Research Article

On the Pressure and Temperature Dependence of the Absorption Coefficient of NH₃

F. Aousgi, S. Hadded, and H. Aroui

Laboratoire de Physique Moléculaire, Ecole Supérieure des Sciences et Techniques de Tunis, 5 Avenue Taha Hussein, Tunis 1008, Tunisia

Correspondence should be addressed to F. Aousgi, aousgifethi@yahoo.fr and H. Aroui, haroui@yahoo.fr

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The effects of pressure and temperature on the absorption coefficient of ammonia (NH₃) gas self-perturbed and perturbed by nitrogen (N₂) gas have been measured. We varied the gas pressure from 10 to 160 Torr and the temperature from 235 to 296 K in order to study the absorption coefficient at the center and the wings of lines in the ν₄ band of NH₃. These measurements were made using a high resolution (0.0038 cm⁻¹) Bruker Fourier-transform spectrometer. These spectra have been analyzed using the method of multipressure technique permitting to succeed to an evolution of the absorption coefficient with the pressure and the quantum numbers J and K of the NH₃ molecule. The results show that the absorption coefficient varies as a quadratic function of the pressure at the center of a given line. However, it has a linear evolution in the wings of the line. Moreover, the absorption coefficients are inversely proportional to temperature in the wings when NH₃ lines are broadened by N₂. The retrieved values of these coefficients were used to derive the temperature dependence of N₂ broadening NH₃ lines. The absorption coefficients were shown to fit closely the well-known exponential law.

1. Introduction

The infrared spectroscopic investigations of the atmospheres of stars, planets, and their satellites, using infrared spectroscopy, not only provide valuable information about the chemical elements that they consist of, but also about the horizontal and the vertical distribution of their minor constituents. Due to the complexity of the line profiles used to model the spectral shapes (absorption, broadening, intensity), it is necessary to determine experimentally the line parameters of the spectra in order to test the models being used.

Several studies in the literature have investigated the spectral properties of NH₃ in several infrared bands. Aroui et al. [1] have studied the self-broadening and line intensities, Nouri et al. [2] have studied the temperature dependence of pressure broadening, and other authors [3, 4] were interested in the absorption coefficient at the line centers of NH₃. Experimentally absorption coefficients for broadband ArF excimer radiation laser were determined for NH₃ at temperatures up to 3500 K [5]. Measurements of the NH₃ absorption coefficients at CO₂ laser wavelengths have been done by Zelinger et al. [5] using photoacoustic spectroscopy. NH₃ absorption coefficients were also measured by Allario and Seals [6] using several transitions of a CO₂ laser for small concentrations of NH₃ perturbed by N₂. The influence of CO₂ Laser line width on the measured absorption coefficients of atmospheric ammonia has been studied by Voitsanchkova et al. [7].

The focus of the present study is to present absorption line profile measurements of NH₃ in the 6μm region (Pₚ branch of the ν₄ band). In this range, we resolved the spectra for different J and K quantum numbers. We have determined the absorption coefficients in the centers and in the wings of NH₃ lines self-perturbed and perturbed by N₂ at various pressures (10–160 Torr). The measurements were made for different gas temperatures 235, 245, 268, and 296 K. The analysis was made as a function of J and K quantum numbers, and the results were compared to the previous investigations.
2. Experimental

The measurements were made using a high-resolution Bruker Fourier transform spectrometer (Bruker IFS 120 HR) [8, 9]. This spectrometer is equipped with different components: a Globar source, a KBr beam splitter, a filter eliminating infrared radiation above 2500 cm\(^{-1}\), and a photovoltaic HgCdTe detector cooled at 77 K by liquid nitrogen.

The spectral resolution was about 0.0038 cm\(^{-1}\) after apodization with a triangular function. This value is equal to the half-width at half maximum of the apparatus function approximated in the calculations by a Gaussian shape. This approximation has a negligible contribution to systematic errors since the pressure-broadened lines were much larger [2, 10]. Ammonia gas in natural abundances was provided by Air Liquid France with stated purity of 98.5%. The spectra were measured at different pressures covering the lines of the \(\text{P}\text{P}\) branch of the \(\nu_4\) band of ammonia. \(\text{NH}_3\) and \(\text{N}_2\) gases were contained in a metallic cell with a 2.5 cm path length for \(\text{NH}_3\) self-perturbed, and in a Pyrex glass cell with a 15 cm path length for \(\text{NH}_3\) perturbed by \(\text{N}_2\). Both of the absorption cells are sealed by \(\text{CaF}_2\) windows.

