

IR Diode Laser Measurements of the $\text{NH}_3(\nu_2)$ Band at Different Temperatures

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Abstract. A tunable IR diode laser system has been used to measure the temperature dependence of the line strength and the pressure dependence of the nitrogen broadened linewidth of the $aQ(6,6)$ and $aQ(7,7)$ ammonia absorption lines up to temperatures of 660 K. The behavior of the line strength and the pressure dependence of the linewidth coincide with the theoretical prediction while the temperature dependence of the linewidth differs significantly from the predictions of the hard core model.

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The ammonia molecule has been subject of many spectroscopic investigations. In particular the line positions of the ν_2 band have been measured with high accuracy and can be used almost as a calibration standard [1–7]. But up to now data on the line strength and width exist only for room temperature [1, 8–11]. Since ammonia has become of increasing interest not only in astrophysics and as a participant in the photochemistry of the atmosphere, but also as a pollutant emerging from industrial processes [8, 12–18], it is desirable to extend the temperature range investigated.

In this paper we report measurements on the line strength of the $aQ(6,6)$ and the $aQ(7,7)$ ν_2 band absorption lines up to 660 K. The nitrogen broadened width of the $aQ(6,6)$ line has been measured up to 650 K. The data were obtained by using standard absorption spectroscopy with a tunable diode laser system and a heated gas cell. To provide the option of concentration measurements by differential absorption techniques the lines were selected according to the criteria of strong absorbances and lack of interferences with CO_2 or H_2O . This choice was restricted to the spectral range covered by the laser diode used.

A computer simulation of the spectrum between 925 cm^{-1} and 928 cm^{-1} of a mixture of 0.015 atm cm H_2O , 0.015 atm cm CO_2 , 0.002 atm cm N_2O , and 1×10^{-6} atm cm NH_3 diluted in pure nitrogen at STP

is shown in Fig. 1, upper trace. The lower trace is the absorbance due solely to NH_3 . The calculation is based on the data of the AGFL compilation [10]. It confirms that the selected lines do lie in a suitable kind of atmospheric window.

Experimental

The experimental set up is shown schematically in Fig. 2. The diode laser system was built by Müttek GmbH (Herrsching). It consists of a closed cycle helium refrigerator, a high precision current supply and the PbSe semiconductor laser diodes. The cold head contained up to 4 diodes (Müttek, MDS 2040), which could be selected by means of an adjustable sledge. The diodes temperature ranged between 80 K and 90 K, depending on the diode used and the wavelength desired. The diode laser beam was collimated and focussed on a monochromator (Czerny Turner, blaze at $11.9\text{ }\mu\text{m}$), which was used for mode separation if necessary and to roughly determine the absolute wavelength. The relative wavelength scale was established by means of a Ge etalon (free spectral range = 0.049 cm^{-1}) inserted into the beam. The accurate absolute wavelength was determined by using the NH_3 fingerprint spectrum as a calibration standard [1]. After the monochromator the beam passed

