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THE INFLUENCE OF TEMPERATURE AND PRESSURE ON THE RAMAN SPECTRUM OF NITROGEN

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The rotational structure of the Q branch of the vibrational band of the Raman spectrum of nitrogen was studied. The dissimilar nature of the impact broadening of the vibrational and rotational lines of the spectra is established. The following effective collision radii determining the Raman spectrum line broadening were found: for the Q branch of the vibrational band $\rho_\nu = 0.43$ A, for the purely rotational band lines $\rho_\omega = 3.9$ A. It is shown that the experimental results do not contradict the impact theory of spectral line broadening.

THE phenomenon of Raman scattering is fundamentally related to the intramolecular vibrations and rotations of molecules. However, the intermolecular interaction also leaves its imprint on these processes and is reflected in the spectrum. Therefore an investigation of the spectra makes possible the study of the influence of the intermolecular interaction on the processes related to Raman scattering and, besides, allows a more complete disclosure of the dynamics of molecules in the presence of an external perturbation.

The study of the manifestation of the intermolecular interaction in the spectrum begins logically with a gas at moderate pressures, whose kinetics of motion are well known, and therefore the treatment of results is facilitated. Besides, such a study may turn out to be useful in the investigation of phase transitions and the structure of liquids.

The effect of the intermolecular forces is small, and affects mostly the line contours. An investigation of the line contour, as far as the theory of collision broadening is concerned, makes it possible to find the effective optical collision radii for the processes that determine the Raman-scattering line broadening.

Measurement of the line widths involves considerable experimental difficulties, and therefore comparatively little work has been done on intermolecular interactions in Raman scattering. The most interesting in this direction is the work of Sterin.[1] He measured the line widths of the completely symmetrical vibrations of benzene ($\Delta\nu = 992$ cm^{-1}) in the liquid and in the vapor. It turned out that the line width was not changed in the phase transition, a fact explained by the rotational splitting of the Q branch of the vibrational band.[2]

The aim of the present work was to investigate the line broadening of Raman scattering in a gas, to study in more detail the rotational splitting of the vibrational-transition Q branch, and to study the spectrum of a liquid. Nitrogen was chosen as the object of the investigation.

EXPERIMENT

A high-pressure illuminator for the investigation of Raman scattering in gases at various pressures and constant temperature was developed and manufactured jointly with the High-Pressure Physics Institute of the U.S.S.R. Academy of Science; its construction is shown in Fig. 1. Three PRK-2 lamps, surrounded by a running-water cooling filter, were placed parallel to the scattering volume and illuminated it through cylindrical lenses of organic glass. The lenses, placed in a "hot" setting, served simultaneously as seals for the illumination windows. The illuminator withstood a test pressure of 450 atmos. Within the scattering volume was placed a multiply reflecting system with aluminized mirrors, which permitted a shortening of the exposure time by a factor of six

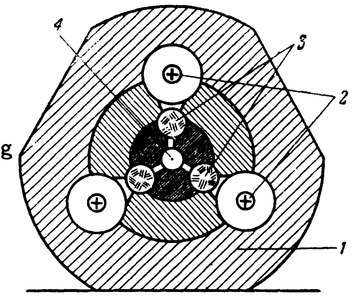

FIG. 1. Diagram of the high pressure illuminator: 1 – housing; 2 – illuminating lamps with water filters; 3 – cylindrical lenses 4 – scattering volume.

or seven.[3] With the help of a specially-designed double-lens condenser, the forward aperture of the mirror system was reflected on the spectrograph aperture, and the rear of the mirror was reflected on the collimator. The gas in the illuminator was supplied directly from cylinders.

A double-lamp illuminator with cylindrical lenses and water-cooled mercury lamps was used to photograph the liquid nitrogen.[4]

The Raman scattering spectrum was excited by the 4047 and 4358 A mercury lines and recorded on a HUET V-III spectrograph with a linear dispersion equal to 22.7 cm^{-1}/mm in the 4047-A region and to 36.2 cm^{-1}/mm in the 4358-A region. The exposure time of the Raman-Ortho Agfa plates ranged from 3 to 40 hours. The spectrograph was thermostatically controlled during the exposure time.

