MEASUREMENT OF HYDROGEN- AND
SELF-BROADENED HALF-WIDTHS
OF AMMONIA AT 200 AND 300°K†

J. S. Margolis and Sunil Sarangi‡

Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91103,
U.S.A.

Abstract—The hydrogen- and self-broadened half-widths have been measured for the $(\nu_1 + \nu_2)$- and $(\nu_2 + \nu_3)$-bands of ammonia at 300 and 207°K. Measurement of hydrogen-broadened widths has been restricted to $J, K \leq 6$, but that of self-broadened widths is done for a few lines outside that range. Assuming a power-law dependence of half-width on temperature given by $\gamma(T) = \gamma(T_0)(T/T_0)^{\alpha}$, the average value of the index α for the lines measured is found to be 0·57 for hydrogen broadening.

INTRODUCTION

IN AN EARLIER publication,[1] the measurements of the room temperature hydrogen-broadened half-widths of the ammonia lines in the $(\nu_1 + \nu_2)$- and $(\nu_2 + \nu_3)$-bands were reported. The primary application of these measurements is to the interpretation of ammonia absorptions in the spectra of the outer planets, in particular, to Jupiter and Saturn where ammonia has recently been observed.[2,3] Since the atmospheres of these planets are cool in the regions where absorptions take place, it is necessary to know the temperature dependence of the broadening parameters. We have extended earlier measurements to lower temperatures and report here on low-temperature hydrogen- and self-broadening of ammonia lines.

EXPERIMENTAL

The spectra used in this study were all obtained in the second order of a 1·8 m Ebert-Fastie scanning spectrometer manufactured by the Jarrell-Ash Company. The grating used is $20 \times 7·5$ cm with 300 l/mm and blazed at 5·7 μ. The spectral resolution was 0·065 cm^{-1} FWHM and the spectral impurity was determined to be less than 1% over the range measured. The low-temperature cell has been described previously;[4] it is equipped with 2·5 cm dia. sapphire windows and is 17·2 cm long. The absorption cell itself is constructed of copper to reduce thermal gradients and is gold-plated internally to eliminate chemical reactions with the ammonia gas. The cell was gold-plated when it was found that chemical reactions of ammonia with the copper walls of the cell interfered with accurate measurements.

The half-widths were measured directly by applying an instrumental correction to the observed line profiles. We used essentially the KOSTKOWSKI–BASS[5] method by computing synthetic spectra; the appropriate instrumental function (which was Gaussian in our case) is convolved into Lorentzian lines of different half-widths and peak absorptions and the resulting half-widths of the distorted lines are noted. In this way, a family of curves is derived relating the measured half-widths to the real half-widths of the lines. This method and results have been given in an earlier publication.[4] The slit-function corrections in this investigation varied from 7 to 43%; most of the measurements were made with a slit-function correction of less than 15%. A more serious correction was that for self-broadening. It was decided, as a criterion for measuring the half-widths of the lines, to consider only lines whose peak absorption was greater than 10%. A typical medium strength line in the $(\nu_2 + \nu_3)$-band (the stronger of the two measured) has $S = 0·05$ cm^{-2} atm^{-1}.[6] Taking $\gamma = 0·065$ cm^{-1} as a minimum desirable measured half-width requires that there be at least 15 Torr of ammonia in the cell to achieve the required peak absorption. On the other hand, the total pressure had to be maintained as small as possible to avoid excessive blending with neighboring lines. The range of pressure used in hydrogen-

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‡NAS–NRC Resident Research Associate in tenure at the Jet Propulsion Laboratory.

broadening measurements was 20–30 Torr of ammonia and 180–300 Torr of hydrogen. Since the NH_3/H_2 ratio is around 10% and the pressure-broadening coefficient for ammonia self-broadening is roughly 5 times that for hydrogen-broadening, self-broadening accounts for roughly a third of the total width. The self-broadening width was accounted for by the relation $\gamma = \gamma^0[NH_3:NH_3]P_{NH_3} + \gamma^0[NH_3:H_2]P_{H_2}$, where $\gamma^0[NH_3:NH_3]$ and $\gamma^0[NH_3:H_2]$ are the self- and hydrogen-broadening coefficients respectively; P_{NH_3} and P_{H_2} are the partial pressures of ammonia and hydrogen respectively. Thus, self-broadening of ammonia at room temperature and at lower temperatures was also measured. The range of pressure used for self-broadening measurements was 60–110 Torr at low temperature and 80–120 Torr at room temperature.

It is fortunate that, in the low-temperature measurements, the decrease of population in the high J, K levels greatly simplified the spectrum and made it relatively easier to determine the continuum level. This measurement was needed to determine the exact position on the line profile for estimation of the half-width. However, the lower temperatures made it impossible to make measurements of the broadening for lines with $J > 6$. The ammonia rapidly condensed at temperatures below 200°K; therefore, the low-temperature measurements were made at 207°K.

