

# Pressure-induced transformation of the Q branch of the rotational-vibrational Raman-scattering spectrum

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We calculate in the strong-collision model the pressure-induced transformation of the contour of the unresolved rotational structure of the Q branch of the Raman scattering spectrum of linear molecules, in the course of which the spectrum becomes homogeneous, its anisotropy component broadens, while the isotropic component is narrowed.

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The rotational fine structure of the shape of the vibrational-transition Q band, resulting from the interaction of the vibrations with the rotation<sup>[1]</sup>, was observed both in anisotropic Raman scattering (RS) of light and in isotropic scattering, when only transitions without a change of the rotational quantum number ( $\Delta J=0$ ) are possible. The experimentally observed<sup>[2]</sup> "non-broadening" of the Q branch with increasing pressure (as contrasted to the increase, proportional to the density, in the width of each rotational component of the O or S branch), gave grounds for proposing, for the first time,<sup>[3]</sup> that the principal mechanism governing the shape of the Q-branch contour is spectral exchange, which leads under certain conditions<sup>[4]</sup> to a narrowing of the spectrum with increasing density. In the same reference,<sup>[3]</sup> the shape of the Q-band contour and its variation with increasing collision frequency were obtained by numerical calculation for the case of weak collisions. The increase in the accuracy and the use of a polarization<sup>[5]</sup> procedure in RS experiments have shown that further increase of the density leads to a narrowing of the isotropic scattering line and a broadening of the isotropic line.<sup>[6–8]</sup> In our present study, using a classical (continuous in the frequency scale) description of the shape of the Q band, we are able to reduce the problem to the integro-differential equations of the theory of sudden modulation,<sup>[9]</sup> which can be solved exactly in the strong-collision approximation. This has made it possible to trace analytically the pressure-induced transformation of both the isotropic and anisotropic Q bands of the RS spectrum of linear molecules and to determine the origin of the difference between them.

When  $J' - J$  transitions are induced between rotational collision terms, a change takes place in the free-path emission-line frequency  $\omega_Q = \alpha_e J(J+1)$  ( $\alpha_e$  is a known constant<sup>[1]</sup>). If the collisions are strong enough, then the probability of changing the frequency does not depend on the value of  $J'$  prior to the collision, and coincides with equilibrium Boltzmann distribution  $\phi(J)$ . Confining ourselves to examination of the unresolved structure, we can assume  $J$  to vary continuously, so that

$$\phi(J) = \beta(2J + 1) \exp\{-\beta J(J + 1)\}; \quad \beta = T^*/T,$$

where  $T^* = \hbar^2/2Ik$  is the characteristic temperature.

Using the correlation theory of line shape,<sup>[9]</sup> we express the spectrum in the form

$$G(\omega) = \frac{1}{\pi} \operatorname{Re} \int_0^{\infty} d_Q(t) \exp\left[-i\omega\left(t + \frac{i\hbar}{2kT}\right)\right] dt = F(\omega) \exp\left[\frac{\hbar\omega}{2kT}\right], \quad (1)$$

where  $d_Q(t)$  is the correlation function of either the scalar (isotropic scattering) or anisotropic (anisotropic scattering) part of the polarizability tensor. If we represent  $d_Q(t)$  in the form

$$d_Q(t) = \int_0^{\infty} d_Q(t, J) dJ,$$

then we can obtain for its  $J$ -component in the usual manner<sup>[9]</sup> the kinetic equation

$$\frac{\partial}{\partial t} d_Q(t, J) = i\alpha_e J(J + 1) d_Q(t, J) - \frac{1}{\tau_J} d_Q(t, J) + \frac{a}{\tau_J} \phi(J) d_Q(t) \quad (2)$$

which is equally valid for the isotropic and anisotropic components, but

$$a = \begin{cases} 1 & \text{for isotropic scattering} \\ \int_0^{\pi} P_2(\cos \alpha) \frac{d\alpha}{\pi} = \frac{1}{4} & \text{for anisotropic scatter (see [10])} \end{cases}$$

where  $\alpha$  is the angle through which the plane of rotation of the molecule is reflected as a result of the collision. The influence of the orientational relaxation on the shape of the anisotropic  $Q$  band is due to the existence of spectral exchange between the  $O$  components of the  $Q$  and  $S$  branches with identical  $J$ .<sup>[10]</sup> At not too large pressures, the overlap of the  $Q$  branch with the  $O$  and  $S$  branches is negligible, the impact operator producing the exchange is diagonalized, and the role of the exchange reduces only to a decrease of the "arrival" term in (2). The initial condition for (2) is

$$d_Q(0, J) = d_Q(0) \phi(J),$$

where  $d_Q(0) = 1$  in isotropic scattering and  $d_Q(0) = 1/4$  in anisotropic scattering, in accord with the fact that  $3/4$  of the intensity of the anisotropic  $O-Q-S$  spectrum, orthonormalized to unity, goes to the  $O$  and  $S$  bands.<sup>[11]</sup>