The pressures of the gases were measured accurately using three calibrated capacitive MKS Baratron transducers with full-scale readings of 10, 100, and 1000 mbar. The accuracy of these manometers is 0.5% of the readout. Ammonia sample pressures were allowed to stabilize for sufficient time before the spectrum of the sample was finally recorded.

For \(\text{NH}_3\) self-perturbed, the pressure was varied from 5 to 120 mbar, whereas for \(\text{NH}_3\) perturbed by \(\text{N}_2\) we varied the gas pressure from 10 to 160 Torr. For the present experiments, the temperatures varies from 235 to 296 K. Each temperature was monitored by three calibrated thermocouples (Pt100).

The measured intensity of the incident light \((I_0)\) and the transmitted light \((I)\) at wave-number \(\sigma\) were converted to transmission spectra \(\tau(\sigma, T)\) using Lambert-Beer’s law

\[
\tau(\sigma, T) = \frac{I(\sigma, T)}{I_0(\sigma, T)}. \tag{1}
\]

Table 1 summarizes the experimental parameters. The spectral region for this study is between 1470 and 1600 cm\(^{-1}\). Figure 1 shows short transmittance spectra of \(\text{NH}_3\) around 1550 cm\(^{-1}\) exhibiting some prominent lines of the \(\text{P}\text{P}\) branch. These spectra were recorded at \(T = 296\) K. At low pressure, the lines are separated, but when the pressure increases the lines widen and begin to overlap.

![Figure 1](image_url)

**Table 1: Experimental parameters.**

<table>
<thead>
<tr>
<th>Studied gas</th>
<th>Temperature (K)</th>
<th>Pressure of the perturbed gas (mbar)</th>
<th>Cell length (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NH}_3)–(\text{NH}_3)</td>
<td>296</td>
<td>10–141</td>
<td>2.5</td>
</tr>
<tr>
<td>(\text{NH}_3)–(\text{N}_2)</td>
<td>235, 245, 268, 296</td>
<td>10–141</td>
<td>15</td>
</tr>
</tbody>
</table>

3. Fitting Procedures

The absorption coefficient of an isolated line of the \(\nu_4\) band is obtained by comparing the recorded line with a synthetic line. The adjustment is performed using the Rosenkrantz profile given [11, 12] by

\[
\alpha(\sigma) = \frac{P_{\text{NH}_3}}{\pi} \sum_{\text{line } k} S_k \left( \frac{P Y_k(\sigma - \sigma_k) + P Y_k(\sigma - \sigma_k)' + P Y_k(\sigma - \sigma_k)''}{(\sigma - \sigma_k)^2 + (P Y_k)^2} \right), \tag{2}
\]

where \(P_{\text{NH}_3}\) is the \(\text{NH}_3\) pressure, \(P\) is the partial pressure of the perturbing gas, \(k\) represents the line \(\nu_i f_j → \nu_i f'_j\), \(S_k\) its intensity, \(\sigma_k\) its wave number including the collisional shift \(\delta = \sigma_k - \sigma_0\), \(\sigma_0\) the unperturbed or zero pressure wave number, \(Y_k\) its broadening coefficient, and \(Y_k\) its mixing parameter.

The modelled transmission \(\tau(\sigma)\) is the result of a convolution of \(\alpha(\sigma)\) with a Doppler profile \((\alpha_{\text{Dop}})\) and the apparatus function of the spectrometer \((F_{\text{App}})\) [10].

\[
\tau(\sigma) = \int_{-\infty}^{+\infty} F_{\text{App}}(\sigma - \sigma') \exp \left[ -l \int_{-\infty}^{+\infty} \alpha_{\text{Dop}}(\sigma' - \sigma'') \alpha(\sigma''')d\sigma''' \right] d\sigma', \tag{3}
\]

where \(l\) represents the length of the absorption cell.

