

Pressure-induced change of the shape and width of the Q branch of the coherent anti-Stokes light scattering spectrum of the ν_2 oscillations of acetylene

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We investigated in the pressure range 10–120 atm the width and shape of the Q branch of the ν_2 oscillation of acetylene dissolved in nitrogen gas. We observed narrowing of the Q branch with increasing density. The measurements were performed by the method of coherent anti-Stokes light scattering (CALS).

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At high gas densities, the main contributions to the contour width of the isotropic Q band of the Raman-scattering spectrum of molecules is made by resonant collisional energy exchange, by collisions that alter the character of the vibrational motion, and by rotationally inelastic collisions. In the investigation of gases dissolved at small concentrations in an extraneous gas, the resonant exchange processes can be neglected, and at a $\hbar\Omega_j \gg kT$ (T is the gas temperature and Ω_j is the frequency of the vibrational-rotational transition) the main contribution to the transformation of the Q band is made by rotationally inelastic collisions. It was first shown in^[1] that at gas densities such that the width of the individual J components becomes larger than the distance between them, rotationally inelastic collisions lead to a narrowing of the Q band. This phenomenon (motional narrowing) was observed experimentally in the Raman spectra of the gases CO, N₂, HD, and N₂O,^[2–4] and analytic expressions that describe the transformation of the isotropic and anisotropic Q bands of the Raman spectra of linear molecules, as functions of the density, were derived in^[5].

In the present study we investigated the shape, width, and shifts of the Q -band of the oscillation $\nu_2 = 1974 \text{ cm}^{-1}$ of acetylene (C₂H₂) dissolved in nitrogen gas. We used for this purpose a high-resolution CALS method ($\sim 10^{-3} \text{ cm}^{-1}$) employing single-frequency cw lasers.

The experimental setup of the high-resolution CALS spectrometer is described in detail in^[6]. We used collinear beam interaction. The frequency shift of the position of the maximum of the investigated line was calibrated accurate to 500 MHz against the simultaneously registered absorption spectrum of molecular-iodine vapor. The polarizations of the interacting waves were the same, and in as much as for the ν_2 Q band of C₂H₂ the degree of polarization is $\rho = 0.03$,^[7] the contribution of the anisotropic component to the registered radiation did not exceed 4% of the maximum intensity.

Figure 1 shows the dependence of the width (full width at half height) of the CALS line of the Q -band spectrum on the gas-mixture pressure. At pressures ~ 10 atm

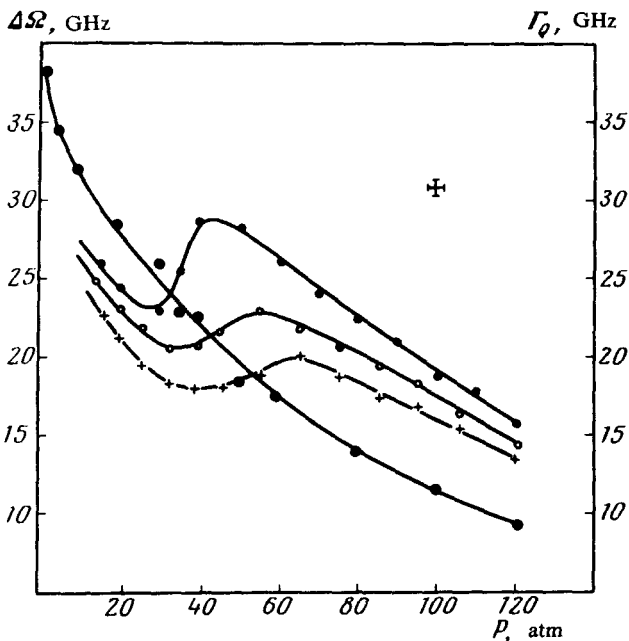


FIG. 1. Total width Γ_Q :
 +—0.55, atm C_2H_2 , o—1.7
 C_2H_2 , ·—3.7 atm C_2H_2 and
 ●—shift of Q branch relative to
 the frequency reference point.

one observes a line narrowing due to the fact that, starting with a certain density value at which the collision frequency becomes comparable with and exceeds the frequency splitting $2\alpha J$ (where α is the vibrational-rotational interaction constant and J is the rotational quantum number), further increase of the density alters the character of the vibrational-rotational interaction. Following the results of^[5] and assuming $\alpha = 5.91 \times 10^{-3} \text{ cm}^{-1}$ for ν_2 of C_2H_2 ,^[8] calculation shows that the line narrowing should begin in the pressure region 20 atm, in good agreement with experiment.

