

Diode laser spectroscopy of the ν_2 fundamental and hot bands of NH_3^+

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The nondegenerate $\nu_2 \leftarrow 0$ and $2\nu_2 \leftarrow \nu_2$ bands of the ammonia cation NH_3^+ have been observed using tunable diode lasers combined with the velocity modulation technique. The ion was produced in a water-cooled 6 kHz ac glow discharge cell with a gas mixture of $[\text{He}]:[\text{N}_2]:[\text{H}_2] = 9:0.06:0.3$ (Torr). From the observed spectra, the band origins were determined to be $\nu_{1-0} = 903.3898 \text{ cm}^{-1}$ and $\nu_{2-1} = 939.771 \text{ cm}^{-1}$. Vibration-rotation interaction constants and potential constants were derived. The missing of $K = 0$ R -branch transitions with $N = \text{odd}$ in the $\nu_2 \leftarrow 0$ band and $N = \text{even}$ in the $2\nu_2 \leftarrow \nu_2$ band clearly shows the characteristics of a D_{3h} planar structure with a ${}^2A_2''$ ground electronic state, just like its isoelectronic case CH_3 radical. Spin-rotation doublets were well-resolved in R -branch transitions and spin-rotation interaction constants of the ground, ν_2 , and $2\nu_2$ states were determined. A potential function consisting of a quadratic term and a quartic term was used for modeling the out-of-plane bending vibration of NH_3^+ . In comparison with the methyl radical, the ammonia cation is more rigid and closer to a harmonic oscillator.

I. INTRODUCTION

Spectroscopic studies of the ν_2 nondegenerate bending mode of XH_3 -type molecules, such as the pyramidal NH_3 ,^{1,2} SiH_3 ,³ and $\text{H}_3\text{O}^{+4-7}$ with tunneling inversion motion and the planar CH_3 ,^{8,9} are of great importance in elucidating their molecular structure and intramolecular potential. In this paper, we report our high resolution spectroscopic study of the ν_2 fundamental band and the $2\nu_2 \leftarrow \nu_2$ hot band of the ammonia cation NH_3^+ . The recent spectroscopic study of the ν_3 band of this ion has been published,¹⁰ where the theoretically expected planar structure and the symmetry of the electronic state ${}^2A_2''$ was confirmed.

While the work in this paper represents the first direct observation of the ν_2 band, there had previously been several papers which contained information on the ν_2 vibration of NH_3^+ . Since the early years of ultraviolet spectroscopy of NH_3 , it was known that excited electronic states of NH_3 have vibrational frequencies of $\sim 900 \text{ cm}^{-1}$. Early in 1933, Dixon¹¹ reported 890 cm^{-1} as the ν_2 fundamental frequency in the electronic excited state. His work was extended and made more accurate by subsequent works.^{12,13} Douglas and Hollas¹⁴ have studied the 1600 \AA band system extensively and determined the series expression of the $n\nu_2$ state for the $B {}^1E''$ electronic state, in which the equilibrium structure of NH_3 is planar. Since the electronic configuration for the state $(1a_1')^2(2a_1')^2(1e')^4(1a_2'')(3pe')$, is identical to that of NH_3^+ except for the last nonbonding orbital ($3pe'$), the structure and the vibrational potential (and thus the vibrational frequencies) of the electronic state are expected to be close to those of NH_3^+ . Thus Walsh and Wassop,¹⁵ from the studies of several such Rydberg transitions, have estimated the ν_2 frequency of NH_3^+ to be $920 \pm 10 \text{ cm}^{-1}$, which is close to the value reported in our paper. More recent works of multiphoton ionization of NH_3 have provided a wealth of accurate information on the ν_2 band of the Rydberg state

which are not accessible by conventional spectroscopy.¹⁶⁻¹⁹ The high resolution laser spectroscopy of the \tilde{B} and \tilde{C} states by Ashfold *et al.*^{18,19} has extended the observed number of levels and accuracy considerably. The relation between the structure and the vibrational frequencies of a molecular ion and those of its parent molecule in Rydberg states are interesting subjects and provide a practical use in estimating these values. This topic will be discussed later in this paper for a few molecular ions.

Other studies available at the initiation of our work that provided information on the ν_2 band were photoionization studies,²⁰⁻²² photoelectron spectroscopy,^{23,24} and photodissociation studies,²⁵ all of which give values of ν_2 consistent with that from Rydberg spectra. In particular, the high resolution photoelectron spectroscopy by Ågren, Reineck, Veenhuizen, Maripuu, Arneberg, and Karlsson,²⁴ after a reassignment by Botschwina,²⁶ gave $\nu_2 = 903 \text{ cm}^{-1}$, a value that agrees exactly with our value of $\nu_2 = 903.3898(40) \text{ cm}^{-1}$. Their $2\nu_2$ value of 1831 cm^{-1} , however, differs significantly from our value 1843.161 cm^{-1} . An extensive *ab initio* calculation on the ν_2 mode has been recently reported by Botschwina²⁶ using a basis set of 57 contracted GTOs and the unrestricted Hartree-Fock-coupled-electron pair approximation (UHF-CEPA-1) which gave the value of $\nu_2 = 898 \text{ cm}^{-1}$ and $2\nu_2 = 1839 \text{ cm}^{-1}$. Botschwina's calculation also indicated an abnormally large transition dipole moment of $\mu_2 = 0.323 \text{ D}$ for $\nu = 1 \leftarrow 0$, which increases with the vibrational excitation.

