

Position and width of Q -band of nitrogen molecules in cryogenic mixtures

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We measured the broadening and shift of the center of the vibrational resonance $\nu = 2326.5 \text{ cm}^{-1}$ of liquid nitrogen following addition of liquified argon and oxygen. In the N_2 -Ar mixture, the line width increases monotonically from 2 GHz in pure N_2 to 4 GHz at 60% Ar and more, and in the N_2 - O_2 mixture a maximum width ~ 2.4 GHz is reached at 40% concentration of O_2 , followed by a narrowing of the line. The shift induced by Ar is almost twice as large as the shift produced by O_2 , and at 70% concentration of Ar it amounts to 15 GHz. The experimental data are interpreted within the framework of the theory of impact broadening of lines in a liquid, using the concept of "collapse" of the Q band on account of the collisions that participate in the liquid phase.

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1. We report in this communication the results of an experiment of the measurement of the width and position of an ultranarrow (width $\Delta\nu = 0.066 \pm 0.002 \text{ cm}^{-1}$) Raman-scattering (RS) line of nitrogen molecules (N_2) with frequency $\nu \approx 2326.5 \text{ cm}^{-1}$ in pure liquified N_2 and in other solvents.

The measurements were performed for the first time ever at high spectral resolution (0.002 cm^{-1}) by the method of active Raman spectroscopy (ARS) of light. The results show that the parameters of the RS line of N_2 molecules dissolved in a monatomic liquid (liquid argon, Ar) and in a diatomic molecule liquid (liquid oxygen, O_2) behave quite differently. Whereas when N_2 is dissolved in Ar the N_2 line width increases monotonically from 2 GHz in pure N_2 to 4 GHz at a 60% Ar concentration and more, in liquid oxygen the N_2 line width changes nonmonotonically with increasing O_2 concentration and the maximum broadening does not exceed 20%.

Since the Ar atoms and O_2 molecules influence quite differently the rotational relaxation of the N_2 molecules, the obtained data can be regarded as an experimental confirmation of the notion of the "collapse" of the rotational structure of the Q band of nitrogen molecules in the liquid phase.

2. The pure vibrational transition of liquid nitrogen $\nu \approx 2326.5 \text{ cm}^{-1}$ is one of the narrowest in condensed media.^[1-3]

The prevalent opinion is that this is due to interference phenomena following superposition of individual Q -band J components that have become broadened because of the collisions that take part in the liquid phase and cause a change in the angular momentum ("motional narrowing").^[2,4]

This effect, with N_2 gas as an example, was first considered in^[5] and experimen-

tally observed in^[4]. A complete classical theory of the effect was presented recently in^{[6,1)}

However, the very fact of the strong "narrowing" of the RS line of liquid N₂ can itself not yet be regarded as unequivocal proof of a manifestation of this effect in the liquid phase.

From this point of view, particular interest attaches to experiments with solutions of N₂ in liquids that alter substantially the character of the rotational relaxation of the N₂.

This is precisely the method chosen by us to study the nature of the ultranarrowing of the Q band of N₂ molecules.

3. We measured in the experiment the width and the position of the maximum of the RS line of N₂ molecules following addition of inert solvents (liquid argon and oxygen) to the Dewar with the liquid nitrogen. Both the nitrogen itself and the employed solvents are characterized by a small specific heat of evaporation and are simple non-associated liquids. The gas-kinetic diameters of their molecules are close and amount to ~3.5 Å.

The measurements were carried out in accordance with the ARS scheme using narrow-band stabilized cw lasers (the experimental setup is described in^[7]; see also^[8]). The spectral resolution, determined by the laser-emission line widths, was ~60 MHz (~0.002 cm⁻¹). The frequency was scanned discretely in steps of 390 MHz.

The character of the variation of the parameters of the RS line of nitrogen follow-

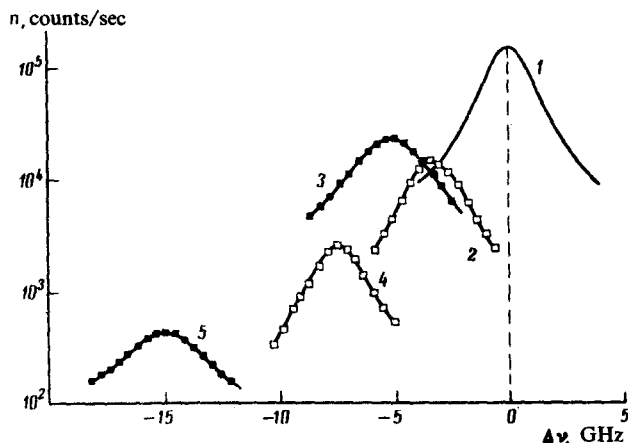


FIG. 1. Deformation of the contour and shifts of the center of the RS line of nitrogen molecules in the liquid phase following addition of liquified argon or oxygen. An ARS scheme is used with registration of the signal in the anti-Stokes region ($\lambda_a \approx 4595 \text{ \AA}$) and photon counting. The noise-count level is less than 40 counts/sec: 1—pure liquified N₂, continuous scanning of the frequency of a dye laser; 2, 4) solution of N₂ in O₂, the molar concentrations of N₂ are 75 and 35% respectively; 3, 5) solution of N₂ in Ar, the molar concentrations of N₂ are 75 and 35% respectively; ■, □—experimental points. The shift of the central frequency of the RS line is towards lower frequencies in either case.

