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Shift and broadening of the lower inversion-rotational transition of the $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ molecules

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(Received 8 June 1982)

Opt. Spektrosk. 56, 828-832 (May 1984)

The frequencies and parameters of the shift and broadening by pressure of the lower inversion-rotational transition of the molecules of ordinary and isotopic ammonia in the ground vibrational state have been measured. The frequencies of the transition not shifted by pressure are 572,497.99(4) and 572,112.65(4) MHz for $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$, respectively. The parameters of the shift and broadening of both spectral lines by a pressure of ammonia and phosphine have been determined. A marked difference in the parameters of the frequency shifts of the lines for $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ has been detected.

Present day studies of spectral lines have reached such a level of accuracy that the usual single measurement of their frequencies in a number of cases is becoming insufficient. The reason is the shift of the frequencies of the lines by gas pressure, which in the submillimeter range may reach several MHz/Torr for an accuracy of the measurement of the frequencies of the lines equal to several kilohertz.¹⁻³ At the same time, there is no sufficiently reliable theory of the phenomenon of the frequency shifts of lines by pressure, and this makes it impossible to obtain the necessary corrections by calculation.^{4,5} For a number of years, we have been studying modern spectroscopic methods for obtaining the absorption spectrum of the ammonia molecule,⁶⁻⁹ which is a traditional object for molecular spectroscopy. In fact, it was during these studies that the marked shifts of the ammonia lines by pressure were detected.^{6,7} The present study is devoted, on the one hand, to obtaining accurate data on the frequencies of the only lower inversion-rotational transition of the molecules of ordinary $^{14}\text{NH}_3$ and isotopic $^{15}\text{NH}_3$ ammonia accessible to microwave spectroscopy and, on the other hand, to a study of the shift and broadening of these lines by pressure. These studies supplement the previously obtained² picture of the shifts of the lines of ammonia by pressure in the excited

vibrational state ν_2 and are also of interest for the study of the details of intermolecular interactions and the construction of a corresponding theory of the shifts.

The rotational-inversion transition $s(1,0) \rightarrow a(0,0)$ of ammonia was studied using an RAD (acoustic-detector)¹⁰ and a submillimeter frequency synthesizer.¹¹ The modulation and tuning of the frequency of the SHF radiation, required for the production of the signal from the absorption line, were carried out by applying the corresponding voltages to the variable capacitor of the interpolation generator of the kilohertz decade of the base low-frequency synthesizer Ch6-31. The magnitude of the frequency deviation of the radiation was chosen to be appreciably smaller than the width of the line being studied, so that the signal at the output from the RAD corresponded to the first derivative of the contour of the absorption line. In the experiment we measured both the frequency of the center of the line, corresponding to the zero value of the output signal, and the frequencies of the extremal points of the signal ν_{\max} and ν_{\min} , which, assuming a Lorentzian line contour and a short optical path length in the gas, are related to the linewidth by the familiar expression:

$$2\Delta\nu = \sqrt{3}(\nu_{\max} - \nu_{\min}). \quad (1)$$

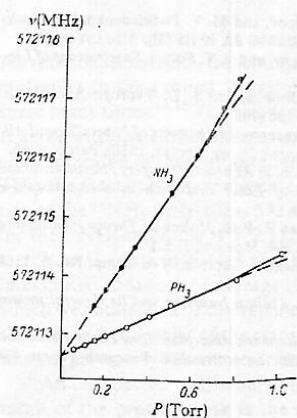


FIG. 1. Dependence of the frequency of the $s(1,0) \leftarrow a(0,0)$ transition of the $^{15}\text{NH}_3$ molecule on the pressure of ammonia and phosphine; the cell length was 10 cm in both cases.

where Δv is the half-width of the absorption line at the level of half intensity. The pressure was measured by a VDG-1 membrane gas-discharge vacuum meter. The accuracy of the reading of the VDG-1 scale in the 0.01–1.0-Torr pressure range was 0.005 Torr. The vacuum meter was calibrated beforehand at two points: from the water vapor pressure above the surface of melting ice, equal to 4.579 Torr, and in a high vacuum at $\sim 10^{-5}$ Torr. The chief difficulty in the measurements of the pressure of ammonia, as is well known, is related to its strong absorption by the walls of the gas cell. To decrease the error associated with this process, the measurements were carried out as follows. The ammonia was first kept for 10–15 min to saturate the walls of the cell. It was then passed from the walls of the cell to a prepared vacuum system, the volume of which was ~ 0.1 times the volume of the cell, and the first reading of the pressure on the VDG-1 scale was carried out. The cell was then separated from the vacuum system, and the latter was rapidly evacuated (which completely excluded the influence of the VDG-1 zero drift on the results of the measurements) to a dynamic vacuum of $\sim 10^{-5}$ Torr, at which the second reading was carried out. The difference between the first and second VDG-1 readings determined the magnitude of the ammonia pressure in the cell before the start of the measurements. When the frequency measurements were complete, the pressure in the cell was measured again. It generally did not differ from the initial value by more than 2–3%. The average value from these two measurements was taken as the pressure of ammonia in the experiment.

