Determination of the translational-relaxation cross section from the measured Dicke contraction in the coherent anti-Stokes Raman spectra of the D_2 molecule

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The widths of the Q_0 and Q_2 lines of the D_2 molecule have been measured at various densities over the range from 0.01 to 40 amagat with a resolution of $0.001\ cm^{-1}$. The translational-relaxation contribution to the line widths has been determined. The cross section for the process has been measured.

One of the interesting spectral manifestations of the molecular collision processes currently under study is the contraction of a spectral line with increasing gas density (the contraction of the Doppler line or "Dicke contraction," first discussed by Dicke,[1] and the contraction of the isotropic Q branch, first explained by Alekseev and Sobel'man[2]). The reason for the importance of this contraction is that additional information can be extracted from the way in which a line contracts with increasing density and also from the very fact that this contraction occurs, when the contributions of the

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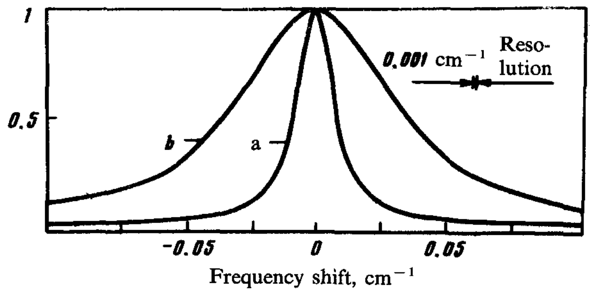

FIG. 1. Shape of the Q_2 line in the coherent anti-Stokes Raman spectrum of deuterium at two densities: a—0.1 amagat; b—15 amagat.

various collision processes to the line shape are sorted out, and information is obtained from the cross sections.

The basic purpose of the present study was to measure the cross section for the translational relaxation of the D_2 molecule through a detailed study of the density-associated broadening of the Q_0 and Q_2 lines of vibrational-rotational transitions in the "Dicke contraction region." Theory has been derived for the shape, width, and shift of the line in the transition from Doppler broadening to homogeneous collisional broadening with allowance for Dicke contraction.[1,3–6] Experimentally, this effect has been observed in Raman spectra only for H_2 and D_2 molecules.[7,8] Detailed experiments on the shapes of individual rotational lines in the Raman spectra of low-density gases have been hindered by the finite spectral resolution and sensitivity of spontaneous Raman spectroscopy. The development of the method of coherent anti-Stokes Raman spectroscopy (CARS) has substantially changed the situation and has made it possible to study line shapes with an instrumental resolution of 0.001 cm^{-1} over the density range 10^{-2}–10^2 amagat.[9–11] By using CARS we have been able to follow the evolution of the line shape over a dynamic range of 10^3–10^4, which corresponds to deviations of hundreds of half-widths from the frequency at the center of the line. Figure 1 shows

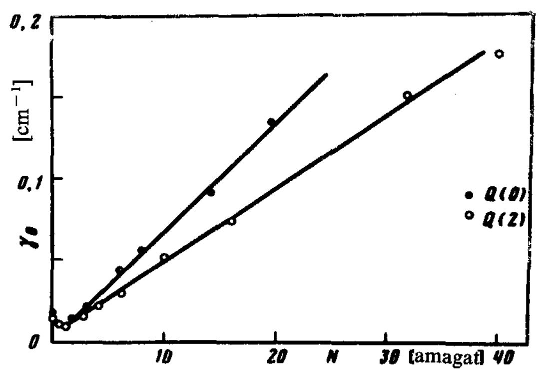

FIG. 2. Density dependence of the widths of the Q_0 and Q_2 lines of deuterium.