Each experimental point for a given pressure was obtained as an average from three to four photographs. The photographs were processed on an MF-4 microphotometer; the total width of the excitation line, of the slit, and of the apparatus function of the spectrograph and the emulsion ($\sim 1.5\ \mathrm{cm}^{-1}$ for the gas and $\sim 1\ \mathrm{cm}^{-1}$ for the liquid) was excluded from the results of the measurements[8] in the subsequent processing. The average error in the measurements of the line widths comprised about 10%.

The Raman scattering spectrum of nitrogen (gas) consists of O and S branches of rotational bands situated on both sides of the excitation line, and a Q branch of the vibrational band. The scattering spectrum in nitrogen was studied at 27° C in the pressure interval from 7 to 114 atmos.

The rotational spectrum for low pressures consists of sharp equidistant lines of alternating intensities with component distances of 8.0 cm^{-1}; up to 15 lines of the O branch and 25 lines of the S branch were observed. On increasing the pressure, the lines of the rotational spectrum broadened; at a pressure of 20 atmos they began to overlap and for $p > 80$ atmos they blended into a continuous band with weakly defined maxima at its width in the region of pressure investigated the positions of the intense rotational lines (Fig. 2).

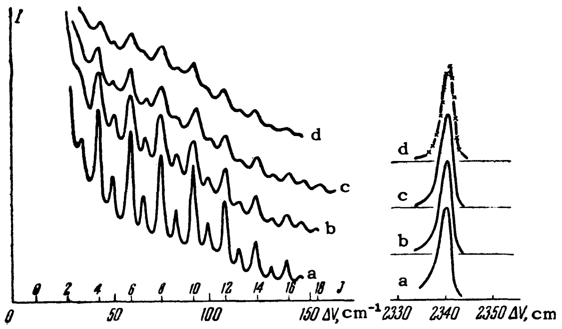

FIG. 2. Raman scattering spectra of nitrogen at pressures a) 15, b) 25, c) 40 and d) 60 atmos; t = 27°C.

Only the Q branch of the vibrational-rotational transition is observed in the vibrational band of nitrogen ($\Delta\nu = 2340\ \mathrm{cm}^{-1}$); the O and S branches, being weaker in intensity, were not observed on the photographs.

The Q branch of the vibrational band of nitrogen is narrow ($\sim 2\ \mathrm{cm}^{-1}$) and has an asymmetric form with an arm on the violet side. On increasing the pressure the Q branch broadens slightly, being less than the width of the pure rotational band component.

The variation with pressure of the rotational ($\delta\omega$) and vibrational ($\delta\nu$) Raman scattering line widths of nitrogen is shown in Table I and in Fig. 3; the average width for the transitions with J = 0 — 15 is given for the rotational lines.

To clarify the role of the temperature, the spectrum of nitrogen was investigated by us at t = 200° C (pressure p = 90 atmos, reduced to 27° C) and at the temperature of liquid nitrogen, at t = − 190° C. The investigation showed that the nitro-

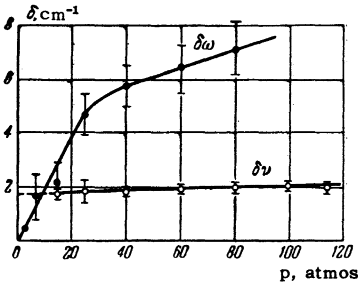

FIG. 3. Pressure dependence of the widths of the rotational, $\delta\omega$, and the vibrational, $\delta\nu$, lines of the nitrogen Raman scattering.

TABLE I. Dependence of the nitrogen Raman scattering line width on pressure (t = 27° C)

p, atmos	$\delta\omega$, cm^{-1}	$\delta\nu$, cm^{-1}	p, atmos	$\delta\omega$, cm^{-1}	$\delta\nu$, cm^{-1}
3	~0,5*	—	60	6,4±0,9	1,9±0,2
7	1.75±0.9	—	80	7.1±1,0	1,95±0,2
15	2,2±0,7	1.7±0.4	100	—	2,1±0,2
25	4,7±0,7	1,85±0.5	114	—	2,4±0,3
40	5,8±0.8	1,8±0.2	—	—	—

*Measured by V. A. Iozenas, Moscow State University.

gen lines are wider at 200° C than at room temperature: $\delta\omega = 8.5 \pm 2\ \text{cm}^{-1}$, $\delta\nu = 5.4 \pm 1.5\ \text{cm}^{-1}$. Only the Q branch of the vibrational band is observed in the liquid nitrogen spectrum with a width $\delta\nu = 0.4 \pm 0.2\ \text{cm}^{-1}$, the rotational bands being absent.[6]

The frequency shift of the Raman scattering lines lies within the limits of the errors of measurement ($\sim 1\ \text{cm}^{-1}$).