The differences between the experimental and calculated spectra were minimized by adjusting the parameters \(PS_k\), \(\alpha_k\), \(P Y_k\), and \(PY_k\) using a nonlinear least-squares multipressure fitting technique where all spectra at various pressures are successively adjusted using (3). An example of multipressure fit in the case of \(\text{P}\text{P}(7, 3)\) line for four \(\text{NH}_3\) pressures (30, 60, 91, and 120 mbar) is shown in Figure 2. Residual (measured minus calculated) spectra are shown in the lower part of graphs.

As illustrated by this figure, the theoretical model given by (3) proves sufficiently accurate to fit very well the observed spectral lines without accounting for Dicke narrowing and/or speed dependence and demonstrates at the same time that the line coupling cannot be neglected.
calculated) spectra are shown in the lower part of the graphs.

In the low-pressure regime, we notice that the absorption coefficient of lines at various pressures of NH$_3$ depends on the statistical weight factor $g_s$. In the case of NH$_3$–NH$_3$ interaction having a statistical weight $g_s$, one can see that the absorption coefficient of the considered line [4].

According to the literature [10, 13], the line intensity $I_{n}$ depends on the quantum numbers $J$ and $K$. The intensities of the transition having a statistical weight $g_s = 2$ (i.e., for $K = 3n, n = 1, 2, 3, \ldots$) are generally higher than of those lines having a statistical weight $g_s = 1$ for $K \neq 3n$. As illustrated by Table 4, one can conclude that the absorption coefficients and the line intensities vary in the same way as a function of the quantum numbers.

These results are in agreement with those published in [4], where the author studied some lines of the $v_2$ band of NH$_3$.

The inverse of the absorption coefficient $(1/\alpha)$ as a function of the square of the pressure of NH$_3$ is plotted in Figure 3(b) for the $P(8, 3)$ line. Indeed, one can see that these two parameters vary linearly. The slope of the obtained straight line is related to the line intensity and self-broadening coefficient of the considered line [4].

Results obtained for NH$_3$ perturbed by N$_2$, show that the peak absorption coefficient, for the 60 lines studied in this work, is decreasing with the N$_2$ pressure. Figure 4 illustrates the variation of the line center absorption coefficients versus the N$_2$ pressure for the $P(J, 1)$ lines at $T = 296$ K. This figure also shows that the absorption coefficient $\alpha$ decreases with the pressure of the perturbing gas. Moreover, it illustrates that $\alpha$ decreases with quantum number $J$ for a given $K$. For example, the $\alpha$ of $P(2, 1)$ line is greater than that of $P(8, 1)$ line.

Figure 5 represents the evolution of the absorption coefficient $\alpha$ with the quantum number $J$ in the case of NH$_3$–NH$_3$ gas mixture at $T = 296$ K and $P = 32$ Torr. The coefficient $\alpha$ has a maximum at $J = 4$ for the $P(J, 1)$ lines and decreases monotonically for $K \geq 2$ with increasing $J$.

4. Results Analysis

4.1. Line Center Absorption Coefficients. We have made measurements of the absorption coefficients for 60 isolated lines of NH$_3$ in the spectral region between 1470 and 1600 cm$^{-1}$. For illustration, the evolution of the absorption coefficient at $T = 296$ K for the $P(8, 3)$ line at various pressures of NH$_3$ is shown in Figure 3(a).

In the low-pressure regime, we notice that the absorption coefficient of a given line varies as a quadratic function of pressure as given by the following equation:

$$\alpha = C^n P_{\text{NH}_3}^2,$$

where $C^n$ is a constant value depending on the individual line.

This figure shows that at high-pressure region, the absorption coefficient tends towards a constant value and hence becomes independent of pressure.
Table 2: Self-absorption coefficient of the two wings of \(^{\text{P}}P(5, 2)_a\) and \(^{\text{P}}P(7, 4)_a\) lines as a function of the square of NH\(_3\) pressure (\(P_{\text{NH}_3}\)) at \(T = 296\) K.