Finally we notice the recent photoion-fluorescence coincidence experiments by Dujardin and Leach,²⁷ which indicated that due to intramolecular fluorescence quenching (*the Douglas effect*²⁸), the lifetime of the \tilde{A} excited state of NH_3^+ could be very long and fluorescence difficult to observe. This perhaps leaves the infrared spectrum of NH_3^+ or microwave spectrum of NH_2D^+ as the only direct means to study this astrophysically interesting species in interstellar

space and in planetary ionosphere. Recent discovery of the H_3^+ emission spectrum in the aurora region of the Jovian ionosphere²⁹⁻³² and the well-known great abundance of NH_3 in Jupiter³³ also suggests the existence of NH_3^+ in Jovian atmosphere in large quantity. It is our hope that the 10 μm spectrum reported in this paper will someday lead to the detection of NH_3^+ in space.

II. EXPERIMENTAL

The absorption spectrum of the ν_2 band of NH_3^+ was observed using a diode laser spectrometer (LS-3, Laser Photonics, formerly Laser Analytix) combined with the velocity modulation technique.^{34,35} NH_3^+ was produced in a water-cooled ac glow discharge cell (0.5 in. i.d.) using a gas mixture of $[\text{He}]:[\text{N}_2]:[\text{H}_2] = 9:0.06:0.3$ (Torr). There is no apparent increase in the signal intensity by changing He pressure from 9 to 20 Torr. A gas mixture of $\text{He}/\text{NH}_3/\text{H}_2$ was also tried, but a poorer signal-to-noise ratio of the NH_3^+ absorption line and stronger NH_3 interference were found. Spectroscopy using a liquid-nitrogen cooled discharge tube was also attempted. In this case, we could not use the $\text{He}/\text{NH}_3/\text{H}_2$ mixture because NH_3 condensed on the cell wall. When the $\text{He}/\text{N}_2/\text{H}_2$ mixture was used, we noticed that the optimum chemistry condition changed slightly (N_2 concentration ~ 0.1 Torr), but the NH_3^+ signal intensities were lower than observed by using the water cooled discharge cell. Even in this case, we noticed the condensation on the cell wall of NH_3 produced from chemical reactions in N_2/H_2 discharge. Therefore most of the measurements have been carried out by using $\text{He}/\text{N}_2/\text{H}_2$ discharge in the water cooled cell. Using an audio amplifier with a step-up transformer, the discharge frequency was kept at 6 kHz with a current of ~ 200 mA rms and voltage of ~ 5 kV, peak to peak. Four laser diodes were used to scan the spectral region from 9.1 to 11.7 μm , corresponding to the *R* and *Q* branches of the ν_2 band; approximately 75% of the region was covered. The tunable infrared radiation from the diode spectrometer was unidirectionally multiple passed through the discharge cell (Fig. 1): The advantage of this "bow-tie" configuration is that the discharge cell can be placed toward the two half-mirrors as close as possible to minimize cutoff of the laser beams. It is especially critical when a smaller diameter cell is used. The effective absorption path length was 240 cm.

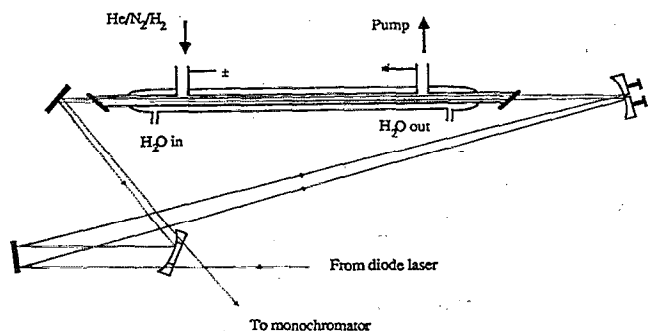


FIG. 1. The bow-tie configuration of the unidirectional multiple reflection white cell.

