

OBSERVATION OF THE LOWEST ROTATIONAL TRANSITION OF NH^+ WITH RESOLVED HYPERFINE STRUCTURE

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Received 8 September 1986; in final form 9 October 1986

The rotational transition $J=3/2 \leftarrow 1/2$ of the $X^2\Pi$, $v=0$ ground state of NH^+ has been observed with resolved hyperfine structure. Spectra were recorded using a sub-millimeter tunable laser sideband spectrometer. Accurate hyperfine constants were obtained which show good agreement with ab initio calculated constants.

1. Introduction

In this Letter we report the first observation of the lowest rotational transition of NH^+ . This molecular ion is expected to be present in interstellar clouds and comets [1], but has not yet been detected. Optical laboratory spectra of NH^+ were first observed by Lunt et al. [2]. Feast [3] re-examined these bands and identified them as arising from a $C^2\Sigma^+ - X^2\Pi$ transition. Additional transitions were observed by Colin and Douglas [4] ($A^2\Sigma^- - X^2\Pi$ and $B^2\Delta - X^2\Pi$), by Krishnamurthy and Saraswathy [5] ($C^2\Sigma^+ - X^2\Pi$) and by Kusunoki and Ottinger [6] ($B^2\Delta - X^2\Pi$). It was found that the $X^2\Pi$ ground state is perturbed by a low-lying $^4\Sigma^-$ state [3-5]. This interaction was theoretically studied by Wilson [7] and Farnell and Ogilvie [8]. Recently Kusunoki et al. [9] presented ab initio calculations on electronic doublet states of NH^+ and Kristiansen and Veseth [10] calculated the hyperfine constants for the $X^2\Pi$ state of NH^+ .

In the present work we have studied the rotational transition $J=3/2 \leftarrow 1/2$ in the $X^2\Pi$, $v=0$ ground state. This transition at 34 cm^{-1} was detected using the laser sideband technique. The hyperfine structure due to both nitrogen and hydrogen nuclei was resolved. This yielded most of the hyperfine parameters for this ion and allowed a comparison with ab initio calculations.

2. Experimental details

Spectra were recorded with the same absorption spectrometer as used in our studies of OH^+ [11] and OD^+ [12]. Tunable radiation in the sub-millimeter region is generated by mixing HCN laser radiation (891 and 964 GHz) with tunable microwave radiation from klystrons (50-110 GHz) in Schottky-barrier diodes. By using fundamental and second-harmonic frequencies of the klystrons, a frequency range from 700 to 1200 GHz can be covered with a maximum power of $\approx 50 \mu\text{W}$. In the present investigation measurements were performed at 1012 and 1019 GHz with a typical sideband power of $5 \mu\text{W}$. The NH^+ ions were produced in a hollow cathode dc discharge tube [13]. The cathode tube was cooled with liquid nitrogen, which proved to be essential for observation of the signals. A fast-flowing mixture of He with $\approx 2\%$ admixture of equal amounts of H_2 and N_2 was used. The total pressure in the pumping line just below the absorption cell was $\approx 5 \times 10^{-2}$ mbar and the discharge current was ≈ 500 mA. Modulation of the discharge current at ≈ 300 Hz was applied for phase sensitive detection. Unfortunately this type of modulation causes periodic variations in the background signal [12]. When necessary, these were reduced by subtracting scans without H_2 in the discharge mixture and, consequently, without signals from NH^+ . Efforts to produce detectable amounts of NH^+ in a discharge of He and NH_3 [2-5] with a

water-cooled hollow cathode were unsuccessful. Signals were very sensitive to the presence of a small magnetic field longitudinal to the discharge, indicating that they arise from a free radical or ionic species.

3. Theory

From the ratio $A/B \approx 5$ of the spin-orbit constant A and the rotational constant B in the $X^2\Pi$ ground state of NH^+ it follows that there is a considerable degree of mixing between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ ladders, which affects the splitting of the hyperfine levels. The two hyperfine-free frequencies of both parity components of the $J=3/2 \leftarrow 1/2$ transition are however insufficient to determine any of the rotational, spin-rotation or A -doubling parameters of NH^+ . For the calculation of the hyperfine structure we therefore used the rotational, spin-orbit, spin-rotation and A -doubling parameters obtained by Brown [14] from a fit of all available spectroscopic data for NH^+ .

