

Difference frequency laser spectroscopy of the ν_3 fundamental band of NH_2^+

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The ν_3 band of NH_2^+ in the \tilde{X}^3B_1 ground electronic state was observed in direct absorption with a tunable difference frequency laser spectrometer in the $3\ \mu$ region, using velocity modulation detection. NH_2^+ and NH_3^+ ions were generated in an ac discharge of He and NH_3 , or of He, N_2 , and H_2 . Fifty-three rovibrational transitions were measured and fit to a triplet A -reduced Hamiltonian to determine rotational, centrifugal distortion, and spin-rotation constants. The band origin was found to be $\nu_0 = 3359.932\ \text{cm}^{-1}$, in excellent agreement with a recent calculation of Jensen, Bunker, and McLean. Indirect evidence from the spectrum suggested that NH_2^+ is quasilinear, but selection rules prevented a determination of the A rotational constant.

I. INTRODUCTION

Quasilinear molecules, which possess very low potential barriers at linearity, are an important case of molecules with large amplitude vibrations. An example of fundamental interest is the methylene diradical CH_2 , which in its ground state has a barrier of $1170\ \text{cm}^{-1}$. Only two bending vibrational levels lie below the barrier.¹ The amidogen cation NH_2^+ is isoelectronic with CH_2 , and its ground \tilde{X}^3B_1 state is also expected to be quasilinear. Although there are a number of elegant spectroscopic and theoretical studies of CH_2 in the triplet state,²⁻⁴ there has been little work on the NH_2^+ ion.

There have been a few *ab initio* calculations of NH_2^+ at the configuration interaction (CI) level, all of which predict that NH_2^+ will possess a low barrier at linearity. Peyerimhoff and Buenker⁵ have obtained a barrier of $330\ \text{cm}^{-1}$, and an equilibrium bond angle of 149.6° . In the most recent calculation, performed concurrently with our work, Jensen, Bunker, and McLean have found that the linear geometry is only $209\ \text{cm}^{-1}$ above the energy minimum.⁶ The equilibrium geometry is calculated to have a bond angle α_e of 153.17° , at a NH bond length of $r_e = 1.0338\ \text{\AA}$. The bending potential energy function (with the bond lengths fixed to r_e) obtained from their calculation is shown in Fig. 1. NH_2^+ is predicted to be much closer to linear than CH_2 , for which $\alpha_e = 135^\circ$ as derived from experiment. Jensen *et al.* predict that the zero point energy of the bending vibration ν_2 is $290\ \text{cm}^{-1}$, slightly above the barrier. Experimental studies of NH_2^+ should therefore provide an important test for theoretical models of quasilinear molecules.

Herzberg observed emission lines in the vacuum ultraviolet from ammonia ionized by low energy electron bombardment,⁷ which were thought to arise from either NH_2^+ or NH_3^+ . Both of these ions are expected to exist in molecular clouds in the interstellar medium.^{8,9} Although initially unassigned, the NH_2^+ spectrum has recently been tentatively identified; these results will be discussed below. Dunlavey,

Dyke, Jonathan, and Morris observed the photoelectron spectrum of the NH_2 radical,¹⁰ and found $\nu_2 = 840 \pm 50\ \text{cm}^{-1}$ for the ground state of the ion.

In this paper, we report the first high resolution study of NH_2^+ . We have observed the ν_3 fundamental band in the infrared, using velocity modulation detection of the ions created in an ac discharge.

II. EXPERIMENTAL

The spectrum was recorded with a difference frequency spectrometer initially developed by Pine,¹¹ which has been described in detail in a previous paper.¹² Briefly, the radiation from an argon ion laser ($\sim 500\ \text{mW}$) was mixed with radiation from a ring dye laser ($\sim 500\ \text{mW}$) in a tempera-

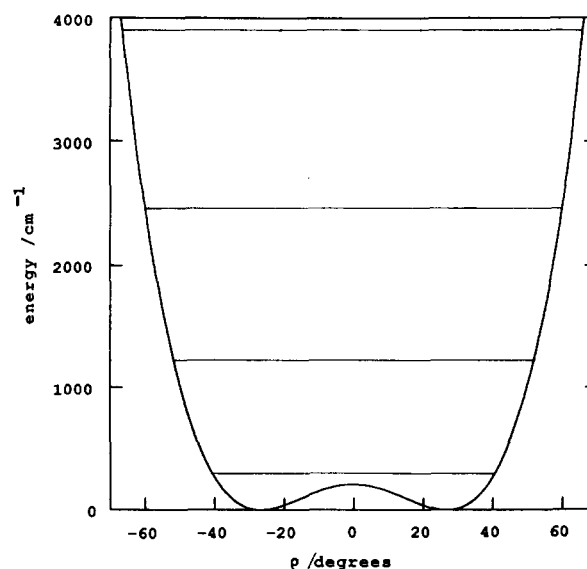


FIG. 1. The bending potential energy function of NH_2^+ \tilde{X}^3B_1 obtained from the calculation by Jensen, Bunker, and McLean, in Ref. 6. The function is a fit to *ab initio* points from a SOCI (second order configuration interaction) calculation with Davidson correction. The angle ρ is defined as $\rho = \pi - \alpha$, where α is the bond angle; the NH bond length is fixed here at $r = r_e = 1.0338\ \text{\AA}$.