The outgoing beam, passing through a 0.5 m monochromator, was focused on a liquid-nitrogen cooled HgCdTe detector (Santa Barbara Research Center $D^* \approx 2 \times 10^{10}$ $\text{cm Hz}^{1/2}/\text{W}$). The detector was placed far from the discharge cell to avoid the electromagnetic pick-up noise. The preamplifier signal was demodulated with a phase sensitive detector and recorded on an *X-Y* recorder. All transitions are measured with a time constant of 3 s. NH_3 ,³⁶ PH_3 ,³⁷ and AsH_3 ,³⁸ were used for frequency calibration. Relative spacings between the reference lines were calibrated using a 1 in. Ge etalon of 0.0482 cm^{-1} free spectral range. Both the reference lines and the etalon fringe were recorded by frequency modulation at 10 kHz. We estimate the accuracy of our measurement to be 0.005 cm^{-1} .

III. OBSERVED SPECTRUM

Altogether 53 vibration-rotation transitions of NH_3^+ have been observed and assigned; 45 transitions have been assigned to the ν_2 fundamental band and seven transitions to the $2\nu_2 \leftarrow \nu_2$ hot band. All of the *R*-branch transitions appeared as well-resolved doublets due to spin-rotation interaction; the doublets were not observed in *Q*-branch transitions except for *Q*(8,6). A computer generated stick spectrum of observed transitions with calculated intensities and examples of observed lines are shown in Fig. 2. The observed absolute intensities of the lines and the signal-to-noise ratio indicate the ion concentration of $\sim 3 \times 10^{10} \text{ cm}^{-3}$ and the detection sensitivity of $\sim 5 \times 10^{-6}$, respectively, as discussed later. Table I lists hypothetical unsplit frequencies of the vibration-rotation transitions in which the doublings due to spin-rotation interaction are eliminated according to the analysis given below. The observed spin-rotation splittings are listed separately in Table II.

IV. ANALYSIS

A. Least-square fitting

The vibration-rotation transitions listed in Table I have been fitted using the standard rotational energy expression

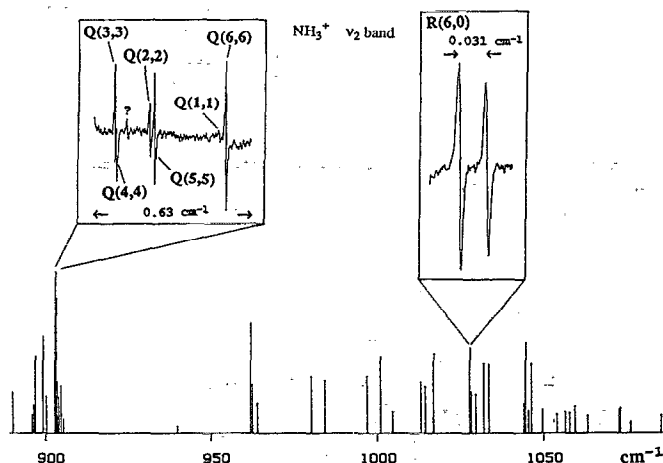


FIG. 2. Spectrum of the ν_2 band of NH_3^+ . Bottom—computer generated stick spectrum; top—examples of observed spectral lines of the $\nu_2 \leftarrow 0$ band. The transition with a question mark "?" is unassigned.

TABLE I. Observed transitions for the $\nu_2 \leftarrow 0$ and $2\nu_2 \leftarrow \nu_2$ bands of NH₃⁺ (cm⁻¹).

	N'	N''	K''	ν_{obs}	Obs.-calc.
$\nu = 1 \leftarrow 0$	8	8	6	889.904	0.007
	9	9	8	895.817	0.002
	8	8	7	896.250	-0.005
	4	4	2	896.580 ^a	-0.016
	7	7	6	896.788	-0.009
	4	4	3	899.078 ^a	-0.012
	3	3	2	900.082 ^a	-0.012
	3	3	3	902.640	0.001
	4	4	4	902.643	-0.004
	2	2	2	902.765	0.006
	5	5	5	902.781	0.000
	1	1	1	903.015	0.006
	6	6	6	903.040	0.000
	7	7	7	903.423	0.003
	8	8	8	903.920	-0.002
	9	9	9	904.550	0.008
	10	10	10	905.275	-0.004
	3	2	0	961.835 ^a	-0.018
	3	2	1	962.354	-0.009
	3	2	2	963.905 ^{a,b}	0.005
	4	3	1	980.053	0.000
	4	3	3	984.121	-0.007
	5	4	1	996.855 ^a	-0.021
	5	4	3	1000.863 ^a	-0.012
	5	4	4	1004.466	0.008
	6	5	1	1012.997 ^a	0.126
	6	5	2	1014.317	-0.004
	6	5	3	1016.767	-0.005
	7	6	0	1027.626	0.009
	7	6	1	1028.101 ^a	0.018
	7	6	2	1029.506 ^a	0.015
	7	6	3	1031.887 ^a	0.019
	8	7	2	1043.968 ^a	0.036
	7	6	6	1045.365 ^a	-0.025
	8	7	3	1046.226	0.003
8	7	4	1049.562 ^a	0.064	
8	7	5	1053.864 ^a	0.042	
9	8	1	1056.409 ^a	-0.010	
9	8	2	1057.715	-0.001	
8	7	6	1059.307 ^a	0.016	
9	8	4	1063.092 ^a	0.047	
9	8	6	1072.507 ^a	0.074	
10	9	3	1073.007	-0.002	
10	9	4	1076.050 ^{a,b}	0.061	
10	9	6	1085.076 ^a	0.145	
$\nu = 2 \leftarrow 1$	9	9	9	939.719	-0.000
	5	4	3	1033.402	-0.004
	6	5	0	1044.408	0.010
	7	6	1	1059.459	-0.012
	7	6	3	1063.128	0.001
	8	7	0	1072.915	0.003
	7	6	6	1075.919	0.002

