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INFRARED ABSORPTION IN GASEOUS AMMONIA AT PRESSURE

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Introduction

The authors previously reported the infrared absorption in gaseous acetylene at pressure¹⁾. Now they have investigated as an example the gaseous ammonia which is a strong polar molecule of non-planar pyramidal structure. The infrared and Raman spectra of compressed gases show significant differences from the spectra of low pressure gases. The differences are caused by intermolecular forces in the course of collision, being usually small for non-polar molecules but large for strongly polar molecules such as ammonia. Many works have been reported on the spectroscopic investigations for ammonia at and below the atmospheric pressure,²⁾ but for compressed gaseous ammonia, no work except the investigations which were performed on the Raman bands near 3μ by Welsh *et al.*^{3,4)}

In the present investigation the authors have measured the infrared absorption spectra of gaseous ammonia compressed up to 5 kg/cm^2 over the frequency range of $1300 \sim 6500\text{ cm}^{-1}$, and have found the remarkable increases of the intensity of the absorption bands with increasing pressure of gaseous ammonia. At the same time, the influence of pressures (1, 10, and 20 kg/cm^2) of the foreign gases (oxygen and hydrogen) on the most strong absorption band (1627.5 cm^{-1}) of gaseous ammonia has been investigated. The experimental curve showing the increase of the integrated absolute absorption coefficients in the gaseous mixtures with the Amagat density of the foreign gases has been obtained. The integrated absolute absorption coefficient of free ammonia molecule has been estimated by the extrapolation of the linear portion of the experimental curve, showing the dependence of the integrated absolute absorption coefficient in the gaseous mixtures on the Amagat density of the foreign gases, to zero density of the foreign gases, and the absolute value for the absorption induced by the foreign gases has been calculated from the slope of the linear portion.

Experimentals

The infrared absorption cell for high pressure gases and the infrared spectrometer which were employed in the present work were the same as described in the previous report. The absorbing path length of the cell was 17.31 cm . It was difficult to seal

- 1) R. Kiyama, S. Minomura and K. Ozawa, *Proc. Japan Acad.*, **30**, 758 (1954)
- 2) G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., 1945), p. 294
- 3) C. Cumming and H. L. Welsh, *J. Chem. Phys.*, **21**, 1119 (1953)
- 4) C. A. Plint, R. M. B. Small and H. L. Welsh, *Can. J. Phys.*, **32**, 653 (1954)

between the optical window (KCl-crystal) and its supporting plug by using glyptal-varnish and polyvinylacetate-cement, because ammonia molecule has strong chemical activity. However, the sealing was performed by using rubber-cement without difficulty. Gaseous ammonia was distilled from liquid ammonia in a commercial bomb, and oxygen and hydrogen were taken directly from commercial bombs without further purification.

The following two series of experiments were performed.

Exp. 1: the infrared absorption spectra in gaseous ammonia at pressures of 1.0, 2.9, and 5.0 kg/cm² were measured over the frequency range of 1300~6500 cm⁻¹ at room temperature of 19°C.

Exp. 2: the infrared absorption of ν_4 -band of gaseous ammonia of partial pressures of 27.2~102.0 mmHg pressurized with oxygen or hydrogen as foreign gas up to the total pressures of 1, 10, and 20 kg/cm², was measured over the frequency range of 1350~2000 cm⁻¹.

The optical density $\log_{10}(T_0/T)$ was measured at the wavelengths 0.1 μ apart. Here, T_0 represents the light transmitted through oxygen at a pressure of 1 kg/cm² in Exp. 1 and through the foreign gas at the same pressure as the total pressure of the measuring gases in Exp. 2 and T is the light transmitted through the measuring gas.