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ture tuned LiNbO_3 crystal, to produce $100 \mu\text{W}$ or more of infrared. The infrared beam made four unidirectional traversals through a 1.2 m long discharge cell (12 mm bore) to probe the discharge. Dual beam noise subtraction was used to reduce laser amplitude noise. Ammonia was used as a reference for frequency calibration.

The ions were produced in an ac positive glow discharge, and detected by velocity modulation.¹³ The absorption lines of NH_2^+ , initially seen in our search for NH_3^+ ,²³ were easily distinguished from the ammonia ion lines due to their distinctive triplet pattern (Fig. 2). The transitions were observed in an air-cooled multi-inlet-multi-outlet discharge cell ("spider") with a mixture of 20 mTorr NH_3 , 100 mTorr H_2 , and 6 Torr He, but were enhanced when we eliminated the hydrogen and increased the ammonia to 50 mTorr. This absence of H_2 also decreased the NH_3^+ signal, so we had very specific chemical evidence for the two species. NH_2^+ was also seen in a liquid-nitrogen cooled discharge (the "black widow" cell), but N_2 (~ 60 mTorr) and H_2 (~ 100 mTorr) had to be used in place of ammonia, which would freeze to the walls of the inlet ports before entering the discharge region. Figure 3 illustrates the effect of H_2 pressure on the relative strengths of NH_2^+ and NH_3^+ lines. The NH_2^+ signal was still observed using N_2 as the source of nitrogen instead of ammonia; surprisingly, the signal was enhanced for all lines, especially for the $K_a = 0$ transitions. The $K_a = 1$ transitions were only slightly stronger. White powder, most likely ammonia, deposited on the walls of the liquid-nitrogen cooled discharge over the course of several hours.

As in the case of hydrocarbon discharges, helium was

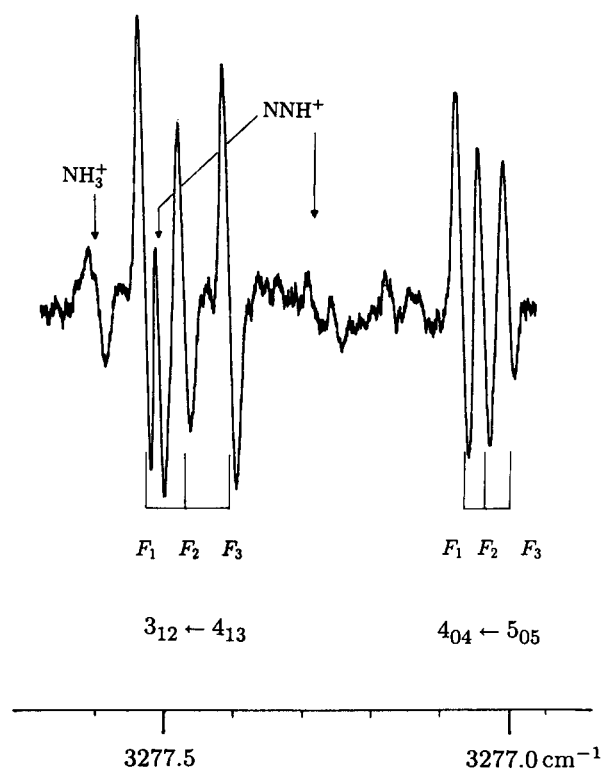


FIG. 2. Example of observed lines of the ν_3 band of NH_2^+ . Also seen are the ${}^oP(7,4)$ transition of NH_3^+ as well as two transitions of N_2H^+ [the strong $R(14)$ line amid the $4_{13} \rightarrow 3_{12}$ triplet and the weak $R(23)$ hot band line].