Table 1. The self-broadening of NH_3 at 300 and 207°K (half-widths are given in cm^{-1} atm^{-1})

Line ($J_{K'}^{K''}$)	γ^0 (207°K)	γ^0 (300°K)	γ^0 (300°K) Ref. (6)	α
1_0	$0\cdot685 \pm 0\cdot042$	$0\cdot368 \pm 0\cdot003$	$0\cdot31$	$1\cdot67$
1_1				
2_0	$0\cdot722 \pm 0\cdot030$	$0\cdot339 \pm 0\cdot039$	$0\cdot27$	$2\cdot04$
2_1	$0\cdot659 \pm 0\cdot039$	$0\cdot411 \pm 0\cdot024$	$0\cdot38$	$1\cdot27$
2_2	$0\cdot862 \pm 0\cdot018$	$0\cdot584 \pm 0\cdot011$	$0\cdot53$	$1\cdot05$
3_0	$0\cdot722 \pm 0\cdot035$	$0\cdot393 \pm 0\cdot061$	$0\cdot25$	$1\cdot64$
3_1	$0\cdot599 \pm 0\cdot061$	$0\cdot353 \pm 0\cdot025$	$0\cdot32$	$1\cdot42$
3_2	$0\cdot742 \pm 0\cdot036$	$0\cdot452 \pm 0\cdot063$	$0\cdot44$	$1\cdot34$
3_3	$0\cdot979 \pm 0\cdot033$	$0\cdot604 \pm 0\cdot023$	$0\cdot55$	$1\cdot30$
4_0	$0\cdot549 \pm 0\cdot043$	$0\cdot367$	$0\cdot24$	$1\cdot08$
4_1	$0\cdot560 \pm 0\cdot035$	$0\cdot327$	$0\cdot29$	$1\cdot45$
4_2	$0\cdot664 \pm 0\cdot020$	$0\cdot459 \pm 0\cdot025$	$0\cdot38$	$1\cdot00$
4_3	$0\cdot840 \pm 0\cdot032$	$0\cdot534 \pm 0\cdot043$	$0\cdot47$	$1\cdot22$
4_4	$0\cdot930 \pm 0\cdot046$	$0\cdot600 \pm 0\cdot012$	$0\cdot56$	$1\cdot18$
5_0	$0\cdot593 \pm 0\cdot048$		$0\cdot23$	
5_1	$0\cdot509 \pm 0\cdot038$		$0\cdot28$	
5_2	$0\cdot650 \pm 0\cdot035$	$0\cdot389 \pm 0\cdot027$	$0\cdot35$	$1\cdot38$
5_3	$0\cdot732 \pm 0\cdot065$	$0\cdot407$	$0\cdot42$	$1\cdot58$
5_4	$0\cdot838 \pm 0\cdot031$	$0\cdot631$	$0\cdot50$	$0\cdot76$
5_5	$0\cdot833 \pm 0\cdot042$	$0\cdot595$	$0\cdot56$	$0\cdot91$
6_0	$0\cdot409 \pm 0\cdot032$	$0\cdot346$	$0\cdot21$	$0\cdot45$
6_1	$0\cdot543 \pm 0\cdot032$	$0\cdot367 \pm 0\cdot032$	$0\cdot27$	$1\cdot06$
6_2	$0\cdot548 \pm 0\cdot023$	$0\cdot383 \pm 0\cdot008$	$0\cdot34$	$0\cdot96$
6_3	$0\cdot704 \pm 0\cdot040$	$0\cdot438 \pm 0\cdot035$	$0\cdot40$	$1\cdot28$
6_4	$0\cdot679 \pm 0\cdot021$		$0\cdot46$	
6_5	$0\cdot791 \pm 0\cdot029$	$0\cdot312 \pm 0\cdot004$	$0\cdot51$	
6_6		$0\cdot665$	$0\cdot57$	
7_0				
7_1	$0\cdot413 \pm 0\cdot027$	$0\cdot286 \pm 0\cdot016$	$0\cdot26$	$0\cdot99$
7_2	$0\cdot425 \pm 0\cdot001$		$0\cdot31$	
7_3	$0\cdot587 \pm 0\cdot015$	$0\cdot385 \pm 0\cdot004$	$0\cdot37$	$1\cdot14$
7_4	$0\cdot619 \pm 0\cdot044$		$0\cdot41$	
7_5	$0\cdot747 \pm 0\cdot003$		$0\cdot46$	
7_6	$0\cdot653$		$0\cdot51$	
7_7	$0\cdot864 \pm 0\cdot031$		$0\cdot57$	
8_0	$0\cdot267 \pm 0\cdot062$		$0\cdot18$	
8_3	$0\cdot470 \pm 0\cdot042$	$0\cdot362 \pm 0\cdot023$	$0\cdot34$	$0\cdot70$
8_5	$0\cdot676$		$0\cdot42$	
8_6	$0\cdot728 \pm 0\cdot030$		$0\cdot47$	
8_7	$0\cdot783 \pm 0\cdot028$		$0\cdot52$	
8_8	$0\cdot886 \pm 0\cdot030$		$0\cdot56$	
9_3		$0\cdot348$	$0\cdot30$	
9_6	$0\cdot636 \pm 0\cdot049$		$0\cdot44$	
9_9	$0\cdot852 \pm 0\cdot021$		$0\cdot55$	

The temperature of the absorption cell was measured near the window with a copper–constantan thermocouple referred to an ice water bath. The maximum temperature difference along the cell was measured to be less than $2°K$. The pressure in the cold cell was directly measured with a Wallace & Tiernan absolute pressure gauge at room temperature, calibrated by an oil manometer. There was no observable pressure change during a scan.