Figure 1 gives the results of the measurement of the dependence of the frequency of the $s(1,0) \leftarrow a(0,0)$ transition of the $^{15}\text{NH}_3$ molecule on the pressure of ammonia and phosphine. The experimental points are effectively approximated by a linear relationship. At a pressure > 0.5 Torr the $v(p)$ relationship becomes nonlinear due to the influence of the wing, whose frequency is higher than that of the stronger transition of $^{14}\text{NH}_3$. The inverse influence is not observed, since for the natural concentration of the isotopes, the $^{15}\text{NH}_3$ line is weaker by a factor of 300. It may also be noted that the large absorption coefficient of the $s(1,0) \leftarrow a(0,0)$ transition of ordinary ammonia (0.37 cm^{-1}) (Ref. 9) not only makes it difficult to measure its width but also may influence the accuracy of the measurement of the shift of the frequency by pressure. Thus the parameters of the self-broadening and self-shift of this transition were measured in a cell with a length of only 13 mm. The experimental data were treated on a computer by the method of least squares. The results of the treatment are given in Table I. The magnitude of the confidence limit of the determination of the frequency v_0 not shifted by pressure and the parameters of the shift Δv_b and broadening Δv_d of the lines by pressure is given in brackets in units of the last significant figure. In the measurement of the shift of the frequencies of the transitions of ammonia by a pressure of phosphine, we made use of the fact that it is difficult to evacuate ammonia from the cell, and small quantities of ammonia are present for a long time in the cell as a result of its liberation from the walls. In this case, as a consequence of the high sensitivity of the RAD and the high intensity of the line being studied, the traces of ammonia in the cell were quite sufficient for the observation and measurement of the line.¹⁰ Before each experiment, the cell was evacuated by a backing pump, and the phosphine was admitted anew to the required pressure. This excluded the accumulation of ammonia in the cell from one experiment to another and the associated systematic error. All the experiments were carried out using highly pure ammonia and chemically pure phosphine, obtained in the Institute of Chemistry of the Academy of Sciences of the USSR.

The broadening of the lines by ammonia and phosphine was measured in parallel with the study of the shifts. Figure 2 gives the experimentally observed $v_{\max}(p)$ and $v_{\min}(p)$ relationships for the $^{15}\text{NH}_3$ molecule. The unsymmetrical character of the relationships is naturally due to the displacement of the frequency of the center of the line by pressure, which takes place at the same time as its broadening.

The experimental data obtained make it possible to determine the parameters of the broadening of the transitions studied. For this purpose, we can consider the relationship between the linewidth and the experimentally measured val-

TABLE I.

Molecule studied	Perturbing gas	v_0 , [MHz]	Δv_b , MHz/Torr	Δv_d , MHz/Torr
$^{14}\text{NH}_3$	Ammonia	572 497.99 (4)	6.10 (7)	44.20 (40)
$^{15}\text{NH}_3$	Ammonia	572 412.65 (4)	5.71 (10)	41.90 (50)
$^{14}\text{NH}_3$	Phosphine	572 497.98 (2)	1.86 (8)	3.85 (30)
$^{15}\text{NH}_3$	Phosphine	572 412.65 (2)	1.67 (7)	5.55 (30)

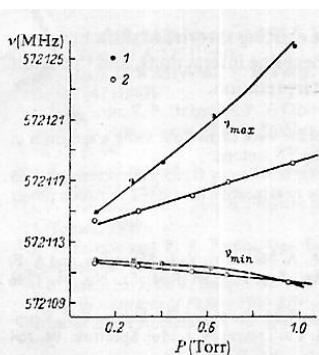


FIG. 2. Pressure dependence of ν_{\max} and ν_{\min} for the broadening of the $s(1,0) \rightarrow a(0,0)$ line of the $^{14}\text{NH}_3$ line by a pressure of ammonia (1) and phosphine (2); cell length: 10 cm.

ues of ν_{\max} and ν_{\min} . For a Lorentzian contour of the absorption line, modulation of the frequency of the radiation by a meander with a frequency ω , and a value of the deviation Δf , the distance between the extremal points of the response from the absorption line is equal to¹²

$$\nu_{\max} - \nu_{\min} = \frac{2\Delta\nu}{\sqrt{3}} \left[1 + \left(\frac{\Delta f}{2\Delta\nu} \right)^2 + \left(\frac{\omega}{\Delta\nu} \right)^2 \right]. \quad (2)$$

