

The $\nu_2 + \nu_3 - \nu_2$ Band of NH_3^+ T. R. HUET,¹ Y. KABBADJ,² C. M. GABRYS, AND T. OKA*The Department of Chemistry and the Department of Astronomy and Astrophysics,
The University of Chicago, Chicago, Illinois 60637*

The $\nu_2 + \nu_3 - \nu_2$ hot band of NH_3^+ (\tilde{X}^2A_2') has been observed on the absorption spectrum recorded by using a difference frequency laser spectrometer combined with the velocity modulation technique in the region between 3500 and 2900 cm^{-1} . The molecular ions were produced in the positive column of a glow discharge with a gas mixture of $\text{N}_2/\text{H}_2/\text{He}$ in a ratio around 1/1/100. From the observed spectrum, the band origin was determined ($\nu_0 = 3371.5607(21) \text{ cm}^{-1}$) and the rotational structure characterized up to $N, K = 10, N - 4$. A symmetric rotor Hamiltonian with A_1-A_2 splittings and l resonance was used for the analysis and the spin-rotation constants were determined. The values obtained for the centrifugal distortion constants of both states do not satisfy the planarity relations. This fact is interpreted as an evidence for the presence of an x - y Coriolis interaction between the ν_2 and the ν_4 states, in agreement with theoretical predictions by Kraemer and Spirko (*J. Mol. Spectrosc.* **153**, 276–284, 1992). The lack of experimental observation on ν_4 prevented a full treatment of the perturbation. © 1994 Academic Press, Inc.

I. INTRODUCTION

The spectroscopic study of $X\text{H}_3^+$ molecular ions ($X = \text{C}, \text{N}, \text{O}$) has received much attention in our laboratory during the past few years in part because of their astrophysical interest. The presence of H_3O^+ in the interstellar medium has recently been reported in detail by Phillips *et al.* (1) and references therein). Detection of other molecular ions in space with high-resolution spectroscopic techniques is expected.

The NH_3^+ ion has been studied experimentally, at low resolution, over the years by electron spin resonance (2, 3), photoionization (4), and photoelectron (5, 6) spectroscopies. However, it is only in the past few years that this molecular ion has been investigated at high resolution, by absorption spectroscopy in the infrared region.

The ν_3 fundamental band, around 3388 cm^{-1} , was first observed by Bawendi *et al.* (7), using a difference frequency laser. The planar structure of the ground electronic state (\tilde{X}^2A_2') was established and the rovibrational structures of ν_3 , the antisymmetric stretching vibrational mode, and of the ground state were characterized.

The ν_2 out-of-plane bending vibrational mode has been investigated by Lee and Oka (8) using tunable diode lasers. The observation of the fundamental and first hot bands in the region of 900 cm^{-1} allowed the determination of the potential function along this coordinate. The rotationally resolved zero kinetic energy (ZEKE) electron spectrum of ammonia has also been reported recently (9). The principal rotational constants B and C of the $\nu_2 = 1, 2$ states have been determined within 10^{-2} cm^{-1} , in good agreement with the results obtained by Lee and Oka (8).

The number of ab initio studies on NH_3^+ are also limited (10–14). Meanwhile,

¹ Senior Research Assistant with the F.N.R.S. (Belgium). Present address: Laboratoire de Chimie Physique Moléculaire CP160/09, Université Libre de Bruxelles, 50 Avenue F.D. Roosevelt, 1050 Brussels, Belgium.

² Present address: Belgian Institute for Space Aeronomy, 3 Ringlaan, 1180 Brussels, Belgium.

extensive calculations have been performed recently by Kraemer and Spirko (13). Predictions are available for the vibrational and rotational structures of the ground electronic state which are in good agreement with the existing experimental results.

Our recent study of spectra recorded in an $\text{N}_2/\text{H}_2/\text{He}$ glow discharge (15) revealed that the chemical conditions we used to produce the ions favor the observation of highly excited vibrational states, especially in the case of HN_2^+ and NH_2^+ . The results obtained for these two ions are published separately (16, 17).