In the pressure region 10–60 atm, one observes a nonmonotonic variation of the line width, due to the presence of smoothed-out “steps” (Fig. 2, curve b) on the line contour, whose frequency positions do not coincide with the positions of the J components and remain unchanged when the pressure is varied, whereas the position of the maximum shifts monotonically. At pressures above 60 atm, the contour becomes fully smoothed out and symmetrical, while at 120 atm it hardly differs from a Lorentz line (points on curve d of Fig. 2).

Using the expressions obtained in^[5], we calculated the cross section $\sigma_J = \pi\rho_J^2$ of the inelastic collisions of $C_2H_2-N_2$, and found it to be $\sigma_J = 6.5 \times 10^{16} \text{ cm}^2$ ($\rho_J = 1.4 \text{ \AA}$) much lower than the gas-kinetic cross sections of $C_2H_2-C_2H_2$ ($\rho_0 = 2.52 \text{ \AA}$) and N_2-N_2 ($\rho_0 = 1.85 \text{ \AA}$) calculated from data on the viscosity,^[9] as well as the cross sections of the collisions that broaden the Q_0 line in the resolved spectrum of the Q band of C_2H_2 ($\rho_0 = 2.32 \text{ \AA}$).^[8] Since the effect of the broadening of the line by the resonant $C_2H_2-C_2H_2$ collisions is superimposed on the effect of the collision narrowing, the calculations were performed for the case of a minimal molar concentration of C_2H_2 in N_2 , equal to 1 : 200. The presence of resonance broadening is attested by the fact that the $\Gamma(P)$ curves for large partial pressures of C_2H_2 lie much lower than the curves for the smaller partial pressures (see Fig. 1).

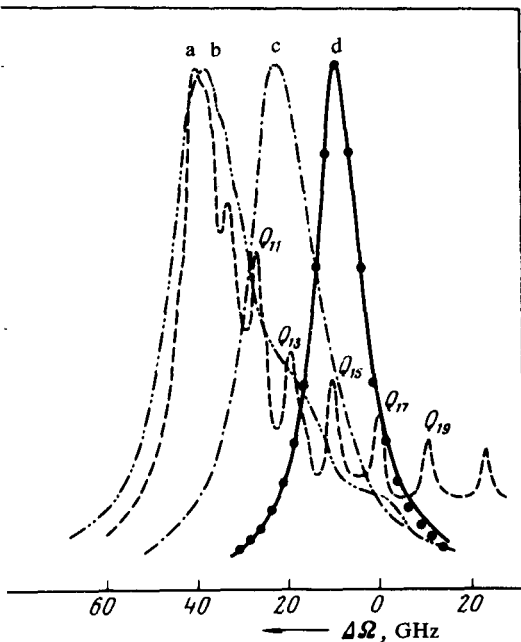


FIG. 2. a—0.55 atm C_2H_2 ;
 b—1.7 atm C_2H_2 ; ○—1.7 atm
 $C_2H_2 + 40$ atm N_2 ; d—1.7
 $C_2H_2 + 120$ atm N_2 .

Figures 1 and 2 show the shift of the position of the maximum of the Q band as a function of the gas density; this shift, as seen from the figures, greatly exceeds the one that follows from the theory.^[5] (According to^[5], the band should contract towards the center of gravity of the resolved spectrum, located at a distance 21 GHz from the position of the frequency reference.) The apparent reason is that the surrounding molecules already exert a noticeable influence on the vibrational motion.

It should be noted in conclusion that the use of the CALS method to investigate molecular interaction in high-pressure gases combines such advantages as high spectral resolution (up to 40 MHz) at high signal-noise ratios (up to 10^3 in the present experiments), and greatly extends the experimental capabilities in the investigation of mechanisms of line broadening in Raman-scattering spectra.

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