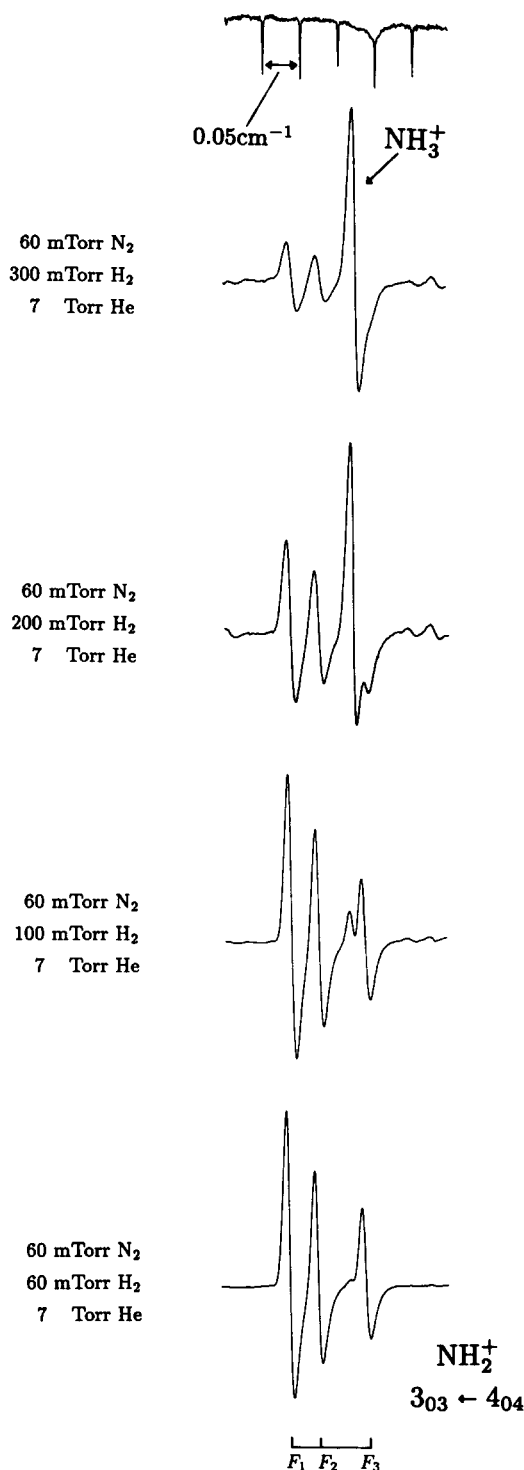


FIG. 3. Effect of H_2 pressure on NH_2^+ and NH_3^+ lines in liquid-nitrogen cooled discharge of H_2 , 60 mTorr N_2 and 7 T He. Note that the NH_3^+ transition nearly disappears at low H_2 pressure.

necessary for the production of free radical ions. The NH_2^+ and NH_3^+ lines vanished at He pressures of 1 Torr or less. By contrast, the closed shell protonated ammonia NH_4^+ ion was enhanced at high hydrogen pressures and low He pressures. The electron temperature is believed to be higher in helium discharges, and Penning ionization is far more energetic, resulting in significantly more bond breaking. Helium is also a poor partner in the vibrational relaxation of excited

ions. Furthermore, stable discharges of helium can be operated at higher total pressures, thus increasing the ion density.

Spectral lines were observed between 3180 and 3510 cm^{-1} , except for a small gap between 3450–3480 cm^{-1} , where the output of the LiNbO_3 crystal is typically low due to OH absorption within the crystal itself. Lines up to $J = 10$ for $K_a = 0$ and $J = 11$ for $K_a = 1$ were assigned, although many lines still remain unassigned.

III. RESULTS AND ANALYSIS

NH_2^+ is an open shell ion with two unpaired electrons, and in its ground electronic state has a total electron spin of $S = 1$. This spin is coupled to the total rotational angular momentum N according to the Hund's case (b) scheme

$$\mathbf{J} = \mathbf{N} + \mathbf{S},$$

and a Hund's case (b) basis set is the most suitable representation for the NH_2^+ energy levels.

The geometrical structure of this ion is predicted to be similar to that of CH_2 . If we consider the molecule as bent, we can use the asymmetric top formalism and can label the energy levels using the quantum numbers $J, N, K_a,$ and K_c . The net electronic spin splits each rotational level into three components labeled $F_1, F_2,$ and F_3 , for $J = N + 1, J = N,$ and $J = N - 1,$ respectively. With a predicted equilibrium bond angle of 153° , the NH_2^+ geometry is expected to be very close to the linear configuration. Although we treat NH_2^+ as an asymmetric rotor in the following discussion, the molecular parameters obtained from the fit can be transformed into the common linear molecule parameters, as discussed in the next section.

The effective Hamiltonian used for the analysis of the NH_2^+ spectrum can be divided into four parts, each due to a different interaction occurring within the molecule. It can be written as

$$H_{\text{eff}} = H_R = H_{CD} + H_{SS} + H_{SR}. \quad (1)$$

The first two terms are the pure rotational part of the Hamiltonian. H_R is the rigid rotor Hamiltonian:

$$H_R = A\hat{N}_a^2 + B\hat{N}_b^2 + C\hat{N}_c^2, \quad (2)$$

where $a, b,$ and c are the principal axes, and $A > B > C$. H_{CD} is the centrifugal distortion correction to the rotational Hamiltonian. We use here the A -reduced expression given by Watson¹⁴:

$$\begin{aligned} H_{CD} = & -\Delta_N \hat{N}^4 - \Delta_{NK} \hat{N}^2 \hat{N}_a^2 - \Delta_K \hat{N}_a^4 \\ & - \frac{1}{2} [\delta_N \hat{N}^2 + \delta_K \hat{N}_a^2, \hat{N}_+^2 + \hat{N}_-^2]_+ \\ & + \Phi_N \hat{N}^6 + \dots, \end{aligned} \quad (3)$$

where $[,]_+$ is the anticommutator.