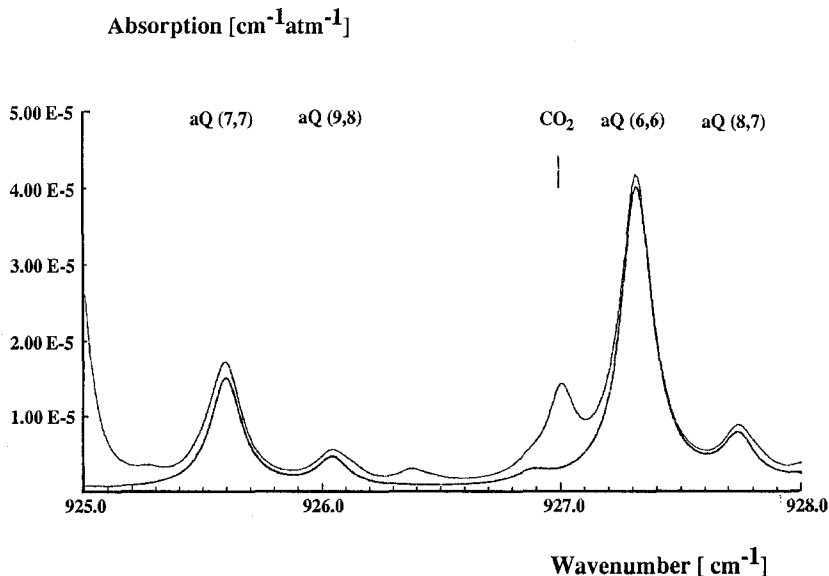


Fig. 1. Computer generated absorption spectrum between 925 cm^{-1} and 928 cm^{-1} for $1 \times 10^{-6}\text{ atm cm NH}_3$ (lower trace) and for $1 \times 10^{-6}\text{ atm cm NH}_3$ with interferences of $0.015\text{ atm cm H}_2\text{O}$, 0.015 atm cm CO_2 , and $0.002\text{ atm cm N}_2\text{O}$ at STP (upper trace)

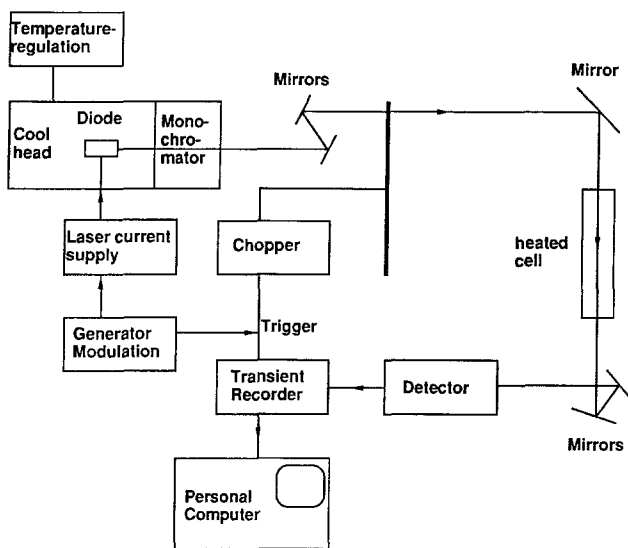


Fig. 2. Experimental set up

through the heatable gas cell and was then focussed on a liquid nitrogen cooled HgCdTe detector (Infrared Associates, HCT 70). Its electrical signal was preamplified and recorded with a transient recorder (Krenz, TRC 2000). A desk top calculator (HP 9800) was used for data acquisition.

The diode current was modulated by an external saw-tooth generator (Krohn-Hite KH 5100B), which also provided a reference for the transient recorder. A chopper, synchronised to the saw-tooth generator and phase adjusted so as to alternately transmit and block a full scanned ramp, defined the zero transmittance detector signal.

The gas cell consisted of a quartz tube with carefully polished grindings at the ends. KCl windows were fitted to these and tightened with silicon grease. The cell length amounted to 19.5 cm ; it was enclosed in an oven, which had a length of 30 cm and was carefully isolated against heat losses. Thus the temperature

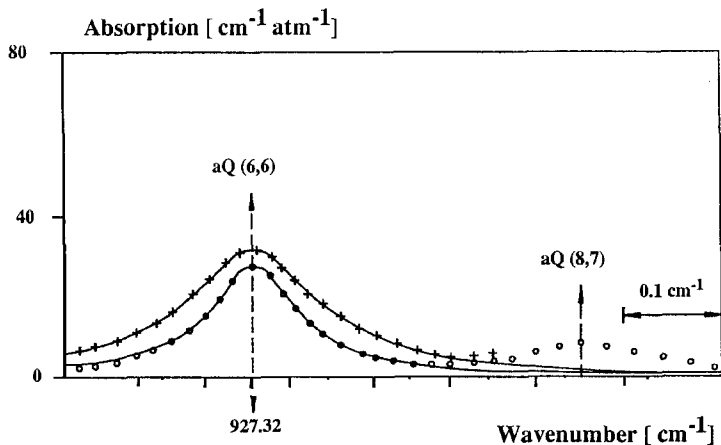


Fig. 3. Measured absorption profiles of the $aQ(6,6)$ line at 296 K (crosses) and 443 K (circles). For clarity the experimental data at room temperature have been drawn in only in the center of the $aQ(6,6)$ line, while the whole scan is shown at 443 K . The solid lines represent the fitted Lorentzian curves

variations along the cell axis were kept less than 5% at all temperatures. The temperature was measured in the oven center by a PtNi thermoelement. The cell was filled with well-defined amounts of ammonia ranging between 0.5 mbar and 2 mbar, and then filled up with pure nitrogen to the total pressure intended.