^a Not included in the fit.^b Only one component of the doublet was observed, calculated from fitted ϵ_{bb} and ϵ_{cc} .

for an oblate symmetric rotor in a nondegenerate state

$$E_R(N, K) = BN(N+1) + (C-B)K^2 - D_{NN}N^2(N+1)^2 - D_{NK}N(N+1)K^2 - D_{KK}K^4, \quad (1)$$

where B and C are rotational constants and D_{NN} , D_{NK} , andTABLE II. Observed spin-rotation splittings of NH₃⁺ in ground, ν_2 , and $2\nu_2$ states (cm⁻¹).

	N'	N''	K''	Δ_r	Obs.-calc.
$\nu = 1 \leftarrow 0$	3	2	0	0.0346	-0.0000
	3	2	1	0.0420	0.0016
	4	3	1	0.0369	0.0005
	4	3	3	0.0604	-0.0010
	5	4	1	0.0335	-0.0004
	5	4	3	0.0486	-0.0012
	5	4	4	0.0668	0.0031
	6	5	1	0.0308	-0.0011
	6	5	2	0.0381	0.0020
	6	5	3	0.0416	-0.0014
	7	6	0	0.0297	0.0005
	7	6	1	0.0275	-0.0027
	7	6	2	0.0337	0.0004
	7	6	3	0.0396	0.0012
	8	7	2	0.0301	-0.0009
	7	6	6	0.0660	-0.0002
	8	7	3	0.0343	-0.0007
	8	7	4	0.0334 ^a	-0.0071
	8	7	5	0.0481	0.0004
	8	7	6	0.0545	-0.0020
9	8	1	0.0335 ^a	0.0056	
9	8	2	0.0320	0.0030	
9	8	4	0.0340	-0.0027	
9	8	6	0.0501	0.0007	
10	9	3	0.0305	0.0007	
10	9	6	0.0449	0.0010	
$\nu = 2 \leftarrow 1$	5	4	3	0.0469	-0.0025
	6	5	0	0.0347	0.0017
	7	6	1	0.0338	0.0007
	7	6	3	0.0369	-0.0030
	8	7	0	0.0323	0.0009
	7	6	6	0.0645	0.0016

^a Not included in the fit.

D_{KK} are the quartic centrifugal distortion constants. In view of the absence of P -branch lines in our spectrum (due to the limited coverage of diodes) and the few observed transitions in the hot band, we fixed the ground state rotational and centrifugal distortion constants to the values obtained from the combination differences of the ν_3 band¹⁰ and fitted the fundamental and the hot band simultaneously. The band origins and the rotation and centrifugal distortion constants thus determined are listed in Table III. We noted that the band origin of the fundamental band agrees very well with the photoelectron spectroscopic result of 903 cm⁻¹ by Ågren *et al.*²³ as reinterpreted by Botschwina.²⁶

The residual discrepancies between the observed and calculated frequencies are listed in the last column of Table I. These discrepancies are much greater than the accuracy of measurement which is ~ 0.005 cm⁻¹. The patchy coverage of frequencies and unavoidable mode hopping of diode lasers cause errors, but they cannot be so large as to explain the discrepancies. Initially some perturbation on the ν_2 vibration-rotation levels due to another vibrational state was suspected, but we eliminate this possibility on the following two grounds: (a) although there have not been *ab initio* predic-

TABLE III. Fitted molecular constants of NH₃⁺ in ground, ν_2 , and $2\nu_2$ states (cm⁻¹).