The last term in Eq. (2) can be neglected, since in the RAD spectrometer, $\omega = 180 \text{ Hz} \ll \Delta\nu \gtrsim 1 \text{ MHz}$. The magnitude of the deviation Δf was chosen so that the contribution of the term $(\Delta f/2\Delta\nu)^2$ did not exceed 2% of the original line width $2\Delta\nu$; i.e., this accuracy can be regarded as the accuracy with which the response from the absorption line coincides with the first derivative of its contour with respect to frequency. There are other reasons for the broadening of the line, in particular, the broadening by the radiation power, the apparent broadening as a result of the influence of the cell, etc. Here we can examine in more detail the broadening as a result of the RAD cell, which has not been taken into account before. In the RAD spectrometer, the signal from the line is proportional to the power absorbed by the gas. In the absence of saturation effects, the power absorbed by the gas is equal to

$$P_{\text{abs}} = P(1 - e^{-\gamma l}), \quad (3)$$

where P is the power of the radiation at the entrance to the cell, l is the length of the cell, and γ is the absorption coefficient of the line. As noted above, under certain conditions, the response from the line is close to the first derivative of its contour. By substituting in Eq. (3) the expression for $\gamma(\nu)$ and equating to zero the second derivative of P_{abs} with respect to frequency, we readily obtain

$$(\nu_{\max} - \nu_{\min})^2 = \frac{(2\Delta\nu)^2}{3} [\sqrt{1 + 3(\gamma l + 1)^2} - (1 + \gamma l)]. \quad (4)$$

In the derivation of Eq. (4) it was assumed that P is independent of the frequency. The applicability of the equation obtained for a uniformly broadened isolated line will break down only when γl is appreciably greater than 1, when the associated nonuniformity of the liberation of heat throughout the volume of the gas cell causes the time constant τ of

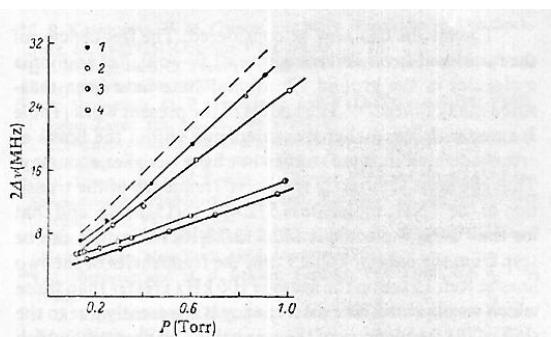


FIG. 3. Pressure dependence of the width of the absorption line $s(1,0) \rightarrow a(0,0)$ of the ammonia molecule, determined from experimental data using Eq. (4); for comparison, the broken line gives the pressure dependence of the width $2\Delta\nu$ of the $^{14}\text{NH}_3$ line for broadening by ammonia obtained from Eq. (1): 1— $^{14}\text{NH}_3-\text{NH}_3$; 2— $^{15}\text{NH}_3-\text{NH}_3$; 3— $^{14}\text{NH}_3-\text{PH}_3$; 4— $^{15}\text{NH}_3-\text{PH}_3$.

the cell,¹³ and hence the amplitude of the output signal, to depend on the frequency. For $\gamma l \ll 1$, the influence of the cell on the linewidth is negligible. Thus, e.g., for the $^{15}\text{NH}_3$ transition ($\gamma \approx 1.3 \times 10^{-2}$), the correction is $\lesssim 1\%$. For the $^{14}\text{NH}_3$ line ($\gamma = 0.37 \text{ cm}^{-1}$, $l = 1.3 \text{ cm}$), however, it reaches 13% (Fig. 3).

The dependence of the linewidths of the $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ molecules on pressure, determined from the experimental data using Eq. (4), is given in Fig. 3. In the 0.2–1-Torr pressure range, within the limits of error of the measurements, $2\Delta\nu$ is given by a linear relationship:

$$2\Delta\nu = \Delta + 2\Delta\nu_b P. \quad (5)$$

The values of the parameters $\Delta\nu_b$ and Δ are given in Tables I and II, respectively. The parameters of the broadening $\Delta\nu_b$ of the lines of both molecules were found to have extremely close values; $\Delta\nu_b$ for $^{15}\text{NH}_3$ for broadening by ammonia has a lower accuracy because of the error in the determination of the path length of the radiation in the RAD absorbing cell, which amounts to $\sim 10\%$. The parameter Δ , which is the linewidth obtained by extrapolating the linear part of the $2\Delta\nu(p)$ relationship to zero pressure, in all cases (Table II) was found to be nonzero. A definite fraction of Δ for the $^{14}\text{NH}_3$ line is, of course, due to the presence of its quadrupole hyperfine structure. The nature of Δ for the $^{15}\text{NH}_3$ line is not yet clear, and additional studies are required to investigate this question. It may merely be noted that the order of magnitude of Δ for $^{15}\text{NH}_3$ is close to that of the sum of the Doppler broadening and the broadening due to saturation of the spectral line by the radiation power.²

TABLE II.