The last two terms in Eq. (1) are due to the interactions involving the spins of the two unpaired electrons. H_{SS} is the spin-spin interaction between the two electrons, and is given by^{15,16}

$$H_{SS} = \frac{D}{3} (2\hat{S}_a^2 - \hat{S}_b^2 - \hat{S}_c^2) + E(\hat{S}_b^2 - \hat{S}_c^2). \quad (4)$$

TABLE I. Observed transitions and residuals of the ν_3 band of $\text{NH}_2^+ \tilde{X}^3B_1$.

J'	$N'_{K_a K_c}$	\leftarrow	J''	$N''_{K_a K_c}$	$\nu_{\text{obs}}, \text{cm}^{-1}$	$\nu_{\text{obs}} - \nu_{\text{calc}}, \text{cm}^{-1}$
10	11 _{0 11}		9	10 _{0 10}	3510.677	0.001
11	11 _{0 11}		10	10 _{0 10}	3510.648	-0.006
12	11 _{0 11}		11	10 _{0 10}	3510.648	0.005
11	12 _{1 12}		10	11 _{1 11}	3507.637	-0.004
12	12 _{1 12}		11	11 _{1 11}	3507.637	0.015
13	12 _{1 12}		12	11 _{1 11}	3507.594	-0.012
10	11 _{1 10}		9	10 _{1 9}	3502.176	-0.004
11	11 _{1 10}		10	10 _{1 9}	3502.176	0.010
12	11 _{1 10}		11	10 _{1 9}	3502.147	-0.007
9	10 _{0 10}		8	9 _{0 9}	3498.941	-0.001
10	10 _{0 10}		9	9 _{0 9}	3498.908	-0.011
11	10 _{0 10}		10	9 _{0 9}	3498.908	0.001
8	9 _{0 9}		7	8 _{0 8}	3486.803	0.005
9	9 _{0 9}		8	8 _{0 8}	3486.769	-0.004
10	9 _{0 9}		9	8 _{0 8}	3486.769	0.008
9	10 _{1 10}		8	9 _{1 9}	3484.214	-0.002
10	10 _{1 10}		9	9 _{1 9}	3484.193	-0.004
11	10 _{1 10}		10	9 _{1 9}	3484.193	0.015
6	7 _{1 6}		5	6 _{1 5}	3450.364	-0.003
7	7 _{1 6}		6	6 _{1 5}	3450.364	0.004
8	7 _{1 6}		7	6 _{1 5}	3450.327	-0.004
5	6 _{0 6}		4	5 _{0 5}	3447.959	0.002
6	6 _{0 6}		5	5 _{0 5}	3447.921	0.000
7	6 _{0 6}		6	5 _{0 5}	3447.906	0.003
7	7 _{1 7}		6	6 _{1 6}	3446.241	0.005
6	7 _{1 7}		5	6 _{1 6}	3446.241	-0.007
8	7 _{1 7}		7	6 _{1 6}	3446.203	0.001
6	6 _{1 5}		5	5 _{1 4}	3436.428	-0.001
5	6 _{1 5}		4	5 _{1 4}	3436.428	0.000
7	6 _{1 5}		6	5 _{1 4}	3436.382	-0.004
4	5 _{0 5}		3	4 _{0 4}	3434.233	0.000
5	5 _{0 5}		4	4 _{0 4}	3434.186	0.001
6	5 _{0 5}		5	4 _{0 4}	3434.162	-0.001
6	6 _{1 6}		5	5 _{1 5}	3432.849	0.001
5	6 _{1 6}		4	5 _{1 5}	3432.849	-0.004
7	6 _{1 6}		6	5 _{1 5}	3432.802	0.000
5	5 _{1 4}		4	4 _{1 3}	3422.129	0.005
4	5 _{1 4}		3	4 _{1 3}	3422.112	0.005
6	5 _{1 4}		5	4 _{1 3}	3422.057	-0.002
3	4 _{0 4}		2	3 _{0 3}	3420.135	-0.005
4	4 _{0 4}		3	3 _{0 3}	3420.064	-0.003
5	4 _{0 4}		4	3 _{0 3}	3420.035	-0.004
5	5 _{1 5}		4	4 _{1 4}	3419.099	-0.009
4	5 _{1 5}		3	4 _{1 4}	3419.093	-0.002
6	5 _{1 5}		5	4 _{1 4}	3419.034	-0.005
4	4 _{1 3}		3	3 _{1 2}	3407.479	0.009
3	4 _{1 3}		2	3 _{1 2}	3407.417	0.012
5	4 _{1 3}		4	3 _{1 2}	3407.357	0.003
2	3 _{0 3}		1	2 _{0 2}	3405.726	0.002
3	3 _{0 3}		2	2 _{0 2}	3405.581	0.005
4	3 _{0 3}		3	2 _{0 2}	3405.540	0.003
4	4 _{1 4}		3	3 _{1 3}	3405.040	0.008
3	4 _{1 4}		2	3 _{1 3}	3404.978	0.007
5	4 _{1 4}		4	3 _{1 3}	3404.918	0.006
3	3 _{1 2}		2	2 _{1 1}	3392.521	0.001
4	3 _{1 2}		3	2 _{1 1}	3392.271	0.003
2	3 _{1 2}		1	2 _{1 1}	3392.271	-0.008
1	2 _{0 2}		0	1 _{0 1}	3391.446	0.004
2	2 _{0 2}		1	1 _{0 1}	3390.718	0.000
3	3 _{1 3}		2	2 _{1 2}	3390.673	-0.004
3	2 _{0 2}		2	1 _{0 1}	3390.654	0.000
2	3 _{1 3}		1	2 _{1 2}	3390.446	0.008
4	3 _{1 3}		3	2 _{1 2}	3390.422	0.002
2	2 _{1 1}		1	1 _{1 0}	3377.664	0.001
2	2 _{1 2}		1	1 _{1 1}	3376.419	-0.005
1	1 _{0 1}		1	0 _{0 0}	3376.224	0.006
3	2 _{1 2}		2	1 _{1 1}	3375.519	-0.005
2	1 _{0 1}		1	0 _{0 0}	3375.353	-0.008
1	2 _{1 2}		0	1 _{1 1}	3374.745	0.012