$\nu_2(1-0)$	903.389 8(40)
$\nu_2(2-1)$	939.771(40)
B_0	10.644 21 (fixed)
B_1	10.196 4(2)
B_2	9.770 7(17)
$C_1 - C_n$	0.066 2(2)
$C_2 - C_1$	0.091 8(24)
$D_{NN}^{(0)}$	$9.109 0 \times 10^{-4}$ (fixed)
$D_{NN}^{(1)}$	$4.221(20) \times 10^{-4}$
$D_{NN}^{(2)}$	$1.30(16) \times 10^{-4}$
$D_{NK}^{(0)}$	-1.635×10^{-3} (fixed)
$D_{NK}^{(1)}$	$-3.560(63) \times 10^{-4}$
$D_{NK}^{(2)}$	$8.97(47) \times 10^{-4}$
$D_{KK}^{(1)} - D_{KK}^{(0)}$	$-7.897(53) \times 10^{-4}$
$D_{KK}^{(2)} - D_{KK}^{(1)}$	$-4.74(37) \times 10^{-4}$
$\epsilon_{bb}^{(0)}$	0.040 98 (fixed)
$\epsilon_{bb}^{(1)}$	0.039 43(7)
$\epsilon_{bb}^{(2)}$	0.038 47(14)
$\epsilon_{cc}^{(0)}$	0.000 91 (fixed)
$\epsilon_{cc}^{(1)}$	0.000 77(22)
$\epsilon_{cc}^{(2)}$	0.000 17(45)

tions of the ν_4 frequency, they are not likely to be much lower than 1400 cm⁻¹, leaving the ν_2 state well isolated just like in other XH₃ molecules; (b) the magnitude of the vibration-rotation interaction constant $\alpha_2 = B_0 - B_1$ does not indicate any large effect of the second-order Coriolis interaction. Some inaccuracy of frequencies and missing of lines are attributable to the extremely strong NH₃ ν_2 band which more or less overlaps with the ν_2 band of NH₃⁺. We cannot find other causes of the discrepancies except possibly some inaccuracy of PH₃ frequencies³⁷ that were used as one of the frequency references. The observed lines which show large discrepancies were not included in the least-square fitting to determine the molecular constants.

As expected, R-branch transitions with $K = 0$ are observed only for even N values in the $\nu_2 \leftarrow 0$ fundamental band and for odd N values in the $2\nu_2 \leftarrow \nu_2$ hot band. This together with the approximate 2:1 intensity ratio for $K = 3n$ and $K \neq 3n$ lines confirm the D_{3h} planar equilibrium structure with an ${}^2A_2'$ ground electronic state. The determined molecular constants are listed in Table III.

The spin-rotation splitting listed in Table II has been fitted to the expression for a symmetric top molecule

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

where ϵ_{bb} and ϵ_{cc} are the spin-rotation coupling constants.^{39,40} Bawendi *et al.*¹⁰ set $\epsilon_{cc}^{(0)} = \epsilon_{cc}^{(1)} = 0$ in the analysis of the ν_3 band. We refitted their data without neglecting $\epsilon_{cc}^{(0)}$ and $\epsilon_{cc}^{(1)}$. Using the resultant values of $\epsilon_{bb}^{(0)}$ and $\epsilon_{cc}^{(0)}$ as fixed, we simultaneously fitted the fine structure splittings of the fundamental and the hot band; the determined values of spin-rotation constants $\epsilon_{bb}^{(v)}$ and $\epsilon_{cc}^{(v)}$ ($v = 0, 1, 2$) are listed in Table III.

B. Potential for the out-of-plane vibration

The ν_2 fundamental of NH₃⁺ is considerably lower than that of the normally behaving CH₃⁺ (theoretically calculated²⁶ to be at 1417.5 cm⁻¹), but is much higher than that of the very abnormal CH₃ (observed frequency⁸ of 606.45 cm⁻¹). This gives us some justification to treat this problem by the conventional method of small vibrational amplitude. If we use the standard vibrational energy expression

$$E_{v_2} = E_0 + \omega_2 v_2 - (\omega x)_{22} v_2 (v_2 + 1), \quad (3)$$

where E_0 is the zero-point vibrational energy, we obtain $\omega_2 = 867.008$ cm⁻¹ and $(\omega x)_{22} = -18.191$ cm⁻¹ as listed in Table IV. When these are compared with the CH₃ values of $\omega_2 = 506.597$ cm⁻¹, $(\omega x)_{22} = -56.901$ cm⁻¹, and $(\omega y)_{22} = -4.29$ cm⁻¹, reported by Hirota and Yamada,⁹ the better convergence of NH₃⁺ is apparent. The values of ω_2 and $(\omega x)_{22}$ allow us to determine the out-of-plane bending potential function which, for a small vibrational amplitude, can be expressed as

$$V(z) = \frac{1}{2!} k_{22} z^2 + \frac{1}{4!} k_{2222} z^4, \quad (4)$$

where z (in Å) is the distance of the center-of-mass from the H₃ plane, or as

$$V(q) = \frac{1}{2!} f_{22} q^2 + \frac{1}{4!} f_{2222} q^4, \quad (5)$$

using the dimensionless normal coordinate q . In Eq. (4), the quadratic and quartic force constants k_{22} and k_{2222} can be expressed in units of mdyn/Å and mdyn/Å³ respectively, while in Eq. (5) both f_{22} and f_{2222} can be expressed in units