DISCUSSION OF RESULTS

1. The broadening due to molecular collisions,[1,2] the analysis of which is best begun with an investigation of the pressure dependence at constant temperature, is the basic cause of the observed line broadening.

For the rotational lines in the region investigated the pressure dependence $\delta\omega(p)$ has the following form: from 0 to approximately 25 atmos it is a straight line, at 25 atmos there is a bend, then the straight line begins anew, but with smaller slope (see Fig. 3). According to the collision-broadening mechanism, this motion of the curve may be explained in the following manner. In the 0 — 25 atmos region the density of molecules is comparatively small, the collision duration is much less than the time between collisions, and the levels do not yet overlap one another, therefore the theory of collision broadening can be applied here. This allows us to estimate the effective optical-collision radius ρ_ω for the rotational levels. From collision theory, the line width is $\delta = 2\pi N\bar{v}\rho^2$ (N is the number of molecules per cm^3, $\bar{v}$ is the average molecular velocity[7]). For nitrogen at 27° C this relation leads to the following dependence of the line width on the pressure:

$$\delta = 0.027\ \rho^2 p$$

(ρ is in A, p is in atmos, and δ is in cm^{-1}). Utilizing the experimental dependence for $\delta\omega(p)$, we find the effective collision radius for the rotational lines of nitrogen $\rho_\omega = 3.3$ A. The value of ρ_ω allows us to estimate the upper bound of the region of the collision broadening influence and, correspondingly, the beginning of the statistical broadening region. The collision theory is accurate[7] for $2\pi\rho^3 N \ll 1$, whence the upper bound of the pressure for collision broadening of the rotational levels is $\rho \ll 100$ atmos.

In the region above 25 atmos the rotational levels overlap, and the slope of the curve becomes smaller. A systematic error in the calculation of the width arises for strongly overlapping lines, i.e., the calculation does not take into account the drop in line intensity at the edge of the rotational spectrum; in addition, the broadening mechanism for the overlapping levels is not completely clear; this fact may be the cause of the change in slope of the curve $\delta\omega(p)$.

Besides the collision broadening, the unresolved rotational structure enters into the observed width for the Q branch of the vibrational band of nitrogen. From the $\delta\nu(p)$ curve extrapolated to zero pressure we can separate out the constant part of the width due to the rotational splitting; the remaining part of the width, which is pressure dependent, naturally belongs to the collision broadening. The magnitude of the rotational splitting coincides with the calculations carried out below, the linear variation of the collision broadening agrees with the theory, and therefore the separation operation is completely admissible.

The width of the Q branch of nitrogen depends weakly on the pressure. Calculations based on collision theory and utilizing the experimental data yield $\rho_\nu = 0.43$ A for the effective optical collision radius for the vibrational line, i.e., significantly less than the kinetic-theory radius, $\rho_{\text{gas}} = 1.84$ A. Such a small value of ρ_ν signifies only a small role of collisions in the broadening of the Q branch. The different values of ρ_ν and ρ_ω observed in practice testify to the different mechanisms of collision broadening of the rotational and vibrational lines. Here, evidently, the following fact plays a role: unlike the O and S branches of the rotational spectra (transitions $\Delta\nu = 0$, $\Delta J = \pm 2$), the Q branch is composed of transitions in which the rotational state does not change ($\Delta J = 0$). Therefore only the perturbation of the vibrational component of the Q-branch structure during a collision influences the width, and perturbation of the rotational components does not manifest itself.

The effective radii found for the nitrogen Raman scattering, $\rho_\omega = 3.3$ A and $\rho_\nu = 0.43$ A, differ from the radii for the nitrogen microwave band $\rho_{\text{mw}} = 1.4 \sim 2.25$ A, quoted in reference 8; the observed difference points out the different effectiveness of the impact for these processes.

2. It was indicated above that the observed width of the Q branch was not due solely to collision broadening. The change of the moment of inertia of the molecules in vibration changes the separation between the rotational levels, and the rotational components of the Q branch are not exactly superimposed one on another, but are somewhat split. This structure, not resolved by the apparatus, introduces an additional contribution into the observed width.