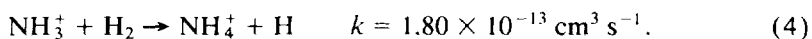
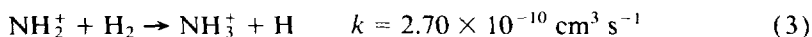
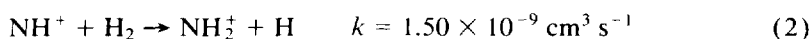
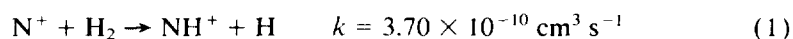
In this paper, we report the observation and analysis of the $\nu_2 + \nu_3 - \nu_2$ band of NH_3^+ . The value of the quartic centrifugal distortion constants that we have determined for both states revealed the presence of a perturbation which is discussed in Section III in relation with the work of Kraemer and Spirko (13).

II. EXPERIMENTAL DETAILS

A difference frequency laser spectrometer was employed to record continuously the spectrum of ions produced in an $\text{N}_2/\text{H}_2/\text{He}$ discharge in the region between 3500 and 2900 cm^{-1} . Our difference frequency laser spectrometer (18) is based on the apparatus initially developed by Pine (19). Briefly, the tunable infrared radiation is generated by mixing radiation from a fixed frequency argon ion laser with tunable radiation from a ring dye laser in a temperature-controlled LiNbO_3 crystal.

The ions were generated in an AC glow discharge with typical voltage and current of 5 kV and 140 mA, respectively. The detection of the absorption signal of the ions was performed, in the positive column region, by using the velocity modulation technique (20), and the noise subtraction was done using counterpropagating beams (21). Both beams each make four unidirectional passes through a glass discharge cell of 1 m long, using a pair of White cell mirrors. Spectra were calibrated using ammonia (22) and ethylene (23) as references. The uncertainty of the line position is estimated to be around 0.003 cm^{-1} .

The gas mixture was $\text{N}_2/\text{H}_2/\text{He} = 60/60/7000$ mTorr flowing into a water-cooled cell, except for the region between 3224 and 3070 cm^{-1} where a liquid nitrogen-cooled cell was employed along with a gas mixture of $\text{N}_2/\text{H}_2/\text{He} = 40/40/7000$ mTorr. These gas mixtures were optimized for the simultaneous observation of the NH_2^+ (17, 24) and HN_2^+ (16) ions. The chemical conditions that were used by Bawendi *et al.* (7) to optimize the intensity of the ν_3 band of NH_3^+ were different, i.e., $\text{He}/\text{H}_2/\text{NH}_3 = 250/8/1$ with a total pressure of 6 Torr. However, strong signals of NH_3^+ , belonging to the ν_3 fundamental band (7), were observed in our spectrum. This is due to the presence of a chain of hydrogen abstraction reactions (25) which takes place in the discharge:



The last reaction is not efficient and this leads to the observation of relatively strong NH_3^+ signals as illustrated in Fig. 1. Series of lines of medium intensity were assigned to the $\nu_2 + \nu_3 - \nu_2$ band of NH_3^+ and the results of the analysis are reported here.