TABLE IV. Derived molecular constants of NH₃⁺.

k_{22}	1.1015(1) mdyn/Å
k_{2222}	23.650(28) mdyn/Å ³
f_{22}	867.008(48) cm ⁻¹
f_{2222}	291.06(35) cm ⁻¹
ω_2	867.008(48) cm ⁻¹
$(\omega x)_{22}$	-18.191(22) cm ⁻¹
α_2^B	0.470(27) cm ⁻¹
α_2^C	-0.041(39) cm ⁻¹
γ_2^B	0.0110(12) cm ⁻¹
γ_2^C	0.013(13) cm ⁻¹
C_0	5.247 6(10) cm ⁻¹
C_1	5.313 8(61) cm ⁻¹
C_2	5.405 6(85) cm ⁻¹
ζ_{23}^2	0.550 2(7) cm ⁻¹
ζ_3	0.100 45(20) cm ⁻¹
k_{122}	420(51) cm ⁻¹
Δ_0	0.044 97(3) amu Å ²
Δ_1	-0.135 35(21) ^b amu Å ²
Δ_2	-0.332 10(26) ^b amu Å ²

^aFor CH₃, see Ref. 8 with $k_{22} = 0.3475$ mdyn/Å and $k_{2222} = 35.61$ mdyn/Å³; we estimate $k_{122} = 1037 \pm 70$ cm⁻¹.

^bCalculated using Eq. (12), $\Delta_1 = -0.1335$ amu Å² and $\Delta_2 = -0.3119$ amu Å².

of cm^{-1} . If we use Eq. (5), a simple perturbation treatment gives

$$f_{22} = \omega_2 \quad \text{and} \quad f_{2222} = -16(\omega x)_{22}. \quad (6)$$

The constants k_{22} and k_{2222} are expressed as

$$k_{22} = 4\pi^2 c^2 \omega_2 \mu f_{22} \quad \text{and} \quad k_{2222} = \frac{16\pi^4 c^3 \omega_2^2 \mu^2}{h} f_{2222}, \quad (7)$$

where μ is the reduced mass $3m_H m_N / (3m_H + m_N)$. The derived constants are listed in Table IV. The quadratic constant $k_{22} = 1.1015 \text{ mdyn}/\text{\AA}$ is three times larger than that of CH_3 ($0.3475 \text{ mdyn}/\text{\AA}$), while the quartic constant $k_{2222} = 23.650 \text{ mdyn}/\text{\AA}^3$ is smaller than that of CH_3 ($35.61 \text{ mdyn}/\text{\AA}^3$). The first hot band to the fundamental band frequency ratio ν_{2-1}/ν_{1-0} of NH_3^+ is 1.040, while that of CH_3 is 1.124; all these indicate that the bending vibration of NH_3^+ is not as anomalously anharmonic as that of CH_3 . Figure 3 shows the calculated potential function of NH_3^+ compared with that of CH_3 .

Yamada, Hirota, and Kawaguchi⁸ explained the anomalously low and anharmonic out-of-plane vibration of CH_3 in terms of a vibronic interaction between the Rydberg $\tilde{B}^2A'_1$ state and the ground $\tilde{X}^2A'_2$ state. As pointed out by Burdett,⁴¹ these states are connected by an operator linear in the out-of-plane coordinate z . Yamada *et al.* succeeded in fitting their observed vibrational levels of 0, ν_2 , $2\nu_2$, and $3\nu_2$ by using only the harmonic potential and this mixing term. While we cannot use a similar analysis because the $\tilde{B}^2A'_1$ state of NH_3^+ is unknown, we can explain the higher rigidity of NH_3^+ . The $\tilde{B}^2A'_1$ state is a Rydberg state in which the outermost electron of NH_3^+ is excited from the $1sa''_2$ to the $3sa'_1$ orbital.⁴² Since such a $3s$ Rydberg electron has the doubly charged NH_3^{++} in the core, the energy of the excited state must be much higher than that of CH_3 , and the effect on the ground state is much smaller. We can use the same argument for the observed near planarity of H_3O^+ as compared to its isoelectronic species NH_3 . Of course for CH_3^+ , the

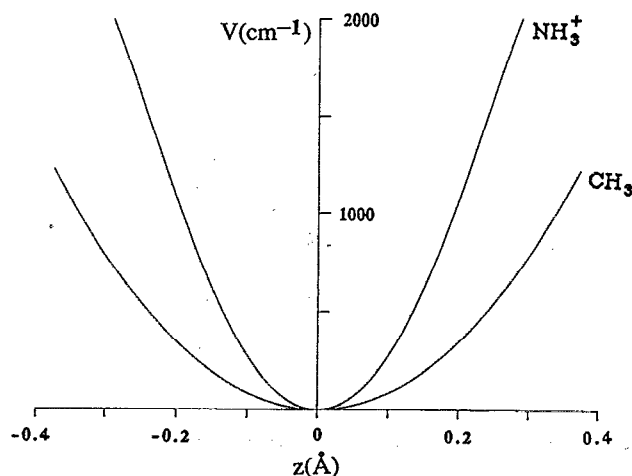


FIG. 3. The calculated ν_2 out-of-plane bending potential functions of NH_3^+ and CH_3 .