Perturbing gas	$\Delta(p=0)$	
	$^{14}\text{NH}_3$	$^{15}\text{NH}_3$
Ammonia	2.88 (64)	2.03 (59)
Phosphine	3.49 (37)	2.92 (42)

The results can now be considered. The frequencies of the rotational-inversion transition $s(1,0) \rightarrow a(0,0)$ of ammonia molecules in the ground vibrational state have been measured many times.^{14,15} The results of the present work (Table I) agree with the earlier measurements within the limits of error indicated in these studies but have a higher accuracy. Thus the most accurately measured frequency of the transition of the $^{14}\text{NH}_3$ molecule is 572,498.15(15) MHz, and that for the $^{15}\text{NH}_3$ molecule is 572,112.78(10) MHz.¹⁵ It can be seen from the data in Table I that the frequencies of the two lines in Ref. 15 are on the average 100 kHz greater than those which we obtained. The discrepancy is apparently due to the shift of the frequencies of the transitions by pressure, which was not previously taken into account in the measurements.

An unexpected and, in our opinion, the most interesting result of the present work is the marked difference in the parameters of the shift for lines which have identical values of the quantum numbers and extremely similar frequencies and which belong to molecules with identical 3-D structures, $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$. The difference in the parameters of the frequency shift of these lines is (7 ± 3) and $(11 \pm 9)\%$ for shift by ammonia and phosphine, respectively, which are appreciably greater than the difference in the average relative velocities of the $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ molecules, the magnitude of which is $< 2\%$. The observed difference cannot be attributed to the influence of the wing of the $^{14}\text{NH}_3$ line on the $^{15}\text{NH}_3$ line, which, although it is revealed in the experiment (Fig. 1), leads to an upward frequency shift of the $^{15}\text{NH}_3$ line. In addition to the mass, the most important physical difference in these molecules, capable of somehow influencing the magnitude of the shift parameter, is the existence of a quadrupole hyperfine structure for the energy levels of the $^{14}\text{NH}_3$ molecule, due to the spin of the ^{14}N nitrogen nucleus; for isotopic ammonia $^{15}\text{NH}_3$ there is no quadrupole

splitting of the levels. The existing theories of shift, however, cannot take account of these fine interactions, and the result obtained still requires interpretation.

¹⁴The experiments with phosphine were carried out using a specimen of ammonia 75% enriched in the ^{15}N isotope.

¹⁵For the $^{15}\text{NH}_3$ line, the Doppler broadening at room temperature is 1.65 MHz, and the broadening due to saturation for a BWT radiation power of 10 mW is ~ 1 MHz.

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Temporal variation in the Raman spectra of $\text{LiNbO}_3:\text{Fe}$ crystals

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(Received 20 September 1982)

Opt. Spektrosk. 56, 833–835 (May 1984)

The experimental data on the variation in the Raman spectra of $\text{LiNbO}_3:\text{Fe}$ crystals with time are given. A different temporal variation is observed for the Raman lines of different symmetry. An energy transfer from a normal beam to an abnormal one is confirmed. The results observed are interpreted by taking into account the optical damage to the crystals. An explanation of the energy transfer is given based on the conditions of spatial phase matching.

The phenomenon of optical damage (OD) to $\text{LiNbO}_3:\text{Fe}$ crystals under the action of laser radiation was investigated, for example, in Refs. 1–4. It was demonstrated in Ref. 5 that the front of variation in the refractive index Δn follows the front of the light wave with an interval of 10^{-9} sec. There are many OD models,^{2–6,7} Some processes that take place after the initial variation Δn for time $t > 10$ min and the transfer of the laser beam energy from the normal to the abnormal with

the passage of light through the crystals were investigated.⁸ However, the mechanisms of these processes remain unclear. An attempt is made in the present paper to explain the long-term temporal variations Δn by using the data on Raman light scattering in $\text{LiNbO}_3:\text{Fe}$ crystals as a function of time.

The Raman spectra were excited with a He–Cd laser $\lambda_0 = 4416 \text{ \AA}$ and recorded photoelectrically on a DFS-12