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COMMUNICATIONS

Infrared studies of molecular ions. I. The ν_3 band of NH_4^+

Mark W. Crofton and Takeshi Oka

Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, Illinois 60637

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Recently Gudeman, Begemann, Pfaff, and Saykally have developed a powerful technique for spectroscopy of molecular ions using an ac discharge cell, and applied it successfully to the observation of the ν_1 band of HCO^+ and HN_2^+ .² In this method, the alternating Doppler shifts of spectral lines due to the drift velocities of molecular ions are used for phase sensitive detection thus discriminating the ion lines from much stronger neutral lines. The existence of a sufficiently large Doppler shift for modulation has been recently demonstrated in a dc discharge.³ In this paper we report our application of this method to the observation of the triply degenerate ν_3 fundamental vibration rotation band of the ammonium ion NH_4^+ .

The discharge cell was similar in design to that used by Gudeman *et al.* but without liquid nitrogen cooling. We used a $\sim 1/1$ NH_3 - H_2 gas mixture and applied a 4 kHz square wave voltage of ~ 6 kV p - p over the discharge length of 80 cm. The current density was typically 200 mA/cm² rms. A difference frequency laser system⁴ was used as the frequency tunable infrared source. Mixing the radiations of an Ar laser and a ring dye laser in a temperature controlled LiNbO_3 crystal produces ~ 20 μW of tunable infrared radiation in the region of 2.2–4.2 μm .^{5–7}

Since the proton affinity of NH_3 is 8.9 eV, NH_4^+ is a very stable molecular ion well known to mass spectroscopists. The spectroscopic studies, however, were limited to solid salt⁸ until recently when Schwarz⁹ observed the 25 cm⁻¹ resolution gas phase spectrum and located the vibrational frequency ν_0 at 3335 cm⁻¹. Based on Schwarz's observation and recent *ab initio* calculations,^{10,11} we searched for the NH_4^+ absorption lines in the region of 3400–3200 cm⁻¹. The identification of the NH_4^+ lines was made possible from the characteristic tetrahedral patterns of the P and R branch lines. Examples of the observed tetrahedral patterns are shown in Fig. 1. So far 150 lines have been measured and assigned to the P , Q , and R transitions up to $J=10$. In addition to the NH_4^+ lines we have observed several lines of H_3^+ , HN_2^+ , and some unassigned ionic species. The absorption lines of NH_3 , which is probably 10^6 times more abundant than NH_4^+ , also appeared but as a distorted first derivative shape.

The observed P and R branch transition frequencies for low J are listed in Table I. While we have not yet done the extensive least square fitting of the spectrum using the full diagonalization,¹² we can accurately determine the most fundamental vibration and rotation constants from the low J spectrum. We used the basic vibration-rotation energy form given by Hecht¹³:

$$W = \nu_0 + B'J^2 - 2(B'_\zeta)'J \cdot 1 - D_\zeta J^4 + Z_{t0pp33}(\text{tensor}) + F_{t0pp33}(\text{tensor})$$

for the ν_3 state. The molecular constants determined from the observed frequencies are listed in Table II. These constants give the observed minus calculated fre-

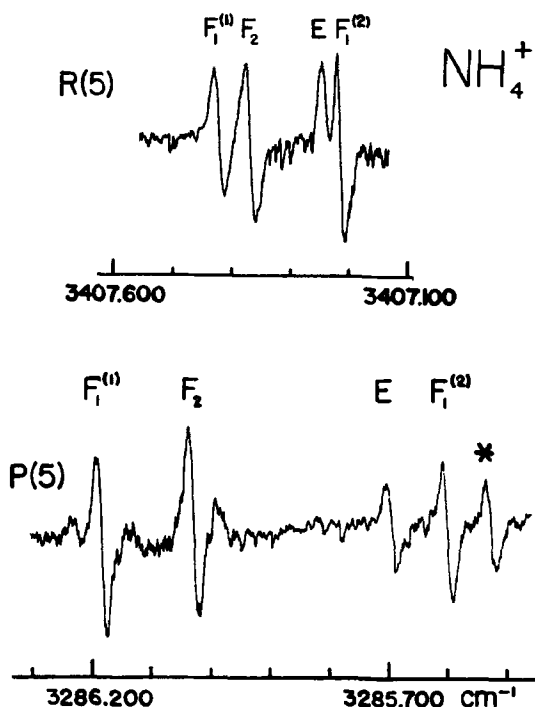


FIG. 1. The $R(5)$ and $P(5)$ transitions of NH_4^+ , showing the tetrahedral pattern. The $R(17)$ line (Ref. 2) of HN_2^+ , denoted by an asterisk, appears in the $P(5)$ trace. A time constant of 3 s was used.

TABLE I. Observed frequencies of the ν_3 fundamental band of NH_4^+ .