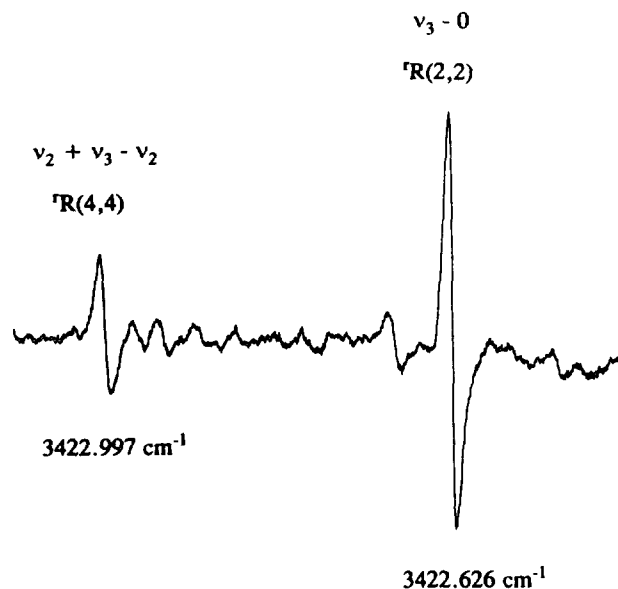


FIG. 1. Portion of the spectrum illustrating the typical signal-to-noise ratios which have been obtained for the NH_3^+ ion in the region of the $\nu_3 - 0$ (Ref. (7)) and $\nu_2 + \nu_3 - \nu_2$ bands. The experimental conditions were optimized for the simultaneous observation of HN_2^+ and NH_2^+ (see text). The weak features remain unassigned.

III. ANALYSIS

The structure of the $\nu_2 + \nu_3 - \nu_2$ band of NH_3^+ has a typical form of a perpendicular band and follows closely the structure of the ν_3 band (7). Its band origin is shifted, from the corresponding value of the fundamental band, by 16.605 cm^{-1} to the lower frequencies. The absence of observed transitions starting from the $J = \text{even}, K = 0$ level of the lower vibrational state is in agreement with symmetry considerations in the D_{3h} point group and gave us additional support to the vibrational assignment.

The observed intensity of the hot band was estimated to be around four times weaker than the intensity of the ν_3 band. If we assume that the transition dipole moment for the hot band is not significantly different from the one associated with the ν_3 fundamental band, we can estimate the vibrational temperature associated with ν_2 to be roughly around 1000 K.

The Hamiltonian model used in the analysis has been already reported in detail in the literature for the analysis of the ν_3 fundamental bands of CH_3 (26), CH_3^+ (18), and NH_3^+ (7). The rotational levels of the ν_2 vibrational state were fitted to the expression

$$E(N, K) = B''N(N+1) + (C'' - B'')K^2 - D''_{NN}N^2(N+1)^2 - D''_{NK}N(N+1)K^2 - D''_{KK}K^4, \quad (5)$$

where B and C are the rotational constants and the D 's are the quartic centrifugal distortion constants.

The diagonal part of the Hamiltonian describing the rovibrational structure of the $\nu_2 + \nu_3$ state is

TABLE I

Observed Transitions for the $\nu_2 + \nu_3 - \nu_2$ Hot Band of NH₃ in the $\tilde{X}^2A_2^+$ State (in cm⁻¹)