The magnetic hyperfine and quadrupole interactions in the $X^2\Pi$ state are due to the two nuclear spins: $I_N=1$ and $I_H=1/2$. We used the coupling scheme $\mathbf{J} + \mathbf{I}_N = \mathbf{F}_1$, $\mathbf{F}_1 + \mathbf{I}_H = \mathbf{F}$. Both A -doublet levels of every rotational state split into six sublevels except for $J=1/2$ where there are four sublevels. Due to the selection rule $\Delta F=0, \pm 1$, seventeen transitions are possible in each parity component of the $J=3/2 \leftarrow 1/2$ transition. The hyperfine and quadrupole interactions of a nuclear spin I are described by the following Hamiltonians [15,16]:

$$H_{\text{hfs}} = aI_zL_z + b_F\mathbf{I} \cdot \mathbf{S} + \frac{1}{3}c(3I_zS_z - \mathbf{I} \cdot \mathbf{S}) + \frac{1}{2}d(e^{-2i\phi}S_+I_+ + e^{2i\phi}S_-I_-) \quad (1)$$

and

$$H_Q = eq_0Q(3I_z^2 - I^2)/4I(2I-1) + eq_2Q(e^{-2i\phi}I_+^2 + e^{2i\phi}I_-^2)/8I(2I-1), \quad (2)$$

where $b_F = b + \frac{1}{3}c$ and a, b, c and d are the Frosch and Foley [17] parameters. The constants eq_0Q and eq_2Q are the quadrupole coupling parameters. L and S are the resultant electronic orbital and spin angular momentum, respectively, ϕ is the electron orbital azimuthal coordinate with respect to the internuclear axis and $-e$ is the electron charge. Integration over ϕ of the $e^{\pm 2i\phi}$ terms and the ϕ -dependent part of

the electronic wavefunctions transforms these expressions into those of ref. [16]. These interactions can be considered as small perturbations on the fine structure Hamiltonian [18], describing rotational and A -doubling structure. Hyperfine matrix elements were calculated using eigenfunctions obtained from diagonalisation of this fine structure Hamiltonian based on symmetrised Hund's case (a) functions

$$|^2\Pi_{|\Omega|}JM_J \pm \rangle = 2^{-1/2}(|^2\Pi_{\Omega}JM_J \rangle \pm |^2\Pi_{-\Omega}JM_J \rangle). \quad (3)$$

The upper and lower sign refer to the different parity states labelled c and d respectively in ref. [4]. In this case the c states are the lower A -doublet states. The resulting eigenfunctions of the fine structure Hamiltonian for the c states are

$$|^2\Pi JM_J \rangle_c = \alpha_c(J)|^2\Pi_{1/2}JM_J + \rangle + \beta_c(J)|^2\Pi_{3/2}JM_J + \rangle \quad (4)$$

and for the d states

$$|^2\Pi JM_J \rangle_d = \alpha_d(J)|^2\Pi_{1/2}JM_J - \rangle + \beta_d(J)|^2\Pi_{3/2}JM_J - \rangle \quad (5)$$

with $\alpha_c(1/2) = \alpha_d(1/2) = 1$, $\beta_c(1/2) = \beta_d(1/2) = 0$ and $\alpha_c(3/2) = 0.91275$, $\beta_c(3/2) = 0.40852$, $\alpha_d(3/2) = 0.91020$, $\beta_d(3/2) = 0.41417$.

The hyperfine matrix elements (diagonal in J) form a 6×6 matrix consisting of two 1×1 and two 2×2 submatrices, except for $J=1/2$ where a 4×4 matrix with only one 2×2 submatrix is obtained. Diagonalisation of this matrix gives the hyperfine energies of each state $|^2\Pi JM_J \rangle_{c,d}$ expressed in terms of the Frosch and Foley a, b, c and d constants for the magnetic hyperfine interaction of both nuclei and in terms of eq_0Q_N and eq_2Q_N for the quadrupole interaction of the nitrogen nucleus.