Table I (continued).

J'	$N'_{K_a K_c}$	\leftarrow	J''	$N''_{K_a K_c}$	$\nu_{\text{obs}}, \text{cm}^{-1}$	$\nu_{\text{obs}} - \nu_{\text{calc}}, \text{cm}^{-1}$
0	1 _{0,1}		1	0 _{0,0}	3374.171	-0.010
4	3 _{1,2}		4	3 _{1,3}	3346.881	0.004
3	3 _{1,2}		3	3 _{1,3}	3346.844	-0.012
2	3 _{1,2}		2	3 _{1,3}	3346.831	-0.015
3	2 _{1,1}		3	2 _{1,2}	3345.995	0.004
1	2 _{1,1}		1	2 _{1,2}	3345.961	-0.004
2	2 _{1,1}		2	2 _{1,2}	3345.961	-0.011
1	1 _{1,0}		1	1 _{1,1}	3345.396	0.017
1	0 _{0,0}		0	1 _{0,1}	3345.348	0.006
0	1 _{1,1}		1	1 _{1,0}	3345.183	-0.018
1	1 _{1,0}		2	1 _{1,1}	3344.968	0.010
2	1 _{1,1}		1	1 _{1,0}	3344.561	-0.006
1	0 _{0,0}		2	1 _{0,1}	3344.161	0.003
1	1 _{1,1}		1	1 _{1,0}	3344.137	-0.005
2	1 _{1,1}		2	1 _{1,0}	3344.137	0.002
0	1 _{1,1}		0	1 _{1,0}	3344.137	0.001
1	0 _{0,0}		1	1 _{0,1}	3343.292	-0.004
1	1 _{1,1}		0	1 _{1,0}	3343.065	-0.013
1	2 _{1,2}		1	2 _{1,1}	3342.252	0.006
2	2 _{1,2}		2	2 _{1,1}	3342.223	-0.012
3	2 _{1,2}		3	2 _{1,1}	3342.223	-0.003
2	1 _{0,1}		3	2 _{0,2}	3327.834	0.006
1	1 _{0,1}		2	2 _{0,2}	3327.758	0.001
0	1 _{0,1}		1	2 _{0,2}	3327.044	-0.003
5	6 _{1,6}		5	6 _{1,5}	3325.232	0.000
6	6 _{1,6}		6	6 _{1,5}	3325.202	-0.002
7	6 _{1,6}		7	6 _{1,5}	3325.188	0.006
0	1 _{1,1}		1	2 _{1,2}	3314.128	-0.010
0	1 _{1,0}		1	2 _{1,1}	3312.885	0.001
2	1 _{1,0}		3	2 _{1,1}	3312.091	-0.004
3	2 _{0,2}		4	3 _{0,3}	3311.217	0.000
1	1 _{1,0}		2	2 _{1,1}	3311.201	0.012
2	2 _{0,2}		3	3 _{0,3}	3311.169	0.000
1	2 _{0,2}		2	3 _{0,3}	3311.032	-0.001
3	2 _{1,2}		4	3 _{1,3}	3296.835	-0.001
1	2 _{1,2}		2	3 _{1,3}	3296.823	0.010
2	2 _{1,2}		3	3 _{1,3}	3296.577	0.008
3	2 _{1,1}		4	3 _{1,2}	3294.942	0.003
1	2 _{1,1}		2	3 _{1,2}	3294.936	0.014
2	2 _{1,1}		3	3 _{1,2}	3294.680	0.005
4	3 _{0,3}		5	4 _{0,4}	3294.294	0.001
3	3 _{0,3}		4	4 _{0,4}	3294.255	-0.001
2	3 _{0,3}		3	4 _{0,4}	3294.192	-0.002
4	3 _{1,3}		5	4 _{1,4}	3280.061	-0.002
2	3 _{1,3}		3	4 _{1,4}	3280.006	0.005
3	3 _{1,3}		4	4 _{1,4}	3279.936	0.002
4	3 _{1,2}		5	4 _{1,3}	3277.529	-0.005
2	3 _{1,2}		3	4 _{1,3}	3277.471	-0.008
3	3 _{1,2}		4	4 _{1,3}	3277.406	-0.002
5	4 _{0,4}		6	5 _{0,5}	3277.060	0.004
4	4 _{0,4}		5	5 _{0,5}	3277.027	0.002
3	4 _{0,4}		4	5 _{0,5}	3276.991	0.004
5	4 _{1,4}		6	5 _{1,5}	3263.002	-0.004
3	4 _{1,4}		4	5 _{1,5}	3262.947	-0.001
4	4 _{1,4}		5	5 _{1,5}	3262.928	0.001
5	4 _{1,3}		6	5 _{1,4}	3259.848	0.000
3	4 _{1,3}		4	5 _{1,4}	3259.789	-0.006
4	4 _{1,3}		5	5 _{1,4}	3259.776	0.004
6	5 _{0,5}		7	6 _{0,6}	3259.510	0.002
5	5 _{0,5}		6	6 _{0,6}	3259.482	0.002
4	5 _{0,5}		5	6 _{0,6}	3259.456	0.002
6	5 _{1,5}		7	6 _{1,6}	3245.662	0.002
4	5 _{1,5}		5	6 _{1,6}	3245.607	-0.001
5	5 _{1,5}		6	6 _{1,6}	3245.607	0.003
6	5 _{1,4}		7	6 _{1,5}	3241.873	-0.003
4	5 _{1,4}		5	6 _{1,5}	3241.821	-0.009
5	5 _{1,4}		6	6 _{1,5}	3241.821	-0.002
7	6 _{0,6}		8	7 _{0,7}	3241.652	-0.004
6	6 _{0,6}		7	7 _{0,7}	3241.626	-0.004
5	6 _{0,6}		6	7 _{0,7}	3241.607	-0.003