To avoid the condensation of ammonia on the windows or the wall of the cell, the cell was warmed at about 50°C and gaseous ammonia was introduced very slowly into the cell. The changes in the pressures of the measuring gas in the cell and in the light transmission of the windows were observed for 100 hours after the end of sealing of gaseous ammonia at 5.0 kg/cm². No change was detected in the first several hours, but the depression by 0.3, 0.4, 0.7, and 0.8 kg/cm² after 12, 28, 50, and 75 hours respectively and then the pressure of the gas was stabilized at 4.2 kg/cm². The decrease of light transmission of the windows was observed in the lapse of 100 hours at gaseous pressure of 5.0 kg/cm² in consequence of the adsorption of gaseous ammonia. However, the adsorbed ammonia on the windows could be desorbed by evacuation and the light transmission of the windows recovered to the same as the initial clarity. A further investigation for the effect of compressed gaseous ammonia on the KCl windows will be necessary.

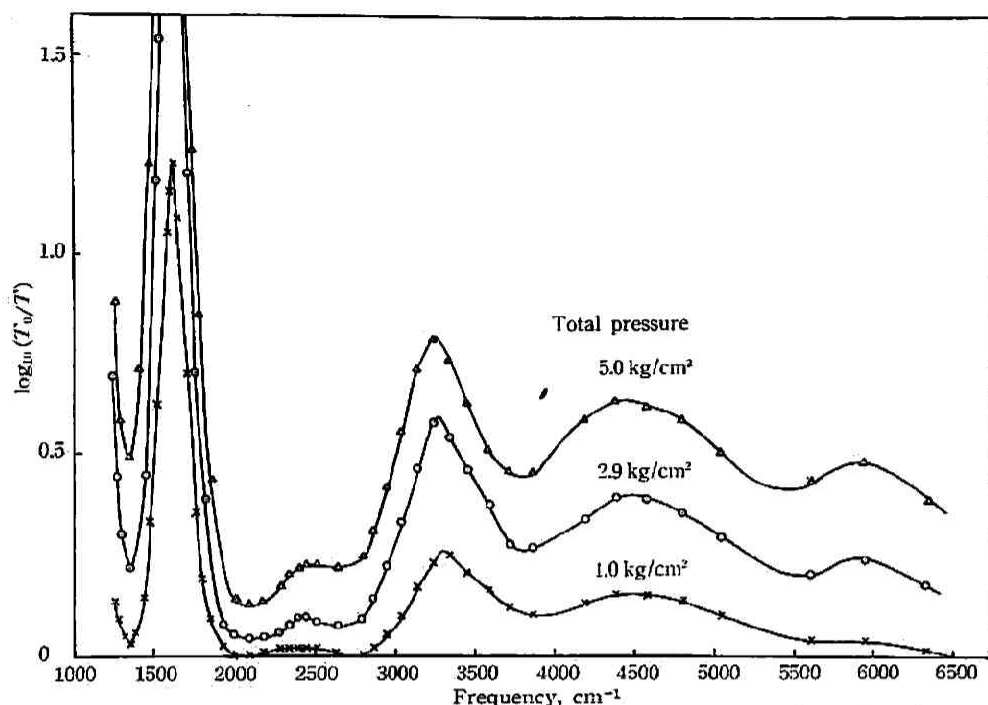
Results

The results of Exp. 1 for gaseous ammonia at pressures are shown in Fig. 1. The assignments and the frequencies corresponding to their absorption bands are listed in Table I.^{2,5,6)} The apparent intensity of each band increases remarkably with increasing pressure.

The results of Exp. 2 for the ν_4 -band of ammonia pressurized with oxygen or

5) G. B. B. M. Sutherland, *Phys. Rev.*, **56**, 836 (1939)

6) F. P. Reding and D. F. Horning, *J. Chem. Phys.*, **19**, 592 (1951)

Fig. 1 Infrared absorption spectra of gaseous NH_3 at pressures of 1.0–5.0 kg/cm^2 at 19°CTable I Infrared absorption in gaseous NH_3

Frequency, cm^{-1}	Assignment
1627.5	ν_4
2440.1	$\nu_2 + \nu_4$
2472.6	
3335.9	ν_1
3337.5	
4433	$\nu_2 + \nu_3$
4505	
6016	$\nu_2 + \nu_3 + \nu_4$

hydrogen are given in Table II. The absorption contours of the band of ammonia at the partial pressure of 27.2 mmHg pressurized with oxygen at 1, 10, and 20 kg/cm^2 are shown in Fig. 2. The rotational branches can be observed in the absorption contour at the total pressure of 1 kg/cm^2 , and not at 10 and 20 kg/cm^2 , because of the pressure broadening of the rotational struc-