4. Results and discussion

We observed seven hyperfine components of the ($J=3/2, d$) \leftarrow ($J=1/2, d$) transition at 1019.2 GHz and five hyperfine components of the ($J=3/2, c$) \leftarrow ($J=1/2, c$) transition at 1012.5 GHz. The signal-to-noise ratio was typically ≈ 5 at $RC=1$ s for the

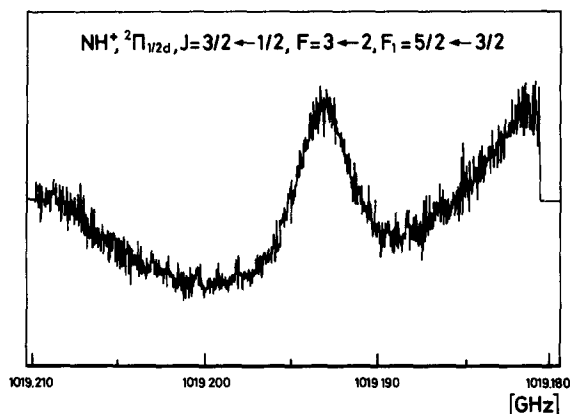


Fig. 1. Recording of the $(F_1, F) = (5/2, 3) \leftarrow (3/2, 2)$ component of the $R_{1d}(1/2)$ transition after 40 scans with an RC time of 1 s. The curved baseline is due to interfering reflections in the experimental apparatus [12].

strongest transitions. Fig. 1 shows a recording of the strongest hyperfine component ($F_1 = 5/2 \leftarrow 3/2$, $F = 3 \leftarrow 2$) of the $R_{1d}(1/2)$ transition at 1019.2 GHz. The observed linewidth is ≈ 4 MHz. Most of the weaker components could only be seen by using signal-averaging techniques. The experimental frequencies of the hyperfine components of the $R_{1d}(1/2)$ and $R_{1c}(1/2)$ transitions are listed in table 1. The assignment of the quantum numbers F_1 and F is based on a hyperfine spectrum and relative intensities [14] calculated with the ab initio hyperfine con-

stants of Kristiansen and Veseth [10]. It should be noted that F_1 is not a good quantum number and is only used for labeling the levels.

Because of the two nuclear spins there are, in principle, 12 parameters to be determined: the Frosch and Foley a , b , c and d constants for both nuclei, eq_0Q_N and eq_2Q_N for the nitrogen nucleus, and the two hyperfine-free frequencies $\nu_{0c}(J=3/2 \leftarrow 1/2)$ and $\nu_{0d}(J=3/2 \leftarrow 1/2)$ for both parity components. However, since the hyperfine matrix elements containing the a , b , and c constants are nearly equal for upper and lower A -doublet states (the difference between the calculated mixing coefficients for both parity states is very small), these three constants cannot be evaluated independently. Instead we introduce parameters abc_i and cba_i (where i refers to the two nuclei N and H), being linear combinations of a_i , b_i and c_i :

$$abc_i = 2[a_i - \frac{1}{2}(b_i + c_i)] , \quad (6)$$

$$cba_i = 3^{1/2} \alpha(3/2) \beta(3/2) b_i + \frac{1}{2} [\beta(3/2)]^2 [a_i + \frac{1}{2}(b_i + c_i)] , \quad (7)$$

with

$$\alpha(3/2) = \frac{1}{2} [\alpha_c(3/2) + \alpha_d(3/2)]$$

and

$$\beta(3/2) = \frac{1}{2} [\beta_c(3/2) + \beta_d(3/2)] .$$

The parameter abc_i and the second term in cba_i orig-

Table 1

Observed frequencies (in MHz) of the $R_1(1/2)$ transitions of NH^+ and deviations from the values obtained by a least-squares fit