| <i>N'</i> | <i>K'</i> | <i>l'</i> | <i>N''</i> | <i>K''</i> | Observed | O - C | <i>N'</i> | <i>K'</i> | <i>l'</i> | <i>N''</i> | <i>K''</i> | Observed | O - C |
|-----------|-----------|-----------|------------|------------|-----------|-------|-----------|-----------|-----------|------------|------------|-----------|-------|
| 11 | 7 | 1 | 10 | 6 | 3512.350 | -9 | 4 | 1 | -1 | 4 | 2 | 3385.502 | -12 |
| 11 | 8 | 1 | 10 | 7 | 3502.718 | -2 | 4 | 0 | -1 | 4 | 1 | 3374.670 | 8 |
| 9 | 5 | 1 | 8 | 4 | 3496.902 | -8 | 5 | 0 | -1 | 5 | 1 | 3373.525 | 4 |
| 10 | 7 | 1 | 9 | 6 | 3494.890 | -1 | 1 | 1 | 1 | 1 | 0 | 3366.051 | 13 |
| 11 | 9 | 1 | 10 | 8 | 3493.218 | -10 | 3 | 1 | 1 | 3 | 0 | 3365.117 | 6 |
| 7 | 2 | 1 | 6 | 1 | 3491.356 | -0 | 5 | 1 | 1 | 5 | 0 | 3363.459 | 8 |
| 8 | 4 | 1 | 7 | 3 | 3488.998 | -1 | 7 | 1 | 1 | 7 | 0 | 3361.071 | 4 |
| 9 | 6 | 1 | 8 | 5 | 3486.939 | -4 | 0 | 0 | -1 | 1 | 1 | 3356.572 | -0 |
| 10 | 8 | 1 | 9 | 7 | 3485.233 | 2 | 2 | 2 | 1 | 2 | 1 | 3354.923 | -2 |
| 11 | 10 | 1 | 10 | 9 | 3483.867* | -16 | 5 | 2 | 1 | 5 | 1 | 3352.143* | -22 |
| 6 | 1 | 1 | 5 | 0 | 3482.464 | -4 | 6 | 2 | 1 | 6 | 1 | 3350.787 | 7 |
| 7 | 3 | 1 | 6 | 2 | 3480.959 | -1 | 1 | 1 | -1 | 2 | 2 | 3346.833 | 9 |
| 8 | 5 | 1 | 7 | 4 | 3478.868 | -4 | 5 | 3 | 1 | 5 | 2 | 3341.713 | -3 |
| 9 | 7 | 1 | 8 | 6 | 3477.117 | 1 | 6 | 3 | 1 | 6 | 2 | 3340.347 | -1 |
| 10 | 9 | 1 | 9 | 8 | 3475.699* | -16 | 2 | 2 | -1 | 3 | 3 | 3336.986 | 6 |
| 11 | 11 | 1 | 10 | 10 | 3474.677 | -8 | 5 | 4 | 1 | 5 | 3 | 3331.384 | -9 |
| 7 | 4 | 1 | 6 | 3 | 3470.680 | 1 | 6 | 4 | 1 | 6 | 3 | 3330.023 | -13 |
| 8 | 6 | 1 | 7 | 5 | 3468.887 | 3 | 7 | 4 | 1 | 7 | 3 | 3328.450 | -3 |
| 9 | 8 | 1 | 8 | 7 | 3467.434 | -0 | 3 | 3 | -1 | 4 | 4 | 3327.046 | 3 |
| 10 | 10 | 1 | 9 | 9 | 3466.341 | -6 | 8 | 4 | 1 | 8 | 3 | 3326.648 | 1 |
| 6 | 3 | 1 | 5 | 2 | 3462.363 | -3 | 2 | 1 | -1 | 3 | 2 | 3326.014* | 18 |
| 7 | 5 | 1 | 6 | 4 | 3460.539 | 3 | 7 | 5 | 1 | 7 | 4 | 3318.266* | -17 |
| 8 | 7 | 1 | 7 | 6 | 3459.026 | -13 | 4 | 4 | -1 | 5 | 5 | 3317.009 | -4 |
| 9 | 9 | 1 | 8 | 8 | 3457.889 | -9 | 3 | 2 | -1 | 4 | 3 | 3315.949 | 2 |
| 5 | 2 | 1 | 4 | 1 | 3453.925 | -2 | 5 | 5 | -1 | 6 | 6 | 3306.881 | -12 |
| 6 | 4 | 1 | 5 | 2 | 3452.070 | 1 | 4 | 3 | -1 | 5 | 4 | 3305.806 | 1 |
| 7 | 6 | 1 | 6 | 5 | 3450.520 | -12 | 3 | 1 | -1 | 4 | 2 | 3304.971 | 6 |
| 8 | 8 | 1 | 7 | 7 | 3449.341 | 2 | 2 | 1 | 1 | 3 | 0 | 3304.271 | 5 |
| 4 | 1 | 1 | 3 | 0 | 3444.940 | -0 | 6 | 6 | -1 | 7 | 7 | 3296.668* | -16 |
| 5 | 3 | 1 | 4 | 2 | 3443.478 | -8 | 5 | 4 | -1 | 6 | 5 | 3295.579 | -2 |
| 6 | 5 | 1 | 5 | 4 | 3441.910 | -0 | 4 | 2 | -1 | 5 | 3 | 3294.699 | -5 |
| 7 | 7 | 1 | 6 | 6 | 3440.670 | -1 | 3 | 0 | -1 | 4 | 1 | 3294.116 | 5 |
| 4 | 2 | 1 | 3 | 1 | 3434.768* | -16 | 7 | 7 | -1 | 8 | 8 | 3286.362* | -28 |
| 5 | 4 | 1 | 4 | 3 | 3433.163 | -13 | 6 | 5 | -1 | 7 | 6 | 3285.268 | -7 |
| 6 | 6 | 1 | 5 | 5 | 3431.893 | 1 | 5 | 3 | -1 | 6 | 4 | 3284.374 | -10 |
| 4 | 3 | 1 | 3 | 2 | 3424.322 | -8 | 8 | 8 | -1 | 9 | 9 | 3276.004 | -6 |
| 5 | 5 | 1 | 4 | 4 | 3422.997 | -9 | 7 | 6 | -1 | 8 | 7 | 3274.887 | -2 |
| 3 | 2 | 1 | 2 | 1 | 3415.362 | -8 | 6 | 4 | -1 | 7 | 5 | 3273.981 | 4 |
| 4 | 4 | 1 | 3 | 3 | 3414.009 | -1 | 5 | 2 | -1 | 6 | 3 | 3273.333 | 5 |
| 2 | 1 | 1 | 1 | 0 | 3406.161 | -8 | 8 | 7 | -1 | 9 | 8 | 3264.446* | 22 |
| 3 | 3 | 1 | 2 | 2 | 3404.909 | 2 | 7 | 5 | -1 | 8 | 6 | 3263.501 | 5 |
| 4 | 2 | -1 | 4 | 3 | 3396.495 | 8 | 6 | 3 | -1 | 7 | 4 | 3262.803 | 10 |
| 2 | 2 | 1 | 1 | 1 | 3395.688 | -10 | 4 | 1 | 1 | 5 | 0 | 3261.720 | 4 |
| 5 | 2 | -1 | 5 | 3 | 3395.385* | 23 | 7 | 4 | -1 | 8 | 5 | 3252.222 | 9 |
| 6 | 2 | -1 | 6 | 3 | 3393.910 | 5 | 6 | 2 | -1 | 7 | 3 | 3251.672 | -6 |