RESULTS

The results of the self-broadening measurements at room temperature and low temperature are listed in Table 1. They are tabulated according to the J, K quantum numbers of the lower energy state in the transition without consideration of their parity or whether they originate in the $(\nu_1 + \nu_2)$- or $(\nu_2 + \nu_3)$-band. The measurement of the self-broadening of ammonia lines has also been carried out by VARANASI[7] and BENEDICT et al.[8] at room temperature. These were both done at lower resolution than used here. Benedict et al. smoothed their results and presented them so as to account for both upper and lower levels in the transitions. Since we have not distinguished between different branches of the bands we have included appropriate averages of these smoothed values in Table 1 for comparison. The errors given in Table 1 represent the standard deviation of the set of measurements for a given value of J, K. The estimated minimum uncertainty in any of the results is 5%. When no error is shown, only one measurement was obtained. Assuming the following power-law dependence of half width on temperature:

$$\gamma(T) = \gamma(T_0)(T_0/T)^\alpha,$$

the index α has been calculated and listed in column 5.

In Table 2, we have listed values of hydrogen-broadening coefficients of ammonia at low temperature and the corresponding room-temperature measurement made previously.[1] We have also given the index α.

According to BIRNBAUM,[9] the temperature dependence should be given by $\alpha = (n + 4)/2n$ where $n = 4$ for dipole–dipole, $n = 6$ for dipole–quadrupole and $n = 12$ for dipole–induced-dipole interactions. The dominant interactions are dipole–dipole in self-broadening and dipole–quadrupole in hydrogen-broadening. Thus, α is expected to be $1·0$ for self-broadening and $0·83$ for hydrogen-broadening. However, in the case of NH_3-H_2 interactions, because of the large difference in rotational constants, the chance of resonance is extremely small. The effective optical collision cross section will be close to the kinetic one and only weakly dependent on temperature and quantum numbers. As the result, values close to $0·5$ are obtained for the index α for all of the lines. Although there is a fair amount of scatter in our determination of α due to the narrow temperature range over which we could make our measurements, the results suggest this dependence within our experimental uncertainty. The average value of α for the hydrogen-broadened case is, indeed, close to $0·5$. The value of α in self-broadening seems to depend strongly on quantum numbers J, K and an average may not have any physical significance.

Table 2. Hydrogen broadening of ammonia at 300° and 207°K (half-widths are given in $cm^{-1} atm^{-1}$)

Line $(J''_{K'})$	γ^0 (207°K)	γ^0 (300°K)	α	Line $(J''_{K'})$	γ^0 (207°K)	γ^0 (300°K)	α
1_0	$0·117 \pm 0·009$	$0·0920$	$0·65$	5_0			
1_1	$0·127 \pm 0·004$	$0·0893$	$0·95$	5_1		$0·0667 \pm 0·0012$	
				5_2	$0·083 \pm 0·009$	$0·0733 \pm 0·0057$	$0·32$
2_0	$0·102 \pm 0·004$			5_3	$0·098 \pm 0·010$	$0·0911 \pm 0·0009$	$0·20$
2_1	$0·125 \pm 0·017$	$0·0920 \pm 0·0071$	$0·83$	5_4	$0·113 \pm 0·010$	$0·0902 \pm 0·0098$	$0·61$
2_2	$0·125 \pm 0·011$	$0·1040 \pm 0·0060$	$0·50$	5_5	$0·113 \pm 0·009$	$0·0914 \pm 0·0059$	$0·57$
3_0	$0·092 \pm 0·008$			6_0	$0·075 \pm 0·002$		
3_1	$0·104 \pm 0·011$	$0·0787 \pm 0·0059$	$0·75$	6_1		$0·0680 \pm 0·0042$	
3_2	$0·112 \pm 0·008$	$0·0936 \pm 0·0014$	$0·48$	6_2		$0·0655 \pm 0·0057$	
3_3	$0·115 \pm 0·006$	$0·0978 \pm 0·0014$	$0·44$	6_3		$0·0857 \pm 0·0060$	
				6_4		$0·0795 \pm 0·0040$	
4_0	$0·096 \pm 0·007$	$0·0865 \pm 0·0076$	$0·29$	6_5	$0·101 \pm 0·006$	$0·0861 \pm 0·0042$	$0·43$
4_1	$0·095 \pm 0·004$	$0·0761 \pm 0·0051$	$0·61$	6_6	$0·114 \pm 0·005$	$0·0832$	$0·85$
4_2	$0·115 \pm 0·010$	$0·0833 \pm 0·0065$	$0·87$				
4_3	$0·109 \pm 0·005$	$0·0956 \pm 0·0007$	$0·35$				
4_4	$0·109 \pm 0·009$	$0·0890 \pm 0·0059$	$0·55$				

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