$F_1, F' \leftarrow F_1, F$	Symmetry	Observed frequency	Obs. - calc.
3/2 2 1/2 1	d	1019366.0(1.5)	-0.19
3/2 1 1/2 1	d	1019361.5(1.5)	0.22
1/2 1 1/2 1	d	1019257.0(1.5)	0.20
1/2 0 1/2 1	d	1019251.0(2.0)	-0.19
5/2 2 3/2 1	d	1019233.0(1.3)	-0.06
5/2 3 3/2 2	d	1019193.1(1.2)	-0.07
3/2 2 3/2 2	d	1019020.9(1.5)	0.05
5/2 2 3/2 1	c	1012571.2(1.2)	-0.01
1/2 0 1/2 1	c	1012560.7(3.0) ^{a)}	-0.32
3/2 1 3/2 2	c	1012560.7(3.0) ^{a)}	-0.19
5/2 2 3/2 2	c	1012554.5(2.0)	0.11
5/2 3 3/2 2	c	1012524.1(1.2)	0.07
3/2 2 1/2 1	c	1012515.5(1.2)	-0.04

^{a)} Overlapping lines.

Table 2

Hyperfine parameters (in MHz) for the X $^2\Pi$, $v=0$ ground state of NH^+ . The errors given in parentheses correspond to one standard deviation

	This work	Ref. [10]
abc_N	301.9(4.5)	308.1
cba_N	61.9(1.6)	63.3
d_N	165.0(2.4)	171.2
eq_0Q_N	-9.6(6.5)	
eq_2Q_N	-37.2(9.8)	
abc_H	142.8(6.4)	131.0
cba_H	-51.4(2.0)	-51.3
d_H	41.7(3.3)	39.8

inate from matrix elements diagonal in $\Omega=1/2$ and $\Omega=3/2$ respectively. The first term in cba_i originates from matrix elements off-diagonal in Ω . The error introduced by averaging the mixing coefficients for both parity components is much smaller than the experimental uncertainties in the hyperfine splittings. The values of all parameters, resulting from a least-squares fit are listed in table 2. The differences between the observed frequencies and those calculated with the best-fit parameters are well within the experimental uncertainties, as can be seen in table 1. The experimentally obtained hyperfine parameters show excellent agreement with the ab initio calculated values of ref. [10]. This demonstrates the reliability of this kind of ab initio calculation for the evaluation of hyperfine parameters for the electronic ground state of diatomic open-shell molecules.

The hyperfine constants can be written in terms of averaged electron densities, in particular [19]:

$$d_N = \frac{2}{3} g g_N \mu_n \mu_B \langle \sin^2 \vartheta / r^3 \rangle_U, \quad (8)$$

$$q_2 = -3 \langle \sin^2 \vartheta / r^3 \rangle_T, \quad (9)$$

where the subscript U refers to unpaired electrons and T to all electrons and where g , g_N , μ_n and μ_B are the g factor for the free electron, the g factor for the nitrogen nucleus, the nuclear magneton and the Bohr magneton respectively. The symbols r and ϑ denote the spherical coordinates of the electrons with respect to the nitrogen nucleus and the internuclear axis. The electronic configuration of NH^+ in its X $^2\Pi$ ground state is $(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)$. Since the integration over the azimuthal angle ϕ yields zero for σ electrons, the averages over U and T in the expressions for d_N and q_2 both reduce to an average over the one unpaired π electron [20]. The values of $\langle \sin^2 \vartheta / r^3 \rangle$ calculated from d_N and q_2 are $19.2(0.3) \times 10^{-30} \text{ m}^{-3}$ and $21.5(5.7) \times 10^{-30} \text{ m}^{-3}$, respectively. The constants $Q_N = 2.66 \times 10^{-49} \text{ C m}^2$ and $g_N = 0.40365$ were taken from ref. [21]. The two values for the averaged electron densities are in good agreement.

In table 3 the hyperfine-free origins of both transitions are compared with the term values given by Colin and Douglas [4]; the agreement is good. The difference $\nu_{od}(3/2 \leftarrow 1/2) - \nu_{oc}(3/2 \leftarrow 1/2)$ represents the difference of the A -doubling separations in the $J=3/2$ and $J=1/2$ states. In case of NH^+ these separations are caused by interactions with the A $^2\Sigma^-$ and C $^2\Sigma^+$ states as well as with the low-lying a $^4\Sigma^-$ state as shown by Wilson [7]. There is good agreement with the previous experimental results of Colin and Douglas [4] and reasonable agreement with the theoretical value calculated by Wilson [7].