Note. The transitions marked with an asterisk were not included in the least-squares procedure. The observed minus calculated values are also indicated (O - C, $\times 10^3$ cm⁻¹).

$$\begin{aligned}
 E(N, K, l) = & \nu_0 + B'N(N+1) + (C' - B')K^2 - 2\zeta C'Kl \\
 & - D'_{NN}N^2(N+1)^2 - D'_{NK}N(N+1)K^2 - D'_{KK}K^4 + \eta_N K l N(N+1) + \eta_K K^3 l \\
 & + (-)^N \delta_{K,1} \delta_{l,1} q N(N+1)/2 + (-)^{N+1} \delta_{K,2} \delta_{l,-1} \beta_2 (N+2)! / (N-2)!, \quad (6)
 \end{aligned}$$

where ζ is the first-order Coriolis coupling constant for the $\nu_2 + \nu_3$ degenerate vibrational state and η_N and η_K are the centrifugal distortion constants related to the Coriolis interaction. The l -type doubling effect is responsible for the splitting of the levels with $|K - l| = 3n$. It is expressed by the two last terms of the equation with the constants q and β_2 , for $K = 1$ and $K = 2$, respectively.

The l -type resonance effect is expressed by an off-diagonal element of the Hamiltonian:

$$\begin{aligned} \langle N, K+1, l=1 | H_{\text{eff}} | N, K-1, l=-1 \rangle \\ = \frac{q}{2} \{ [N(N+1) - K(K+1)][N(N+1) - K(K-1)] \}^{1/2}. \quad (7) \end{aligned}$$

The spin-rotation interaction is responsible for the splitting observed for some lines. The constants ϵ_{bb} and ϵ_{cc} characterizing the coupling are fitted, for the upper and lower vibrational states, respectively, to the usual expression (26, 27)

$$\Delta\nu_{sr} = -(N+1/2)[\epsilon_{bb} - (\epsilon_{bb} - \epsilon_{cc})K^2/N(N+1)], \quad (8)$$

where $\Delta\nu_{sr}$ is the spin-rotation splitting of a given rotational level.