<table>
<thead>
<tr>
<th>(P_{\text{NH}_3} \times 10^4) (atm(^2))</th>
<th>(^{\text{P}}P(5, 2)_{\text{left}})</th>
<th>(^{\text{P}}P(5, 2)_{\text{right}})</th>
<th>(^{\text{P}}P(7, 4)_{\text{left}})</th>
<th>(^{\text{P}}P(7, 4)_{\text{right}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.28</td>
<td>14.9</td>
<td>14.4</td>
<td>—</td>
<td>1.64</td>
</tr>
<tr>
<td>18</td>
<td>61</td>
<td>—</td>
<td>48.5</td>
<td>—</td>
</tr>
<tr>
<td>37</td>
<td>123.8</td>
<td>125.9</td>
<td>80.5</td>
<td>81.5</td>
</tr>
<tr>
<td>63</td>
<td>191.5</td>
<td>191.5</td>
<td>122.1</td>
<td>121.5</td>
</tr>
<tr>
<td>140</td>
<td>384.4</td>
<td>382.3</td>
<td>256.5</td>
<td>256.3</td>
</tr>
</tbody>
</table>

Table 3: Absorption coefficient of two wings of the \(^{\text{P}}P(7, 2)_a\) for NH\(_3\)–N\(_2\) mixtures as a function of N\(_2\) pressure (\(P_{\text{N}_2}\)) at \(T = 268\) K.

<table>
<thead>
<tr>
<th>(P_{\text{N}_2} \times 10^4) (atm)</th>
<th>(\alpha/P_{\text{NH}_3} \times 10^2) (cm(^{-1}) atm(^{-1}))</th>
<th>(^{\text{P}}P(7, 2)_{\text{right}})</th>
<th>(^{\text{P}}P(7, 2)_{\text{left}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>29.6</td>
<td>15.1</td>
<td>13.8</td>
<td>—</td>
</tr>
<tr>
<td>59.2</td>
<td>19.4</td>
<td>18.4</td>
<td>—</td>
</tr>
<tr>
<td>89.6</td>
<td>24.1</td>
<td>23.9</td>
<td>—</td>
</tr>
<tr>
<td>121.9</td>
<td>27.7</td>
<td>26.7</td>
<td>—</td>
</tr>
<tr>
<td>138.9</td>
<td>30.8</td>
<td>30.1</td>
<td>—</td>
</tr>
</tbody>
</table>

Figure 5: Variation of the absorption coefficient of \(^{\text{P}}P(J, 3)_a\) and \(^{\text{P}}P(J, 1)_a\) lines with the quantum numbers \(J\) and \(K\). Case of NH\(_3\)–NH\(_3\) gas mixture at \(P = 32\) Torr for \(T = 295\) K.

4.2. Line Wing Absorption Coefficients. According to our analysis, we observe a quadratic dependence of the absorption coefficient as a function of pressure of the NH\(_3\) gas that can be modeled as follows [14]:

\[
\alpha = A_0(\sigma, T)P_{\text{NH}_3}^2, \tag{5}
\]

where \(A_0(\sigma, T)\) is the normalized absorption coefficient depending on the temperature and the wave number \(\sigma\) of the line; \(P_{\text{NH}_3}\) is the NH\(_3\) pressure. Table 2 gives the self-absorption coefficient of the two wings of \(^{\text{P}}P(5, 2)_a\) and \(^{\text{P}}P(7, 4)_a\) lines as a function of the square of NH\(_3\) pressure (\(P_{\text{NH}_3}\)) at \(T = 296\) K.

Table 4 gives the self-absorption coefficient of the two wings of \(^{\text{P}}P(5, 2)_a\) and \(^{\text{P}}P(7, 4)_a\) lines as a function of the square of NH\(_3\) pressure (\(P_{\text{NH}_3}\)) at \(T = 296\) K.

Figure 6 shows the variation of self-absorption coefficient of the right wings of \(^{\text{P}}P(5, 2)_a\) and \(^{\text{P}}P(7, 4)_a\) lines as a function of the square of NH\(_3\) pressure (\(P_{\text{NH}_3}\)). One can see that the wing absorption coefficients increase linearly with pressure.

