonia with a high degree of isotopic invariancy. This problem is now studied in the Prague group (ref. 11) and it will probably be extended by a study of the breakdown of the Born-Oppenheimer approximation in molecules with pyramidal inversion. Such approach requires of course also the knowledge of the vibrational-rotational data of the isotopic species of ammonia. We have recently analyzed with this aim the diode laser spectra of the ν_2 band of $^{14}\text{ND}_3$ and $^{15}\text{ND}_3$ (ref. 27), and work is in progress on the analysis of the submillimeter-wave spectra of $^{15}\text{NH}_3$ and the diode laser spectra of NH_2D and ND_2H .

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