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Vibrational dependence of the hyperfine quadrupole constant in $^{14}NH_3$ observed by saturated absorption spectroscopy

by M. OUHAYOUN, C. J. BORDÉ
Laboratoire de Physique des Lasers, Université de Paris-Nord,
93430 Villetaneuse, France
and J. BORDÉ
Laboratoire de Physique Moléculaire et d'Optique Atmosphérique,
C.N.R.S., 91405 Orsay, France

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Infra-red saturation spectroscopy is a powerful method for investigating the hyperfine structure of vibration–rotation spectra [1–4]. Even for molecules such as NH_3, for which the hyperfine splittings in the lower vibrational state are well known from microwave spectroscopy [5], this technique now allows us to obtain the hyperfine splittings of the vibrationally excited states and it is therefore possible to study the specific influence of the vibration on the hyperfine structure. In this paper we report the first clear evidence for the dependence of the quadrupole coupling constant on the ν_2 vibration in $^{14}NH_3$ [6]. To demonstrate this effect unambiguously, we chose a transition with identical rotational quantum numbers in both states : $\Delta J = \Delta K = 0$. In this case the splitting of the various $\Delta F = 0$ hyperfine components is a direct consequence of the vibrational dependence of eQq. The transition selected is the asQ (8, 7)$^-$ line of NH_3 in close coincidence with the $P(13)$ emission line of the N_2O laser at 927·74 cm^{-1} [12]. Neglecting the magnetic interactions, the expected hyperfine spectrum for this transition consists of seventeen resonances : three main diagonal $\Delta F = 0$ components (see figure 1) ; four very weak $\Delta F = \pm 1$ satellite components ; eight Doppler-generated level crossings (cross-over peaks or three-level resonances) between $\Delta F = 0$ and $\Delta F = \pm 1$ sharing a common upper or lower level ; these have been observed before on both sides of the main components [4] ; two very weak Doppler-generated level crossings between $\Delta F = \pm 1$ components.

The spectrometer consists of two independent optical ring circuits [7, 8] illuminated by two N_2O lasers. One of these systems provides a reference frequency by locking the corresponding laser on a saturation resonance of CF_2Cl_2 [7], 3·97 MHz above the NH_3 frequency. The other laser is tuned across the NH_3 line to be studied, 7·4 MHz higher than the N_2O line centre. The beat note between these two lasers was used only for the frequency calibration of the spectrum but shall be used in the future for frequency offset-locking the tunable laser [2]. Liquid-nitrogen cooled Hg–Cd–Te crystals (bandwidth $\geqslant 50$ MHz) are used both for this beat note and for the detection of the saturated absorption signals. To achieve optical isolation of each laser, perpendicular linear polarizations are used for the counter-propagating beams in each ring. This results in two different selection rules $\Delta M_F = 0$ or $\Delta M_F = \pm 1$ for the two waves in the absorber and consequently only Doppler-generated level crossings can occur.

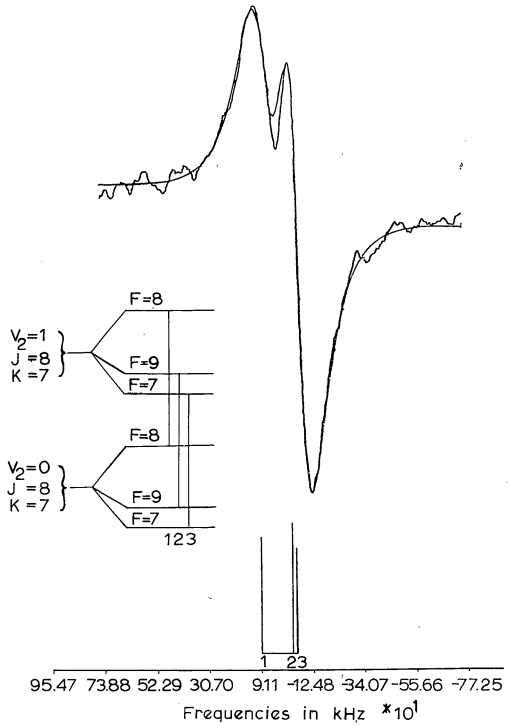

Figure 1. Derivative spectrum of the $\Delta F=0$ quadrupole components of the $asQ(8, 7)$ of the ν_2 band in $^{14}NH_3$ and theoretical spectrum for $\delta(eQq)=-350$ kHz and width $=100$ kHz HWHM ($P_{NH_3}=10^{-3}$ torr). Frequency increases towards the left.

In the absence of Stark or Zeeman effects all of the possible three-level resonances between M_F states have the same frequency, for each of the 17 hyperfine transitions discussed above.

Figure 1 shows the part of the spectrum corresponding to the $\Delta F=0$ central components obtained by frequency modulation of the laser and phase-sensitive detection. This spectrum exhibits a partly resolved structure which can result from a change in the quadrupole coupling constant

$$\delta(eQq)=eQq_{\text{upper}}-eQq_{\text{lower}}.$$

Each $\Delta F=0$ component is frequency shifted by the quantity

$$\delta\nu_F=\delta(eQq)[3K^2/J(J+1)-1]f(I, J, F),$$

where $f(I, J, F)$ is Casimir's function [5]. In first approximation the corresponding intensity is proportional to

$$I_F=\sum_{M_F,\,\epsilon=\pm1}|\langle F, M_F|\mu_Z|F, M_F\rangle|^2|\langle F, M_F|\mu_X|F, M_F+\epsilon\rangle|^2$$
$$\propto(2F+1)[2F(F+1)+1][F(F+1)+J(J+1)-2]^4/[F(F+1)]^3,$$

where μ_X and μ_Z are the components of the dipole moment along the fixed X and Z axes chosen along the polarization directions of the two beams.

Figure 2. Spectrum of figure 1 recorded with a smaller transit-time broadening and theoretical spectrum for $\delta(eQq) = -350$ kHz and width = 27 kHz HWHM ($P_{NH_3} = 2 \times 10^{-4}$ torr).

A theoretical spectrum was calculated using the two formulae above and a lorentzian derivative for the line shape. The best fit was obtained for a half-width at half-maximum (HWHM) equal to 100 kHz and for $\delta(eQq) = (-350 \pm 35)$ kHz. The sign of this last quantity agrees with the predictions of *ab initio* calculations [10].

It is now well-established [2, 9, 11] that the resolving power in saturation spectroscopy is essentially limited by transit-time effects resulting either from an insufficient beam diameter or from a poor quality of the wave fronts. A preliminary attempt to expand the beam further has resulted in an increase of resolution as illustrated by the spectrum of figure 2. Unfortunately, a failure of the reference laser has prevented us from obtaining a precise frequency calibration for this new spectrum. The calculated spectrum obtained with the previous value of $\delta(eQq)$ is found to be in excellent agreement with the experimental data for a width equal to 27 kHz (HWHM). This is still far from the potential 1 kHz [11] obtainable from our new 30 cm diameter optical system. We therefore expect to get considerably more information about the electric and magnetic hyperfine structure of this ammonia line in the near future.

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