The absorption coefficient \(\alpha\) can be described by the following equation [15]:

\[
\alpha = A_0(\sigma, T)P_{\text{NH}_3}^2 + B_0(\sigma, T)P_{\text{NH}_3}P_{\text{N}_2}, \tag{6}
\]

where \(B_0(\sigma, T)\) is the normalized absorption coefficient.

The \(A_0(\sigma, T)\) and \(B_0(\sigma, T)\) parameters were determined using (6) and the absorption coefficient values for the right and left wings of the each line considered in this work. The results at \(T = 296\) K are given in Table 4 for 32 ro-vibrational antisymmetric lines in the \(^{\text{P}}P\) branch of the \(v_4\) band along with the estimated errors given in parentheses.
These errors correspond to the statistical errors expressed as one-time standard deviation for all spectroscopic parameters determined in this work. As expected, the errors vary widely with the lines. The stronger and less blended ones are better determined. For the lines which are too weak or too strongly blended, no reliable fit could be obtained. For this reason, some lines have been disregarded. The assignments of the lines considered in this table are taken from [16]. Within the table, some lines have been disregarded. The assignments of the blended, no reliable fit could be obtained. For this reason, the errors vary widely with the lines. The stronger and less blended ones are better determined in this work. As expected, the errors vary widely with the N₂ pressure for the two wings of the NH₃ pressure (\(\alpha/P\)).

For these spectra, the pressure of NH₃ was fixed. Variation of the absorption coefficient \(\alpha\) with temperature.

According to Shi and Zhang and Bauer et al. [17, 18], the temperature dependence of absorption coefficient \(\alpha(T)\) could be presented by the simple power law:

\[
\alpha = \alpha(T_0) \left( \frac{T}{T_0} \right)^A,
\]

4.3. Temperature Dependence. Spectra of the \(v_3\) band of NH₃ perturbed by N₂ were recorded at four temperatures 235, 245, 268, and 296 K for different pressures of nitrogen (\(P_{N_2}\)). For these spectra, the pressure of NH₃ was fixed. Variation of the absorption coefficient \(\alpha\) with the N₂ pressure for the \(^2P(7, 2)_a\) line for \(T = 268\) K. As shown by this figure, the variation of the absorption coefficient divided by the NH₃ pressure (\(\alpha/P_{N_3}\)) is linear. Also, we observe that the values of \(\alpha/P_{N_3}\) and \(A_0(\sigma, T)\) are practically the same for the left and right wings of the lines.
where $A$ is the temperature exponent and $T_0$ is the reference temperature. In our case $T_0 = 235$ K.

From the measured values of the absorption coefficients for the considered temperatures, one can determine the values of the exponent $A$ as the slope of least square fits from the graphs of $\ln (T/\alpha(T_0))$ as a function of $\ln (T/T_0)$. The straight lines obtained for all the transitions considered in this work validate (7) within the indicated temperature range. Figure 9 illustrates the variation of $\ln (\alpha(T)/\alpha(235))$ as a function of $\ln (T/235)$ for the $P(5,2)_a$ line. The variation is linear; the slope of the line obtained from a linear regression gives a temperature exponent $A = 0.619 \pm 0.016$.

This dependence is in agreement with the work performed by Bauer et al. [18] in their study of the temperature dependence of the absorption coefficient of H$_2$O transitions.

5. Conclusion

Using spectra recorded using a Fourier transform spectrometer and a multispectrum fitting technique, we have determined the absorption coefficients at the center and in the wings of 60 lines pertaining to the $P$ branch of the $\nu_4$ band of NH$_3$ as a function of NH$_3$ and N$_2$ pressures for different temperatures. The present results are in agreement with other recent measurements. In the low-pressure region, the self-absorption coefficient at the center of a given line varies with pressure as a quadratic function. At higher pressures, this coefficient tends to become constant. For NH$_3$–N$_2$ mixture, the values of the absorption coefficients exhibit a decreasing with N$_2$ pressure.

In the wings of the lines, these coefficients show an increasing with the square of NH$_3$ pressure, while for NH$_3$–N$_2$ gas mixtures they increase with N$_2$ pressure.

For this gas mixture, we have studied the temperature dependence of absorption coefficient which fits closely an exponential law. The temperature exponents of this law were derived for the $P(5,2)_a$ line.

References


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