Assignment		Frequency (cm^{-1}) ^a	Obs. - calc. ($\times 10^3$)
R(4)	A_1	3396.860	0
	F_1	3396.817	2
	E	3396.786	1
R(3)	F_2	3396.699	7
	F_1	3386.172	-1
	F_2	3386.127	-6
R(2)	A_2	3386.081	-2
	E	3375.421	4
	F_2	3375.403	4
R(1)	F_1	3364.573	8
R(0)	A_1	3353.634	14
Q(1)	F_1	3342.477	4
P(2)	E	3320.239	10
	F_2	3320.150	0
P(3)	F_1	3308.937	7
	F_2	3308.809	10
	A_2	3308.628	-7
P(4)	A_1	3297.653	-6
	F_1	3297.528	2
	E	3297.437	-2
	F_2	3297.184	9

^aThe uncertainty of measurement is $\leq 0.005 \text{ cm}^{-1}$.

quencies listed in Table I. The standard deviation for the fitting of the P and R branch lines was $\Delta = 0.007 \text{ cm}^{-1}$. For the Q branch lines, Δ was about ten times larger; this could be reduced by using a different value of $B' - B_0$.¹⁴

Although the separation of ν_0 , B' , $(B\zeta)'$, and B_0 has to await observation of weaker forbidden transitions, their values were derived as shown in Table II based on the value of $\zeta_3 = 0.048 \pm 0.005$ calculated from the *ab initio* force field.¹⁰ The procedure used by Kuchitsu and Bartell¹⁵⁻¹⁷ to determine r_e for CH_4 was used to obtain the equilibrium bond length of NH_4^+ . The agreement of ν_0 and r_e with the theoretical values given by Yamaguchi and Schaefer¹⁰ is very good. Our result also confirms the expected tetrahedral structure of NH_4^+ .

These results together with those of Gudeman *et al.*^{1,2} show that the ac modulation method developed by Saykally and his colleagues can be applied to a variety of molecular ions. *Ab initio* predictions of the vibrational frequencies and structure of molecular ions, in particular protonated ions such as CH_5^+ , H_2CN^+ , H_3C_2^+ , etc., are eagerly awaited.

We would like to thank Nathan N. Haese for discussion

TABLE II. Molecular constants of NH_4^+ .

Observed constants ^a			
$\nu_0 - 2(B\zeta)'$	3342.573 (21) cm^{-1}	Z_t ^b	$-7.59 (80) \times 10^{-3}$
$B' - (B\zeta)'$	5.523 53 (70)	F_t	$-1.6 (11) \times 10^{-4}$
$B' - B_0$	-0.049 97 (19)	D_s	$7.2 (32) \times 10^{-6}$
Derived constants [$\zeta = 0.048(5)$ assumed]		Theoretical ^c	
ν_0	3343.130 (56) cm^{-1}		3379 cm^{-1}
B_0	5.852 (31) cm^{-1}		
r_0	1.035 (3) \AA		
r_e	1.026 (5) \AA		1.0215 \AA

^aNumbers in parentheses for the observed constants are three times standard deviation. For the derived constants the 10% error estimate of the assumed ζ value has been included.

^bThe values of smaller parameters may not be accurate because of our neglect of higher order terms.

^cReference 10.

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¹C. S. Gudeman, M. H. Begemann, J. Pfaff, and R. J. Saykally, *Phys. Rev. Lett.* **50**, 727 (1983).

²C. S. Gudeman, M. H. Begemann, J. Pfaff, and R. J. Saykally, *J. Chem. Phys.* **78**, 5837 (1983).

³N. N. Haese, F. S. Pan, and T. Oka, *Phys. Rev. Lett.* **50**, 1575 (1983).

⁴A. S. Pine, *J. Opt. Soc. Am.* **64**, 1683 (1974); **66**, 97 (1976).

⁵T. Oka, *Phys. Rev. Lett.* **45**, 531 (1980).

⁶P. Bernath and T. Amano, *Phys. Rev. Lett.* **48**, 20 (1982).

⁷M. Wong, P. Bernath, and T. Amano, *J. Chem. Phys.* **77**, 693 (1982).

⁸G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1949).

⁹H. A. Schwarz, *J. Chem. Phys.* **72**, 284 (1980).

¹⁰Y. Yamaguchi and H. F. Schaefer III, *J. Chem. Phys.* **73**, 2310 (1980).

¹¹D. A. Dixon (private communication).

¹²D. L. Gray, A. G. Robiette, and A. S. Pine, *J. Mol. Spectrosc.* **77**, 440 (1979).

¹³K. T. Hecht, *J. Mol. Spectrosc.* **5**, 355 and 390 (1960).

¹⁴W. L. Barnes, J. Susskind, R. H. Hunt, and E. K. Plyler, *J. Chem. Phys.* **56**, 5160 (1972).

¹⁵K. Kuchitsu and L. S. Bartell, *J. Chem. Phys.* **36**, 2470 (1962).

¹⁶Y. Morino, K. Kuchitsu, and T. Oka, *J. Chem. Phys.* **36**, 1108 (1962).

¹⁷D. L. Gray and A. G. Robiette, *Mol. Phys.* **37**, 1901 (1979).