The frequencies of the rotational component of the Q branch are described by the formula

$$\nu = \nu_0 - 2x_0\nu_0 - \alpha J(J+1),$$

where $\nu_0 - 2x_0\nu_0$ is the frequency of the undisplaced component, and $\alpha = B_0 - B_1$ is the vibrational-rotational interaction constant. The distribution of intensities among the different components is given by the expression (see reference 2)

$$I_\nu = I_0\sqrt{1+4\nu/\alpha}\; e^{-B\nu/kT\alpha}.$$

The rotational structure of such a type is shown dotted in Fig. 4. Taking into account the dependence on J of the distance between components (which was neglected in reference 2), it is easy to find the averaged intensity distribution in the Q branch:

$$I_{\mathrm{av}} = I_0 \exp\left\{-\frac{B}{kT}\frac{\nu}{\alpha}\right\} \Big/ \left[1 + (1+4\nu/\alpha)^{-1/2}\right],$$

(the cross-hatched contour in Fig. 4). Graphical calculation for N_2 ($B = 1.998$ cm^{-1}, $\alpha = 0.171$ cm^{-1} and $T = 300°$K) leads to a width due to the unresolved rotational structure $\delta\nu_{\mathrm{rot}} = 1.54$ cm^{-1}.

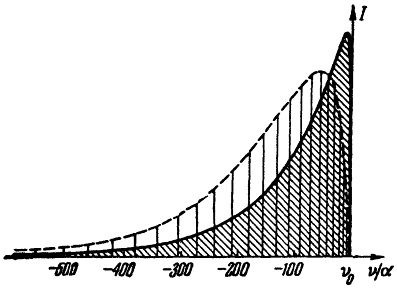

FIG. 4. The rotational structure of the nitrogen Q band at 300°K.

The pressure-independent part of the width, which is separated from the observed dependence of $\delta\nu(p)$ by extrapolating the curve to zero pressure, equals 1.6 cm^{-1}, i.e., it coincides with the calculations, and hence is explained by the rotational structure of the Q branch unresolved by the apparatus.

The asymmetry of the observed contour serves as additional proof of the presence of rotational splitting. For p = 60 atmos, each rotational component of the Q branch was broadened to the magnitude of the collision and apparatus broadening (~ 1.5 cm^{-1}) and a rounded contour was constructed which coincided well with the one observed (in Fig. 2 calculated points are denoted by crosses).

As is evident from Table II, the rotational splitting introduces a basic length into the observed width of the Q branch and a significantly larger collision broadening over a comparatively wide interval of temperature.

3. In conclusion we shall dwell momentarily on the role of the temperature. The frequency and energy of collisions and the distribution of the molecules over the rotational levels changes with the temperature; with an increase in temperature both these factors operate in identical directions: in view of the change of the populations of the rotational levels of the Q branch, more and more components appear and the width of their structure grows, the collision broadening of the rotational and vibrational lines also increasing.

A detailed examination of the rotational structure of the Q branch and of the value obtained for ρ_ν found allows us to calculate the width of the vibrational lines at various temperatures; in Table II the present calculations are compared with the results of measurements for nitrogen at t = 200, 27 and −190° C. The measured values of $\delta\nu$ coincide with the calculations within the limits of error. For −190° C the experimental data belong to the liquid, whereas the calculations were made for the gas. The agreement between the present calculations and the observed width in the liquid may be due to the width being fundamentally caused by rotational splitting, which is also present in the liquid; only a small part is due to the range of the intermolecular interaction.

The present work was conducted at the suggestion of the prematurely deceased Academician G. S. Landsberg, and was conducted under his direction in the first stages. I consider it my duty to thank Profs. P. A. Bazhulin and I. I. Sobel'man for advice in the performance of the work and the discussion of results, and also my associates at the High-Pressure Physics Institute

TABLE II. Comparative contributions of the collision broadening and rotational splitting to the width of the Q branch of nitrogen at various temperatures

t, °C	p at 27°C	Calculated for the gas			Experimental
		$\delta\nu_{\mathrm{rot}}$	$\delta\nu_{\mathrm{col}}$	$\delta\nu=\delta\nu_{\mathrm{rot}}+\delta\nu_{\mathrm{col}}$	$\delta\nu$, cm^{-1}
200	50 atmos	2,34	1.4	3.8	5.4±1.5
27	50 atmos	1.54	0,2	1,75	1.8±0.2
—190	liquid, $\rho = 0.5$ g/cm^3	0,45	0,05	0.5	0.4±0.2

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