Solving (2) formally with respect to  $d_Q(t, J)$  with subsequent integration with respect to  $J$ , we arrive at the integral equation

$$d_Q(t) = \frac{e^{-(t/\tau_J)}}{1 - i\bar{\omega}_Q t} + \frac{a}{\tau_J} \int_0^t \frac{d_Q(t') e^{-(t-t')/\tau_J} dt'}{1 - i\bar{\omega}_Q(t-t')},$$

which can be easily solved by using the Laplace transformation, after which, taking (1) into account, we obtain

$$F(\omega) = \frac{d_Q(0)}{\pi \bar{\omega}_Q} \operatorname{Im} \left\{ \frac{\exp(-z) Ei(z)}{1 + ia \Gamma \exp(-z) Ei(z)} \right\}, \quad (3)$$

where

$$\bar{\omega}_Q = \int_0^{\infty} \omega_Q \phi(J) dJ = a_e (T/T^*); \quad z = x - i\Gamma; \quad x = \omega/\bar{\omega}_Q; \quad \Gamma = 1/\bar{\omega}_Q \tau_J,$$

and  $Ei(z)$  is the integral exponential function (see [12]). Formula (3) gives analytically the dependence of the spectral contour on the gas density  $n$  in terms of  $\tau_J = (n \sigma_J \nu)^{-1}$  ( $\nu$  is the average thermal energy, and  $\sigma_J$  is the cross section for the scattering with change of the rotational state).

As  $\Gamma \rightarrow 0$ , Eq. (3) reduces to the function

$$F_0(\omega) = \lim_{\Gamma \rightarrow 0} F(\omega) = \frac{d_Q(0)}{\bar{\omega}_Q} \exp\left(-\frac{\omega}{\bar{\omega}_Q}\right) \quad (\omega > 0)$$

which is the distribution of the intensity in the  $Q$  band of a free classical rotator. [13] In the opposite limiting case ( $\Gamma \gg 1$ ) expression (3) again simplifies, so that

$$F(\omega) = \frac{d_Q(0)}{\pi \bar{\omega}_Q} \frac{(1-a)\Gamma + \frac{\Gamma}{x^2 + \Gamma^2}}{\left[x - 1 - \frac{x}{x^2 + \Gamma^2}\right]^2 + \left[(1-a)\Gamma + \frac{\Gamma}{x^2 + \Gamma^2}\right]^2},$$

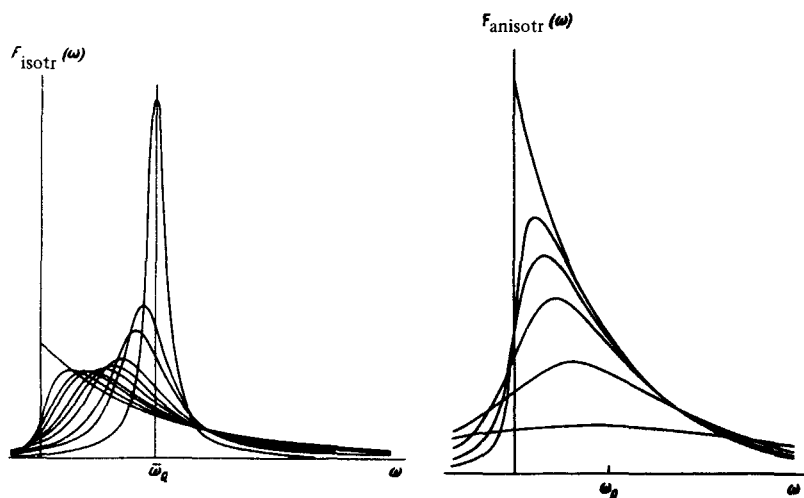


FIG. 1.  $\Gamma = 0; 0,1; 0,2; 0,4; 1; 3$ . FIG. 2.  $\Gamma = 0; 0,1; 0,2; 0,3; 0,5; 0,7; 1; 2; 3; 10$ .

from which we see that the half-width of the isotropic band ( $\Delta\nu_{1/2}^{is} = \bar{\omega}_Q^2 \tau_J$ ) decreases in inverse proportion to the density, while the half-width of the anisotropic Q branch increases in direct proportion to the density ( $\Delta\nu_{1/2}^{anis} = (3/4) \tau_J^{-1}$ ) until the overlap of the Q branch with the O and S branches becomes appreciable. The subsequent behavior of the contour of the vibrational-rotational band of anisotropic scattering is determined entirely by the effects of the O-Q-S exchange. <sup>[10]</sup>

The spectral contours of both components, in the intermediate region of pressures, are shown in Figs. 1 and 2.

It should be noted in conclusion that an equation of type (2) describes not only the RS spectrum of linear molecules, but also the Q branch of IR absorption and RS spectra of spherical tops (the symmetry of the molecule influences only the value of the parameter  $a$  and the form of the  $\phi(J)$  distribution). The ability to solve (2) analytically is useful in those cases when knowledge of the shape of the Q band is essential for the determination of the gain and also for different resonance effects. <sup>[14]</sup>

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