Table II Experimental results for $\text{NH}_3\text{-O}_2$ and $\text{NH}_3\text{-H}_2$ mixtures (ν_4 -band of NH_3)

Ammonia partial pressure mmHg	Total pressure kg/cm^2	$\frac{1}{l} \int \ln(T_0/T) d\nu$ $10^{10} \text{cm}^{-1} \text{sec}^{-1}$	Foreign gas
27.2	1	6.348	O_2
"	10	7.274	"
"	20	7.598	"
50.9	1	13.04	H_2
"	10	14.10	"
"	20	14.35	"
52.1	1	12.86	O_2
"	10	14.40	"
"	20	15.23	"
75.7	1	17.58	"
"	10	21.52	"
"	20	21.73	"
101.1	1	22.61	"
"	10	27.99	"
"	20	29.43	"
102.0	1	23.62	H_2
"	10	28.61	"
"	20	29.41	"

ture of the rotational struc-

ture. Fig. 3 and 4 show the variation of the integrated apparent absorption coefficient $B = \frac{1}{l} \int \ln(T_0/T) d\nu$ (in units of frequency ν , sec^{-1} , per path length l , cm) of the ν_4 -band for six constant partial pressures of ammonia. The Amagat densities of oxygen and hydrogen were calculated from the PV-P data cited in the International Critical Tables.⁷⁾ The quantity B increases with increasing foreign gas density. The variation curves of the quantity B with the partial pressure of ammonia are plotted for three constant total pressures in Fig. 5. The limiting slope of each curve which is estimated by the extrapolation to zero partial pressure of ammonia corresponds to the integrated absolute absorption coefficient $A = \left(\frac{\partial B}{\partial N}\right)_{N=0}$ in the gaseous mixture, where N is the number of ammonia molecules per unit volume. The values of A increases and the curvature of the curves decreases with increasing pressure of the foreign gas. No difference between oxygen and hydrogen as the foreign gas can be detected. The integrated absolute absorption coefficient A in the mixture is plotted against the foreign gas density in Fig. 6. The values of A show a sharp initial rise with increasing foreign gas density, but increase proportionally to the foreign gas density above $10\text{kg}/\text{cm}^2$, because the rate of enhancement of the values between the total pres-

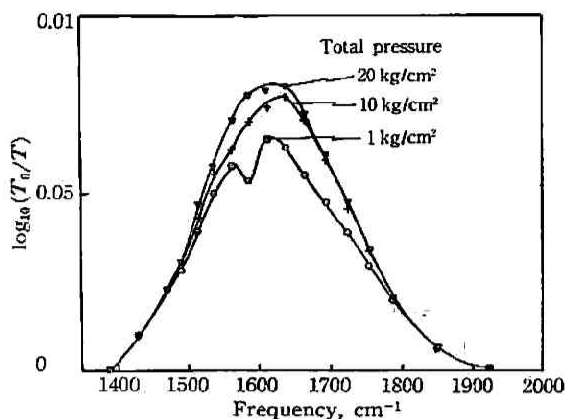


Fig. 2 The pressure effects of O_2 on the contour of the ν_4 -band of ammonia. Partial pressure of ammonia, 27.2mmHg ; Absorbing path length, 17.31cm ; Temperature, 19°C

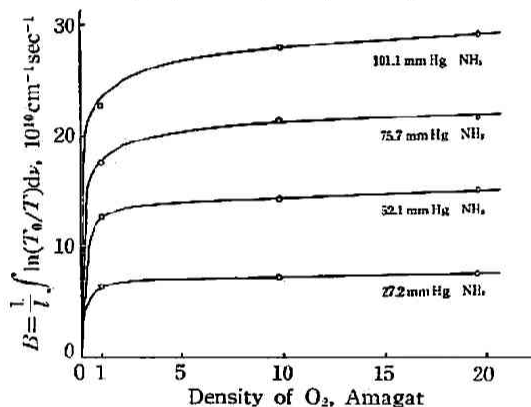


Fig. 3 The variation of the apparent absorption coefficient B in $\text{NH}_3\text{-O}_2$ mixtures