Table I (continued).

J'	$N'_{K_a K_c}$	\leftarrow	J''	$N''_{K_a K_c}$	$\nu_{\text{obs}}, \text{cm}^{-1}$	$\nu_{\text{obs}} - \nu_{\text{calc}}, \text{cm}^{-1}$
7	6 _{1,6}		8	7 _{1,7}	3228.028	0.001
6	6 _{1,6}		7	7 _{1,7}	3227.986	0.004
5	6 _{1,6}		6	7 _{1,7}	3227.986	0.008
7	6 _{1,5}		8	7 _{1,6}	3223.630	0.007
5	6 _{1,5}		6	7 _{1,6}	3223.584	0.002
6	6 _{1,5}		7	7 _{1,6}	3223.584	0.002
8	7 _{0,7}		9	8 _{0,8}	3223.497	-0.009
7	7 _{0,7}		8	8 _{0,8}	3223.470	-0.012
6	7 _{0,7}		7	8 _{0,8}	3223.456	-0.008
8	7 _{1,7}		9	8 _{1,8}	3210.113	0.001
7	7 _{1,7}		8	8 _{1,8}	3210.071	-0.003
6	7 _{1,7}		7	8 _{1,8}	3210.071	0.004
9	8 _{0,8}		10	9 _{0,9}	3205.065	0.000
8	8 _{0,8}		9	9 _{0,9}	3205.045	0.003
7	8 _{0,8}		8	9 _{0,9}	3205.045	0.019
9	8 _{1,8}		10	9 _{1,9}	3191.912	-0.009
8	8 _{1,8}		9	9 _{1,9}	3191.877	-0.011
7	8 _{1,8}		8	9 _{1,9}	3191.877	-0.002
9	9 _{0,9}		10	10 _{0,10}	3186.338	0.019
10	9 _{0,9}		11	10 _{0,10}	3186.338	-0.003
8	9 _{0,9}		9	10 _{0,10}	3186.295	-0.010

H_{SR} is the spin-rotation interaction term given by Raynes¹⁷ and by Brown and Sears¹⁸:

$$H_{\text{SR}} = \epsilon_{aa} \hat{N}_a \hat{S}_a + \epsilon_{bb} \hat{N}_b \hat{S}_b + \epsilon_{cc} \hat{N}_c \hat{S}_c. \quad (5)$$

A triplet asymmetric rotor program was written to calculate the energy levels and to fit the spectrum. The matrix generated by the effective Hamiltonian was set up in a prolate symmetric top basis set, factorized into four submatrices using the Wang transformation, and numerically diagonalized to obtain the energy levels for both the ground and vibrationally excited states.