For data evaluation the measured absorption profile of each single scan was fitted with a Lorentzian curve whereby a constant zero absorption signal C has been taken into account:

$$\alpha = S\gamma_L\pi^{-1}(\Delta\nu^2 + \gamma_L^2)^{-1} + C \quad (1)$$

which is adequate since the pressure was always higher than 200 mbar [19]. S is the line strength and γ_L the pressure broadened halfwidth. The zero absorption signal, the line strength and the linewidth were used as fitting parameters and thus determined by the fitting procedure. As an example fitted absorption profiles of the $aQ(6,6)$ line for two different temperatures are shown in Fig. 3. The uncertainties of the measurements were mainly due to the errors in the determination of the absolute pressure and temperature, which amounted to 3% and 5% respectively.

Results

The experimental data of the $aQ(6,6)$ (open squares) and a $aQ(7,7)$ (filled circles) line-strength at different temperatures are shown in Fig. 4. The error of the absolute values is 10% while the relative variation is 5%.

The line-strength S of a single absorption line originating from a transition $J''K'' \rightarrow J'K'$ is theoretically described by [19,20]:

$$S = S_0\nu\nu_0^{-1} \exp(-hcE/kT)(1 - \exp(-h\nu/kT))gHQ^{-1}, \quad (2)$$

where S_0 is the total band-strength, $\nu = \nu(J''K'' \rightarrow J'K')$ is the wavenumber of the transition, ν_0 is the wavenumber of the bandcenter, $E = E(J''K'')$ is the energy of the lower level involved in the transition, $g = g(J''K'')$ is the statistical weight, $H = H(J''K'')$ is the Hönl-London factor and Q is the total partition function [20].

The data have been fitted with (2) using the band-strength as a fit parameter (solid lines in Fig. 4). The theoretical curves coincide very satisfactorily with the measured ones and the fits yield $S_0 = 637 \text{ atm}^{-1} \text{ cm}^{-2}$ from the $aQ(6,6)$ and $S_0 = 523 \text{ atm}^{-1} \text{ cm}^{-2}$ from the $aQ(7,7)$ line. This should not be regarded as an adequate determination of the band-strength since the data of only two lines have been taken into account. Nevertheless in Table 1 the mean value of $580 \text{ atm}^{-1} \text{ cm}^{-2}$ is compared to the results of other authors.

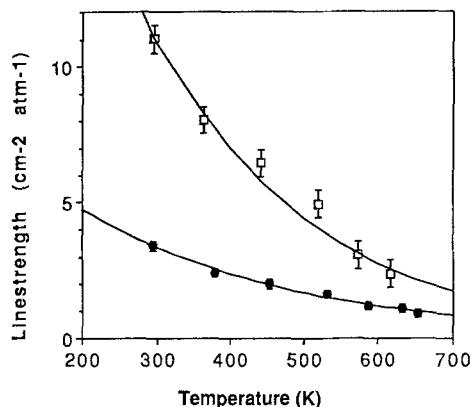


Fig. 4. Temperature dependence of ammonia line-strength: open squares – $aQ(6,6)$ line, filled circles – $aQ(7,7)$ line, solid curve – theoretical prediction of formula (2)

Table 1. Summary of ammonia ν_2 band intensity studies

S_0 atm ⁻¹ cm ⁻²	Author and year of publication
600	McKean and Schatz [21] (1956)
790	France and Williams [22] (1966)
549	Shimizu et al. [23] (1971)
600	Varanasi [24] (1972)
580	Taylor [9] (1973)
535	Krohn and Jones [25] (1981)
616	Koops et al. [26] (1983)
568	Kim [27] (1985)
580	Present work

Table 2. Summary of data of the $aQ(6,6)$ room temperature line-strength

S $aQ(6,6)$ atm ⁻¹ cm ⁻²		Author and year of publication
$aQ(6,6)$	$aQ(7,7)$	
10.02	3.79	Taylor [9] (1973)
10.15	3.8	AGFL compilation [10] (1982)
9.1	3.4	Urban [1] (1983)
11.0	3.4	Present work

Concerning the line-strength of the $aQ(6,6)$ and $aQ(7,7)$ lines comparable data exist only for room temperature. They are shown in Table 2. For both comparisons the agreement is good.