Ninety lines have been assigned, and they are presented in Table I along with the value of the observed minus calculated frequencies. A few lines have been rejected from the fit because of measurement uncertainties due to overlaps or bad signal-to-noise ratios. They are indicated with an asterisk. Twenty-three lines showed a splitting due to the spin-rotation interaction; their values are summarized in Table II. They lead to the determination of the ϵ_{bb} constants with a standard deviation on the observed minus calculated values of the splittings equal to 0.0022 cm^{-1} . The value of the ϵ_{cc} constants were fixed at zero because their effect was found to be negligible. The observation of the strongest component of the ${}^P P(1, 1)$ line 0.010 cm^{-1} above the unsplit calculated value allowed the determination of the absolute sign of ϵ_{bb} as being negative. The unsplit value of all the transitions with the ground state combination differences were included in a least-squares procedure in order to determine the rotation-vibration molecular parameters. They are presented in Table III. It was not found necessary to include in the fit the constant η_N , which was consequently fixed at zero. The standard deviation of the fit is 0.007 cm^{-1} . No systematic perturbation was encountered during the analysis. However, it was noticed that the values of the centrifugal distortion constants D_{NN} , D_{NK} , and D_{KK} were decreasing systematically in magnitude when adding in the fit series of lines with increasing values of $(N-K)$. The final values presented in Table III reproduced very well our data but we believe that they reflect a perturbation.

TABLE II

Observed Spin-Rotation Splittings in the $\nu_2 + \nu_3 - \nu_2$ Hot Band of NH_3^+ in the \tilde{X}^2A_2' State (in cm^{-1})

| N' | K' | l' | N'' | K'' | Observed | O - C | N' | K' | l' | N'' | K'' | Observed | O - C |
|------|------|------|-------|-------|----------|-------|------|------|------|-------|-------|----------|-------|
| 5 | 4 | 1 | 5 | 3 | 0.0552 | 49 | 6 | 2 | -1 | 7 | 3 | 0.0186 | 22 |
| 2 | 1 | 1 | 3 | 0 | 0.0544 | -11 | 5 | 2 | 1 | 5 | 1 | 0.0175 | -42 |
| 2 | 2 | 1 | 2 | 1 | 0.0478 | -11 | 6 | 2 | 1 | 6 | 1 | 0.0152 | -31 |
| 4 | 1 | 1 | 5 | 0 | 0.0473 | -8 | 7 | 3 | 1 | 6 | 2 | -0.0164 | 4 |
| 6 | 4 | 1 | 6 | 3 | 0.0444 | 19 | 5 | 2 | 1 | 4 | 1 | -0.0176 | 15 |
| 7 | 5 | 1 | 7 | 4 | 0.0442 | -31 | 7 | 2 | 1 | 6 | 1 | -0.0220 | 20 |
| 5 | 3 | 1 | 5 | 2 | 0.0384 | 24 | 6 | 2 | -1 | 6 | 3 | -0.0281 | 20 |
| 7 | 4 | 1 | 7 | 3 | 0.0358 | -11 | 4 | 1 | 1 | 3 | 0 | -0.0313 | 11 |
| 8 | 4 | 1 | 8 | 3 | 0.0333 | 8 | 6 | 1 | 1 | 5 | 0 | -0.0328 | 0 |
| 3 | 0 | -1 | 4 | 1 | 0.0315 | 11 | 5 | 2 | -1 | 5 | 3 | -0.0369 | -12 |
| 0 | 0 | -1 | 1 | 1 | 0.0313 | 20 | 4 | 2 | -1 | 4 | 3 | -0.0440 | 1 |
| 6 | 3 | 1 | 6 | 2 | 0.0292 | -12 | | | | | | | |

Note. The observed minus calculated values are also indicated (O - C, $\times 10^4 \text{ cm}^{-1}$).