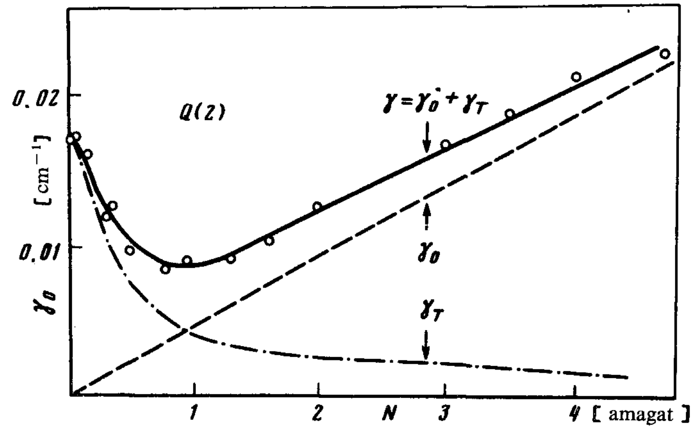

FIG. 3. The widths γ, γ_0, and γ_t of the deuterium Q_2 line in the Dicke contraction region.

parts of experimental spectra for the Q_2 line. Figure 2 shows the density dependence of the widths of the Q_0 and Q_2 lines determined from spectra of this type over the density range from 0.01 to 40 amagat. The line shapes at densities from 0.01 to 0.1 amagat can be described quite accurately by a Gaussian profile (Fig. 1a) with a width $\gamma = (18 \pm 1.5)\times 10^{-3}$ cm^{-1}, indicating that the line broadening in this density range is a purely Doppler broadening. The homogeneous width γ, masked by the Doppler line, is due to rotationally inelastic collisions (for which the cross sections are σ_r) and elastic collisions which alter the velocity vector (σ_t) or the phase of a vibrational motion (σ_v). With increasing density, as the collision rate becomes comparable to the Doppler line width, the further line broadening leads to a contraction of the Doppler line. The line width due to translational relaxation decreases, and the line becomes homogeneously broadened only by rotationally inelastic collisions and collisions which change the phase of a vibrational motion. This range corresponds experimentally to densities of 10 amagat and up. The line shape is approximately Lorentzian in this region (Fig. 1b). With a further increase in the density, the line width increases linearly with the density (Fig. 2). From the slope of the corresponding curves we determined the broadening coefficients $d\gamma_0/dN$ and the Q_0 and Q_2 lines: $(d\gamma_0/dN)(Q_0) = (6.7 \pm 0.1)\times 10^{-3}$ cm^{-1}/amagat and $(d\gamma_0/dN)(Q_2) = (4.6 \pm 0.1)\times 10^{-3}$ cm^{-1}/amagat. The total cross section is calculated from $\gamma_0 = N(\sigma_r + \sigma_v)\langle v\rangle/2\pi c$, where $\langle v\rangle = \sqrt{16kT/\pi m}$, m is the mass of the molecule, and N is the density. The total cross sections are found to be $\sigma_{r+v}(Q_0) = (1.37 \pm 0.03)\times 10^{-16}$ cm^2 and $\sigma_{r+v}(Q_2) = (0.94 \pm 0.02)\times 10^{-16}$ cm^2. At intermediate densities, between 0.1 and 10 amagat (Figs. 2 and 3), a Dicke contraction is observed for the Q_0 and Q_2 lines with minimum widths $\gamma(Q_0) = (10 \pm 1.5)\times 10^{-3}$ cm^{-1} and $\gamma(Q_2) = (9 \pm 1.5)\times 10^{-3}$ cm^{-1}, which are reached at 0.75 and 0.9 amagat, respectively. It should be noted that the line shape remains symmetric in this region, within the experimental error. Extrapolating the linear dependence of γ_0 to a zero density, we were able to determine that part of the total width γ (Fig. 3) which decreased with the density: $\gamma_t = \gamma - \gamma_0$. Using the relation[3,5] $\gamma_T = 4\pi\langle v\rangle v_0^2/3c^3N\sigma_T$, where $\nu_0 = 2986$ cm^{-1} is the frequency of the vibrational transition of the D_2 molecule, we calculated the translational-relaxation cross sections, finding $\sigma_t(Q_0) = (20.7 \pm 0.5)\times 10^{-16}$ cm^2 and $\sigma_t(Q_2) = (21.1 \pm 0.5)\times 10^{-16}$ cm^2. By way of comparison, the value $\sigma_t = 20.2$ is found from the relation $\eta = \langle v \rangle m/3\sigma_T\sqrt{2}$ and experiments on the viscosity coefficient η (Ref. 12).

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