corresponding excited state does not exist and its out-of-plane vibration is normal. Therefore, we can clearly see the trend of the bending rigidity is $\text{CH}_3 < \text{NH}_3^+ < \text{CH}_3^+$. We also expect that the ν_2 out-of-plane bending spectrum of CH_3^+ has a smaller transition moment than that of NH_3^+ . This probably explains why previously we could not observe any transitions in an attempted search for the ν_2 band of CH_3^+ between 1238 and 1397 cm^{-1} (theoretical prediction²⁶ and photoelectron experiment⁴³ showed the ν_2 of CH_3^+ is 1417.5 and 1380 cm^{-1} , respectively).

C. Vibration-rotation interaction

The observed rotational constants B_0, B_1, B_2, C_1-C_0 , and C_2-C_1 allow us to determine the dependence of the rotational constant on ν_2 using the formula

$$B_{\nu_2} = B_0 - \alpha_2^B \nu_2 + \gamma_2^B \nu_2 (\nu_2 + 1), \quad (8)$$

$$C_{\nu_2} = C_0 - \alpha_2^C \nu_2 + \gamma_2^C \nu_2 (\nu_2 + 1), \quad (9)$$

where $\alpha_2^B, \alpha_2^C, \gamma_2^B$, and γ_2^C are vibration-rotation interaction constants. It is not possible to separate C_1 and C_0 until the much weaker $\Delta K = \pm 3$ type forbidden transitions are observed. We repeated the calculation given in Ref. 10, i.e., to use the theoretical expression of inertial defect⁴⁴ in terms of the Coriolis constant as an additional constraint.^{10,45} This repetition was necessary because our observed $\nu_2 = 903.3898 \text{ cm}^{-1}$ is considerably different from the value of 950 cm^{-1} used in Ref. 10. We used $\nu_1 = 3212 \pm 30 \text{ cm}^{-1}$ recommended by Botschwina²⁶ together with the experimentally determined $\nu_2 = 903.3898 \text{ cm}^{-1}$, $\nu_3 = 3388.6453 \text{ cm}^{-1}$, and $\nu_4 = 1500 \text{ cm}^{-1}$ estimated by Bawendi *et al.*¹⁰ We obtained $C_0 = 5.2476(10) \text{ cm}^{-1}$, $\xi_3 = 0.10045(20)$, and $\Delta_0 = 0.04497(3) \text{ amu \AA}^2$ which compare with values given in Ref. 10, $C_0 = 5.2457(59) \text{ cm}^{-1}$, $\xi_3 = 0.1001(10)$, and $\Delta_0 = 0.0461(37) \text{ amu \AA}^2$. All the derived molecular constants are summarized in Table IV.

The vibration-rotation constant α_2^B allows us to determine the value of the cubic anharmonic constant $f_{122} = 420 \pm 52 \text{ cm}^{-1}$ from the equation⁴⁵

$$\alpha_2^B = -\frac{6B^2}{\nu_2} - \frac{8B^2}{\nu_2} \times \left[\frac{\nu_3^2}{\nu_2^2 - \nu_3^2} \xi_{23}^2 + \frac{\nu_4^2}{\nu_2^2 - \nu_4^2} \xi_{24}^2 \right] - f_{122} \left(\frac{B}{\nu_1} \right)^{3/2}, \quad (10)$$

where the second-order Coriolis constants ξ_{23} and ξ_{24} are related to the first-order Coriolis constant ξ_3 as

$$\xi_{23}^2 = \frac{1}{2}(1 + \xi_3) \quad \text{and} \quad \xi_{24}^2 = \frac{1}{2}(1 - \xi_3). \quad (11)$$

The observed inertial defects Δ_0, Δ_1 , and Δ_2 are listed in Table IV together with theoretical values calculated from⁴⁴

$$\Delta_{\nu_2} = \frac{h}{\pi^2 c \nu_2} \left[\frac{\nu_3^2}{\nu_2^2 - \nu_3^2} (1 + \xi_3) + \frac{\nu_4^2}{\nu_2^2 - \nu_4^2} (1 - \xi_3) + \frac{3}{2} \right] \nu_2. \quad (12)$$

The good agreement between observed and calculated iner-

tial defects for the ν_2 and the $2\nu_2$ states gives support of our treatment. We have repeated the structural calculation based on these new constants using the method given in Ref. 10. As before, we obtained $r_e = 1.014 \text{ \AA}$, which disagrees significantly from the most recent theoretical prediction of 1.0241 \AA by Botschwina.⁴⁶