The measured pressure dependence of the nitrogen broadened linewidth of the $aQ(6,6)$ line at different temperatures is shown in Fig. 5. The linewidth at 650 K was measured only for a pressure of 707 mbar.

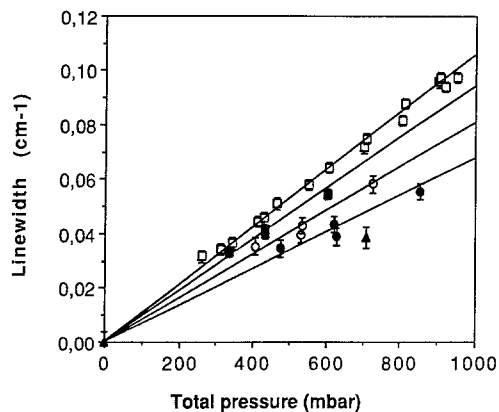


Fig. 5. Nitrogen broadened halfwidth of the $aQ(6,6)$ NH_3 absorption line. Open squares – 296 K, filled squares – 383 K, open circles – 481 K, filled circles – 575 K, triangle – 650 K, solid line – description by formula (3)

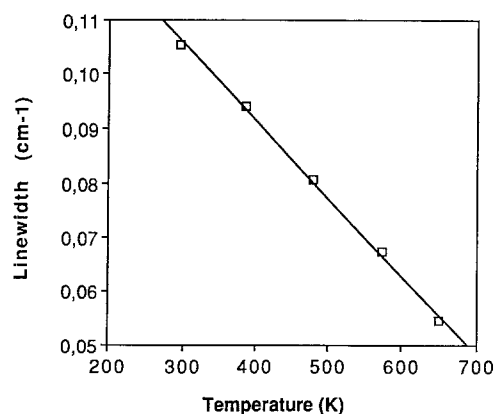


Fig. 6. Temperature dependence of the $aQ(6,6)$ linewidth: Open squares – experimental data, solid curve – fit with formula (5)

The pressure dependence at room temperature is very satisfactorily described by

$$\gamma = \gamma_0 P / P_0 \quad (3)$$

with $\gamma_0(aQ(6,6)) = 0.1054 \text{ cm}^{-1}$. The linewidth of the $aQ(7,7)$ line was measured at STP and found to be $\gamma(aQ(7,7)) = 0.119 \text{ cm}^{-1}$. Due to the lack of comparable data of the nitrogen broadened linewidth of the $aQ(6,6)$, $aQ(7,7)$ lines data for air or hydrogen broadened linewidths and those of other lines have also been listed in Table 3 as a reference.

The temperature dependence of γ_0 is shown in Fig. 6. Rather than by a function of the form

$$\gamma_0 = \gamma_0(T_0) (T_0/T)^\kappa \quad (4)$$

as predicted theoretically (with e.g. $\kappa = 0.5$ for the hard core model), the data are much better described by a fit with

$$\gamma_0 = a - bT. \quad (5)$$

Here we find $a = 0.149 \text{ cm}^{-1}$, $b = 1.43 \times 10^{-4} \text{ cm}^{-1}/\text{K}$. To understand the reasons for this behavior, further theoretical and experimental investigations of the temperature dependence of the line broadening process are needed.

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Table 3. Overview of pressure broadened linewidth at 1 atm of different perturbers. All data in units of cm^{-1}

Author	N_2	Air	H_2	Transition	Band
Hinkley [28] (1971)		0.079		$aQ(9,3)$	ν_2
Varanasi [24] (1972)			0.075	$aQ(J,K)$	ν_2
Margolis [29] (1974)			0.083	$aQ(6,6)$	$\nu_2 + \nu_3$
Margolis [29] (1974)			0.084	$aQ(7,7)$	$\nu_2 + \nu_3$
AGFL [10] (1982)		0.075		$aQ(6,6)$	ν_2
AGFL [10] (1982)		0.075		$aQ(7,7)$	ν_2
Baldacchini [11] (1988)	0.122	0.1	0.089	$aQ(1,1)$	ν_2
Baldacchini [11] (1988)	0.112	0.099	0.089	$aQ(2,2)$	ν_2
Baldacchini [11] (1988)	0.120	0.099	0.091	$aQ(6,4)$	ν_2
Present work	0.107			$aQ(6,6)$	ν_2
Present work	0.119			$aQ(7,7)$	ν_2

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