Fifty-three rovibrational transitions, giving a total of 159 lines and 84 combination differences, were fit using a nonlinear least-squares fitting routine and 25 molecular parameters were calculated. A complete list of the observed transitions is given in Table I. Only the $K_a = 0$ and $K_a = 1$ transitions were assigned. An intensity alternation of approximately 3:1 is observed, with lines assigned to ee ($K_a = \text{even}$, $K_c = \text{even}$) or oo rotational levels of the ground state stronger than the eo or oe lines, as expected for an electronic state with B_1 symmetry. The Q -branch lines are relatively weak for $J \geq 3$, strongly supporting the assignment as an a -type or parallel transition of a nearly linear molecule. No $K_a \geq 2$ lines were observed, despite careful searches. Either the higher order terms in K_a are larger (which was not the case for CH_2), or these states have very low populations due to a very high value of A .

The standard deviation of the fit was 0.007 cm^{-1} , a surprisingly good result considering the large rotational constant of the molecule. In Table II the retrieved molecular parameters are reported. The quoted error bars are one standard deviation. Both ground and vibrationally excited state molecular parameters were determined by simultaneously fitting the observed transitions and the ground state combination differences. We found the origin of the ν_3 band at 3359.932 cm^{-1} . This is reasonably close to the *ab initio* pre-

TABLE II. Derived spectroscopic constants in cm^{-1} for $\tilde{X}^3B_1\text{NH}_2^+$, compared with constants for $\tilde{X}^3B_1\text{CH}_2$ from Ref. 3. Uncertainties in parentheses are 1σ .

	NH_2^+		CH_2
	(000)	(001)	(000)
ν_0	...	3359.931 7(20)	...
A	73.810 575
$A' - A''$...	15.013 7(25)	...
B	8.272 99(34)	8.097 46(33)	3.450 42
C	7.644 43(34)	7.474 36(33)	7.184 31
$\Delta_N \times 10^4$	2.390 (44)	2.440(34)	3.692
Δ_{NK}	-0.097 36(20)	-0.106 03(19)	-0.020 931
Δ_K	2.958 511
$\delta_N \times 10^5$	4.27(13)	4.361(93)	5.
δ_K	0.018 16
$\Phi_N \times 10^8$	-4.6(25)	-1.3(17)	5.0
$\Phi_{NK} \times 10^5$	-3.12(24)	-2.99(17)	-1.15
Φ_K	0.220 221
ϵ_{aa}	0.008 9(27)	0.014 1(34)	0.000 475
ϵ_{bb}	-0.008 79(80)	-0.008 60(89)	-0.005 12
ϵ_{cc}	-0.016 58(80)	-0.016 61(89)	-0.004 12
D	2.058 6(29)	2.049 0(35)	0.778 83
E	0.040 5

diction of 3308 cm^{-1} by DeFrees and McLean,¹⁹ who scaled harmonic frequencies obtained from a Hartree Fock SCF calculation with a fairly small basis set (DZ + P). Our results are in excellent agreement with the value of 3363 cm^{-1} calculated by Jensen, Bunker, and McLean.⁶

Due to the selection rule $\Delta K_a = 0$, we could determine only the difference $A' - A''$, and not the values of A' and A'' separately. Other K related parameters such as δ_K were likewise undetermined, and the differences between the ground and excited states for these parameters were undetermined in the fit.

As in the case of CH_2 ,³ the splittings due to the unpaired spins were dominated by the spin-spin interaction; the D constant was about two orders of magnitude greater than any of the spin-rotation parameters ϵ_{ii} . We also found that ϵ_{cc} was greater than ϵ_{bb} , in contrast to CH_2 , for which $\epsilon_{bb} \approx \epsilon_{cc}$. No significant differences between ground and excited state fine structure constants were determined in the fit. These constants are roughly a factor of 2 to 4 larger than NH_2^+ than in CH_2 , similar to the ratio of spin-orbit interactions in C and N^+ ($13\text{--}16$ vs $41\text{--}49 \text{ cm}^{-1}$),²⁰ CH and NH^+ (28 cm^{-1} vs 82 cm^{-1}),^{21,22} and CH_3 and NH_3^+ (0.01 vs 0.04 cm^{-1}).²³ The spin-rotation interaction in these molecules arises from a second order spin-orbit mechanism, and since the unpaired electron density is predominantly on the heavy atom, one expects the same relative magnitudes for spin-orbit or spin-rotation constants in the isoelectronic hydride series.

IV. DISCUSSION

The observed lines have been fit to a standard asymmetric rotor Hamiltonian. The possibility of large amplitude bending raises the question of whether this approach is valid. As this molecule approaches linearity, the energy level expression for the asymmetric rotor approaches that of the

linear molecule, but the quantum numbers and derived constants must be transformed, as indicated in Table III. Thus, the ambiguity lies not so much in the fit, as in the interpretation of the derived constants. For example, the $\nu_2 = 0$, $K_a = 1$ bent molecule state transforms to the $\nu_2^1 = 1^1$ linear molecule state. The value of the A constant approaches the bending vibrational frequency of the linear molecule limit. The angular momentum about the a axis, K_a , correlates with the vibrational angular momentum l in the linear case, and the K -type doubling can be considered as l -type doubling in the linear molecule limit.