From the agreement of our observed frequencies with earlier experimental results and with ab initio calculations of the hyperfine parameters we conclude that we observed the NH^+ ion in its X $^2\Pi$ electronic and vibrational ground state. The high resolution of our spectrometer allowed us to resolve its hyperfine structure and to determine a set of hyperfine parameters.

Table 3

Hyperfine-free frequencies (in MHz) for the $R_1(1/2)$ transitions of NH^+

	This work	Ref. [4]	Ref. [7]
$\nu_{od}(3/2 \leftarrow 1/2)$	1019210.8(0.6)	1019295(300)	
$\nu_{oc}(3/2 \leftarrow 1/2)$	1012539.5(0.8)	1012100(300)	
$\nu_{od}(3/2 \leftarrow 1/2) - \nu_{oc}(3/2 \leftarrow 1/2)$	6671.3(1.0)	6566(430) ^{a)}	6069(380)

^{a)} Calculated by Wilson [7] from the experimental results of Colin and Douglas [4].

Acknowledgement

The authors wish to thank Messrs. E van Leeuwen, F. van Rijn and L. Hendriks for their excellent technical assistance. Dr. L. Veseth is acknowledged for sending us his unpublished ab initio calculations and Dr. J.M. Brown for making a prediction of the hyperfine splittings using the ab initio parameters.

References

- [1] A.A. de Almeida and P.D. Singh, *Astron. Astrophys.* 113 (1982) 199.
- [2] R.W. Lunt, R.W.B. Pearse and E.C.W. Smith, *Nature* 136 (1935) 32.
- [3] M.W. Feast, *Astrophys. J.* 114 (1951) 344.
- [4] R. Colin and A.E. Douglas, *Can. J. Phys.* 46 (1968) 61.
- [5] G. Krishnamurthy and M. Saraswathy, *Pramana* 6 (1976) 233.
- [6] I. Kusunoki and Ch. Ottinger, *J. Chem. Phys.* 80 (1984) 1872.
- [7] I.D.L. Wilson, *Mol. Phys.* 36 (1978) 597.
- [8] L. Farnell and J.F. Ogilvie, *J. Mol. Spectry* 101 (1983) 104.
- [9] I. Kusunoki, K. Yamashita and K. Morokuma, *Chem. Phys. Letters* 123 (1986) 533.
- [10] P. Kristiansen and L. Veseth, *J. Chem. Phys.* 84 (1986) 6336.
- [11] J.P. Bekooy, P. Verhoeve, W.L. Meerts and A. Dymanus, *J. Chem. Phys.* 82 (1985) 3868.
- [12] P. Verhoeve, J.P. Bekooy, W.L. Meerst, J.J. ter Meulen and A. Dymanus, *Chem. Phys. Letters* 125 (1986) 286.
- [13] F.C. van den Heuvel and A. Dymanus, *Chem. Phys. Letters* 92 (1982) 219.
- [14] J.M. Brown, private communication.
- [15] G.C. Dousmanis, T.M. Sanders Jr. and CH. Townes, *Phys. Rev.* 100 (1955) 1735.
- [16] J.M. Brown, I. Kopp, C. Malmberg and B. Rydh, *Physica Scripta* 17 (1978) 55.
- [17] R.A. Frosch and H.M. Foley, *Phys. Rev.* 88 (1952) 1337.
- [18] J.M. Brown, E.A. Colbourn, J.K.G. Watson and F.D. Wayne, *J. Mol. Spectry.* 74 (1979) 294.
- [19] J.P. Bekooy, W.L. Meerts and A. Dymanus, *J. Mol. Spectry.* 102 (1983) 320.
- [20] W.L. Meerts and A. Dymanus, *Can. J. Phys.* 53 (1975) 2123.
- [21] C.M. Lederer and V.S. Shirley, *Table of isotopes*, 7th Ed. (Wiley, New York, 1978).