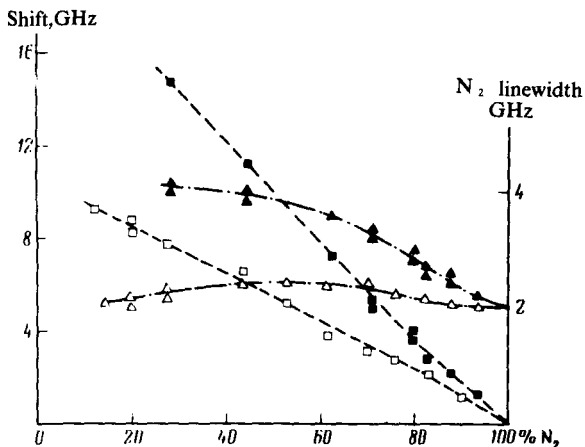


FIG. 2. Summary of experimental data: dark triangles—change of width of $\nu=2326.5\text{ cm}^{-1}$ line following dilution with liquid argon; black rectangles—shift of line center for the same case; triangles—change of width of N_2 line following dilution liquid oxygen; light rectangles—shift of central frequency in this case.

ing addition of liquified Ar and O₂ is shown in Fig. 1. A summary of the experimental data on the width and position of the line as a function of the concentration of the solvent is shown in Fig. 2. The most interesting result is the clearly pronounced difference in the character of the broadening of the RS line of nitrogen following addition of a monatomic (Ar) and a diatomic (O₂) solvent: in the former case a monotonic increase of the width to 4 GHz is observed at 60% Ar and more, while in the latter case the maximum width (~ 2.4 GHz) is reached at a 40% concentration of O₂, and with further increase of the concentration the line begins to narrow. The shift of the RS line center of N₂, due to the oxygen, is almost half the shift induced by the argon atoms.

Although the solutions were at normal pressure, and consequently their temperature ranged from 77 K in pure N₂ to 87 K at the maximum Ar concentration and to ~ 90 K at the maximum O₂ concentration, the effects of temperature on the line width can be neglected, inasmuch as according to^[2] the line width in pure N₂ remains constant at ~ 2 GHz up to ~ 100 K.

4. Despite the relative simplicity of the liquids used in the experiment, and the fact that they have been well studied, it is impossible to present a complete interpretation of the results. An attempt at a qualitative explanation can be made within the framework of the concept of antibroadening of the RS line, where "gas-like" motion of the molecules in the liquid is assumed.^[4-6,12] In fact, addition of a monatomic liquid (Ar) to liquid N₂ hardly changes the frequencies of the collisions of the N₂ molecules with the neighboring molecules, but the character of the N₂-N₂ and N₂-Ar collisions is entirely different. In the first case the angular momentum is easily transferred from one molecule to the other within the time $\tau_J \approx 0.19$ psec,^[9] i.e., on the average after two or three collisions, while in N₂-Ar collisions this transfer is made difficult, inasmuch as in the model of hard rough spheres^[1] the monatomic molecule Ar, which has no intrinsic angular momentum, must be regarded as an ideally smooth sphere. Therefore, even though the N₂ molecule is not ideally spherical (the ratio of the "width" to the "length" is 1:1.3^[11]), the addition of argon to liquid N₂ should apparently lead to an increase in the relaxation time τ_J of the angular momentum of the N₂ molecules. We note that the slowing down of the rotational relaxation in molecular gases follow-

ing addition of heavy noble gas atoms is well known^[10]). The latter, in turn, should broaden the RS line in accord with the theory of the Q-band collapse.^[5,6]

On the other hand, N₂-N₂ and N₂-O₂ collisions do not differ so strongly. Although there are no NMR data on the degree of "roughness" of the paramagnetic molecules O₂, it can be assumed that it differs little in this respect from N₂, while the masses, volumes, and the packing-density parameters of these molecules are quite close. One should therefore not expect a considerable broadening of the RS line of N₂ when some of the N₂ molecules are replaced by an equivalent number of O₂ molecules.

We note finally that the presented interpretation is also favored by our data obtained on the RS line shape and on the degree of its depolarization in pure liquified N₂^[3]: the shape of this line is well described by a Lorentz curve in a signal dynamic band up to 10⁴, and the degree of depolarization of $\rho \leq 0.02$.

It must be emphasized, however, that a quantitative description of the obtained experimental data within the framework of the existing theories^[5,6] is difficult. Estimates show that to obtain quantitative agreement of the data on the N₂-Ar mixture with the calculation^[6] it must be assumed that at a 60% concentration of the Ar the relaxation time τ_j of the angular momentum of the N₂ molecules should increase by almost five times.

In a rigorous description of the situation that arises here it is necessary, besides taking into account the rotational relaxation, to consider also the inhomogeneous broadening of the vibrational transition of N₂ on account of the fluctuations of intermolecular-interaction potential in the liquid, and other mechanisms of pure "vibrational" relaxation (which apparently determines in both cases the shift of the line center), and also the quantum character of the N₂ molecular rotator at $T=77$ K.

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¹¹An analog of the theory of^[6] was recently developed in^[12], where the theory is used in an attempt to describe quantitatively the experimental results of^[2].

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