Although the spectrum can be fit to either a linear or an asymmetric rotor Hamiltonian, the large amplitude of the bending vibration prevents us from determining the molecular structure from the observed constants. For example, if we assume NH_2^+ is a rigid rotor, we estimate using B'' and C'' (ignoring the inertial defect) that $r_0 = 1.029 \text{ \AA}$ and $\theta_0 = 165^\circ$, compared to $r_e = 1.0338 \text{ \AA}$ and $\theta_e = 153.17^\circ$ calculated by Jensen, Bunker, and McLean. Such a discrepancy in the bond angle is rare for small triatomics, and indicates that vibrational averaging is important in this ion.

TABLE III. Correlation between quantum numbers and constants in the transformation from asymmetric rotor to linear molecule energy level expressions.

Asymmetric rotor	Linear molecule
J	J
N	N
K_a	l
$\frac{1}{2}(B + C)$	B
$\frac{1}{2}(B - C)$	q
Δ_N	D
Φ_N	H
$\frac{1}{3}(\epsilon_{aa} + \epsilon_{bb} + \epsilon_{cc})$	γ
$A - \frac{1}{2}(B + C) + \Delta_K + \dots$	$\nu_0, \nu_2 = 1$

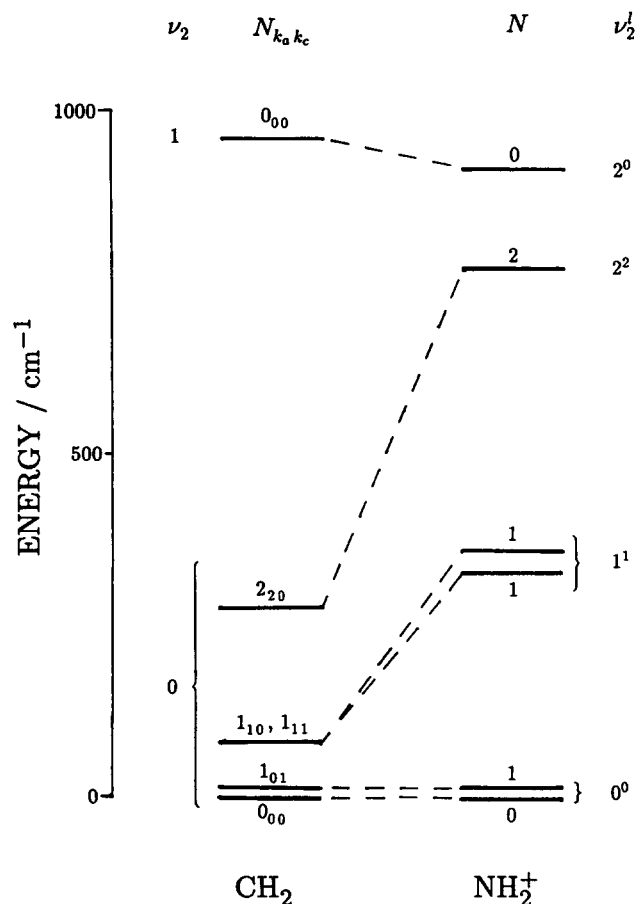


FIG. 4. Comparison of observed CH_2 energy levels (from Ref. 4) labeled with asymmetric rotor quantum numbers, and predicted NH_2^+ levels (from Ref. 6), labeled with linear molecule quantum numbers.

As seen in Fig. 4, the theoretical calculations indicate that NH_2^+ behaves like a badly perturbed linear molecule, while CH_2 is more appropriately described by an asymmetric top molecule. Perhaps the most important parameter for quantifying the quasilinear nature of NH_2^+ is the rotational constant A , but we have been unable to determine it for either state. We have attempted to find the ν_2 band of NH_2^+ without success. We do, however, have indirect estimates of A which are consistent with the large theoretical value of 280 cm^{-1} predicted by Bunker, Jensen, and McLean. We obtain $A'' = 203 \text{ cm}^{-1}$ from an estimated inertial defect $\Delta^0 = 0.08432 \text{ amu } \text{Å}^2$, using experimental vibrational frequencies and $\zeta_{23}^{(c)} \approx 1$. This estimate is crude, because we use $\nu_2 = 840 \text{ cm}^{-1}$ in the calculation without taking into account the low barrier in the bending potential. The approximation assumed in this calculation²⁴ breaks down in NH_2^+ . A value of $A \approx 280 \text{ cm}^{-1}$ is also consistent with the observed

intensity ratio between $K_a = 0$ and $K_a = 1$ lines, if we assume a rotational temperature of 200 K, a value typically found in the positive column of liquid nitrogen-cooled discharges. Recently, Herzberg has communicated to us evidence that A is much lower than our indirect estimates. He has found that an optical spectrum which he assigns to NH_2^+ gives a value of $A \approx 90 \text{ cm}^{-1}$.⁷ A definitive analysis of Herzberg's bands, or observation of either pure rotational transitions or the ν_2 band, would directly yield A'' , and provide experimental information on the bending potential.

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