TABLE III
Molecular Parameters (in cm^{-1}) Characterizing the $\nu_2 + \nu_3 - \nu_2$
Hot Band of NH_3^+ in the \tilde{X}^2A_2' State.

| Constants | This work | Ref. 8 |
|------------------------------------|-------------------------------|-------------------------------|
| $\nu_3 - C' \zeta_{33} - \eta_K/4$ | 3371.560 7(21) | |
| B' | 10.080 47(31) | |
| $C'(1 - \zeta_{33}) + \eta_K$ | 4.742 87(29) | |
| $C' - C'' + 3\eta_K/2$ | -0.051 88(18) | |
| D'_{NN} | $0.388 9(44) \times 10^{-3}$ | |
| D'_{NK} | $-0.268(13) \times 10^{-3}$ | |
| $D'_{\text{KK}} - \eta_K/4$ | $-0.070(11) \times 10^{-3}$ | |
| B'' | 10.195 96(33) | 10.196 4(2) |
| D''_{NN} | $0.401 4(47) \times 10^{-3}$ | $0.422 1(20) \times 10^{-3}$ |
| D''_{NK} | $-0.268(15) \times 10^{-3}$ | $-0.356 0(63) \times 10^{-3}$ |
| $D''_{\text{KK}} - D'_{\text{KK}}$ | $-0.007 7(46) \times 10^{-3}$ | |
| q' | -0.044 90(13) | |
| β_2 | $-0.027 9(15) \times 10^{-3}$ | |
| ϵ'_{bb} | -0.039 07(54) | |
| ϵ'_{cc} | 0.0 ^a | |
| ϵ''_{bb} | -0.039 11(51) | 0.039 43(7) |
| ϵ''_{cc} | 0.0 ^a | 0.000 77(22) |

Note. Error limits are one standard deviation and refer to the last digit.

^a Fixed values (see text).

Indeed, they are quite different from the values obtained for the ground and ν_3 states by Bawendi *et al.* (7) and they do not satisfy the planarity relations (18). Kraemer and Spirko have pointed out in their calculations (13) a strong x - y Coriolis interaction between $n\nu_2$ and $n\nu_4$ (the in-plane doubly degenerate bending mode). They have shown that, by using an effective Hamiltonian as ours, the perturbation is reflected by the unusual values of the distortion constants, similar to those obtained during the analysis of the ν_2 fundamental band by Lee and Oka (8), and also presented in Table III. Our present analysis of the $\nu_2 + \nu_3 - \nu_2$ band confirms this conclusion. It is somewhat difficult to discuss the discrepancies of the values of the quartic centrifugal distortion constants determined in this work and in Ref. (8) for the ν_2 state. We could mention the problem of inaccurate reference lines quoted by Lee and Oka (8) in the region of 900 cm^{-1} , but the discrepancies are most probably due to the adjustment of effective parameters to two different sets of data. In order to go one step further, we looked for a band containing ν_4 . A few series of lines have been identified in the region of the present hot band. They most probably belong to the hot band $\nu_3 + \nu_4 - \nu_4$ which is expected to be less intense than the $\nu_2 + \nu_3 - \nu_2$ band at least by a factor of two. In spite of a careful search, it was not possible to sort out enough lines to

characterize unambiguously the rotational structure of this band and that prevented the treatment of the perturbation with an appropriate model.

CONCLUSION

We have reported in this paper the analysis of the $\nu_2 + \nu_3 - \nu_2$ hot band of NH_3^+ . This band was sorted out from a spectrum very rich in ions signals, produced in a glow discharge with a gas mixture optimized for the observation of HN_2^+ and NH_2^+ in the 3- μm region. Around 90 lines have been assigned and fitted in a least-squares procedure with the model previously used for the analysis of the ν_3 fundamental band (7). A set of molecular parameters has been determined which reproduced very well the observed lines. However, unusual values have been obtained for the quartic centrifugal distortion constants of both the upper and lower states. They are similar to the values obtained for the ν_2 mode by Lee and Oka (8). It seems that they are characteristic of an x - y Coriolis interaction between $n\nu_2$ and $n\nu_4$ as pointed out and discussed in detail by Kraemer and Spirko (13). The full treatment of the perturbation would require the experimental observation of ν_4 . Unfortunately, the search to identify the $\nu_3 + \nu_4 - \nu_4$ band in our spectrum was unsuccessful. It would be therefore more promising to search for the ν_4 fundamental band in the region of 1518 cm^{-1} .

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