D. Plasma diagnostics

The observed absorption intensity $\Delta I/I$ at the peak of a spectral line is expressed as

$$\Delta I/I = n\sigma l, \quad (13)$$

where n is the number density in cm^{-2} and l is the absorption path length. The cross section σ in cm^2 is expressed as

$$\sigma = 5.46 \times 10^{-13} \sqrt{\frac{M}{T}} f(T_R, T_V) |\mu_{ij}|^2, \quad (14)$$

where M is the molecular weight in amu, T is the translational temperature in K, μ_{ij} is the transition dipole moment in D, and $f(T_R, T_V)$ is the fractional population of the ion in the particular vibration-rotation state which is dependent on rotational temperature T_R and vibrational temperature T_V . From a series of $Q(N, N)$ transitions with $N = 1-6$, we obtained the rotational temperature T_R to be 500 K. From the relative intensities of the $R(8, 4)$ transition of the $\nu_2 \leftarrow 0$ fundamental band and of the $R(6, 3)$ of the $2\nu_2 \leftarrow \nu_2$ hot band which happened to be close in frequency, we estimated the vibrational temperature T_V to be 720 ± 100 K. In the estimate of T_V , we used the theoretical prediction by Botschwina²⁶ that the vibrational transition moment of the hot band (0.441 D) is considerably larger than that of the fundamental band (0.323 D) mainly due to the $\sqrt{(v+1)/2}$ factor in the matrix element $\langle v+1 | \mu | v \rangle$.

In order to estimate the absolute concentration of NH₃⁺ in the discharge, we used the two strong lines $R(6, 0)$ and $Q(6, 6)$. We measured the absolute infrared power using chopper modulation and compared it with the ion signal. The absorption was measured to be $\Delta I/I \sim 1.2 \times 10^{-4}$ and 7.6×10^{-4} , respectively, for the path length of 2.4 m. Using the rotational and vibrational temperatures mentioned above and assuming that the translational temperature is equal to the rotational temperature, we find the cross section for these two transitions to be 2.1×10^{-17} and $1.5 \times 10^{-17} \text{ cm}^2$, respectively. These lead us to the estimated NH₃⁺ ion concentration of $\sim 3 \times 10^{10} \text{ cm}^{-3}$.

V. RYDBERG STATES VS IONIC STATES

As extensively discussed by Walsh and Walsop,¹⁵ it is one of the lone pair electrons on the N atom of NH₃ that is excited to high Rydberg orbitals. Since such an orbital is nonbonding, a Rydberg state will show similar structure and vibrational frequencies to those of ionic states. This helps us to estimate the vibrational frequencies, structure, and possibly other properties of molecular ions. Conversely, once information on molecular ions is obtained from direct spectroscopy, we can compare the properties of ionic species and Rydberg states, and examine more fully the subtle bonding or antibonding nature of the Rydberg electrons.

TABLE V. Molecular constants of Rydberg state molecules and molecular ions.

State	ν_2 (cm^{-1})	B_0 (cm^{-1})	Reference	
NH ₃ ⁺	$^2A_2''$	903.3898	10.644	This work
NH ₃	$A^1A_2'' 3sa_1'$	878		15
	$B^1E'' 3pe'$	898.318	10.29	14
		898.208	10.484 4	18
	$C^1A_1' 3pa_2''$	844	10.62	15
		843.87	10.778	17
	$D^1A_2'' 3da_1'$	910.6		15
	$E^1A_2'' 5sa_1'$	927		15
CH ₃ ⁺	$^1A_1'$		9.362 27	45
CH ₃	$B^2A_1' 3sa_1'$	1360		42
	$3p^2A_2''$	1334	10.2	47
	$C^2E'' 3de''$	1360		42
	$D^2A_1' 3da_1'$		10.72	42
	$4p^2A_2''$		9.90	48
H ₃ ⁺	$^1A_1'$	2521	43.56	49
H ₃	$3d^2E'$		42.99	49
	$3p^2A_2''$		47.45	49
	$3s^2A_1'$		44.19	49
	$3p^2E'$		42.15	49
	$2p^2A_2''$		44.57	49
	$2s^2A_1'$		46.8	49

In Table V, we give some comparisons for the combinations of [NH₃, NH₃⁺], [CH₃, CH₃⁺], and [H₃, H₃⁺]. While the number of cases is not sufficient to draw any definitive conclusion, we notice that the rotational constants of Rydberg states *decrease* significantly in degenerate electronic states for all available cases and this indicates the slightly antibonding nature of the orbital. In contrast, the rotational constants *increase* for nondegenerate electronic states indicating that the Rydberg electron in the A_1' or A_2'' states are of bonding character. The effect of electronic excitation on the frequency of out-of-plane vibration is more subtle and no conclusion is drawn from the comparison.

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