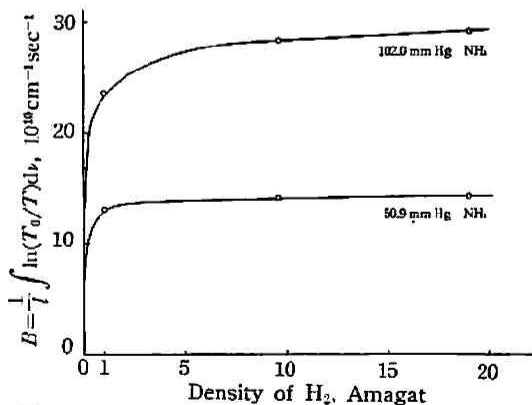


Fig. 4 The variation of the apparent absorption coefficient B in $\text{NH}_3\text{-H}_2$ mixtures

7) *Inter. Crit. Tables*, 3, p. 4 and 8

Table III Absorption coefficients of the ν_4 -band of NH_3

Integrated absolute absorption coefficient ($\text{cm}^{-1} \text{sec}^{-1}$ at N.T.P.)	Pressure-induced absorption coefficient ($\text{cm}^{-1} \text{sec}^{-1}$ at N.T.P. per Amagat unit of density of foreign gas)
208.4×10^{10}	1.385×10^{10}

sures of 1 and 10 kg/cm². According to Welsh *et al.*⁸⁾, the integrated absolute absorption coefficient of free ammonia molecule can be given by the extrapolation of the linear portion of the curve in Fig. 6 to zero foreign gas density, and the pressure-induced absorption coefficient for unit foreign gas density can be estimated by the slope of the linear portion of the curve, being shown in Table III.

It can be concluded from the results obtained above that the remarkable enhancement of the absorption band of gaseous ammonia with increasing pressure (Fig. 1) and the large value of the pressure-induced absorption coefficient for unit foreign gas density (Table III) are due to the polarity of ammonia molecule. That is, a great vibrating dipole is caused by the intermolecular forces in the course of collision, in addition to the original dipole of ammonia.

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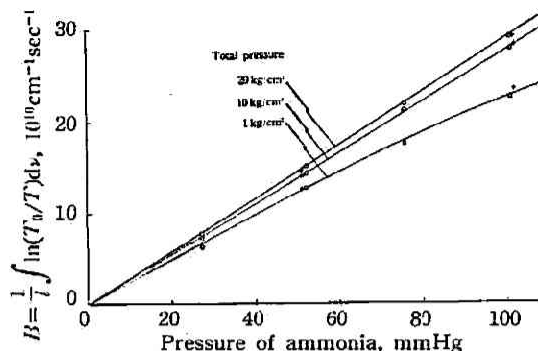


Fig. 5 The variation of the apparent absorption coefficient B as a function of the ammonia partial pressure for various total pressures
 ○ pressurized with oxygen
 + pressurized with hydrogen

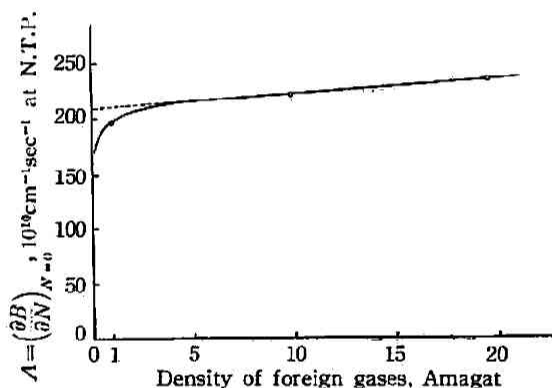


Fig. 6 The variation of the absolute absorption coefficient A in the gaseous mixtures

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8) H. L. Welsh, P. E. Pashler and A. F. Dunn, *J. Chem. Phys.*, 19, 340 (1951)