Spectral manifestations of various mechanisms of rotational relaxation in dense media

S. I. Temkin and A. I. Burshteĭn

Institute of Chemistry of Kinetics and Combustion, Siberian Division, USSR Academy of Sciences
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The transformation of the contour of the Q branch of the CARS (coherent anti-Stokes Raman Spectroscopy) spectrum in the case of strong and weak collisions is calculated. The presence of a initial-broadening stage preceding the narrowing of the spectrum is demonstrated. Methods of experimentally determining the collision forces at high densities are proposed.

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Intermolecular interactions between a spectroscopically active particle and a solvent induce rotational relaxation but cause interference of the overlapping J components of the Q branch (transitions with $\Delta J = 0$) of the vibrational—rotational Raman-scattering spectrum, and consequently lead to a specific character of the change of the shape of its contour as a function of the density or when the solvent is replaced.[1–3] The main experimental features of this phenomenon admit of a simple qualitative interpretation within the framework of the impact line broadening theory.[4,5] In view of the recent advent of new experimental possibilities of investigating spectra with the aid of active Raman spectroscopy (designated ARS or CARS),[6–8] it is of interest to investigate in detail the degree to which changes of the shape and width of the CARS line and its shift are sensitive to different models of rotational relaxation. This is all the more important since the method has a very high spectral resolution (0.001 cm^{-1}). In contrast to ordinary Raman-scattering spectra, the CARS spectrum is a nonlinear function of the cubic susceptibility and, according to Refs. 9 and 10, is proportional to the square of its modulus

$$F^{\mathrm{CARS}}(\omega) \sim |F(\omega)|^2, \tag{1}$$

which in turn is expressed in the known fashion[5]

$$F(\omega) = \int_0^\infty e^{-i\omega t}\, dt \int_0^\infty d_Q(t, J)\, dJ \tag{2}$$

in terms of the correlation function $d_Q(t,J)$. The time evolution of $d_Q(t,J)$ depends on the extent to which J is changed by the collisions. The literature usually deals with two limiting models—weak collisions, which induce transitions only between neighboring J terms,[4] and strong collisions,[5] after which the probability of finding a molecule having a given angular momentum J coincides with the Boltzmann angular-momentum distribution of a linear top $\phi(J) = 2\beta J \exp\{-\beta J^2\}$, $\beta = T^*/T$, where $T^* = \hbar^2/2Ik$ is the characteristic temperature for a molecule with moment of inertia I. In the quasiclassical approximation it is possible to describe in unified form the orientational relaxation for collisions of any strength.[11] Our earlier calculation[5] of the strong-collision model is sufficient for the calculation of the CARS spectrum in the same approximation. In the other limiting case of weak collisions we obtain within the framework of this theory the following relaxation equation

$$\frac{\partial}{\partial t} d_Q(t, J) = i\alpha_e J^2 d_Q(t, J) + \frac{1}{\tau_J}\left[1 + \frac{1}{2\beta J^2}\right] d_Q(t, J) + \frac{1}{\tau}\hat{L} d_Q(t, J),$$

$$\hat{L} = J\left[1 - \frac{1}{2\beta J^2}\right]\frac{\partial}{\partial J} + \frac{1}{2\beta}\frac{\partial^2}{\partial J^2} \tag{3}$$

α_e is the molecular constant and τ_J is the time of rotational relaxation. With the suitable initial conditions indicated in Ref. 5, Eq. (3) admits of an exact solution, which yields after substitution in (2)

$$F(\omega) = \frac{2}{\overline{\omega}_Q (1 + a)^2 \Gamma}\, \frac{\Gamma(p)}{\Gamma(p + 1)}\, {}_2F_1\left(p, 1, p + 1, \left(\frac{1 - a}{1 + a}\right)^2\right), \tag{4}$$

where the following notation is used: $\overline{\omega}_Q = \alpha_e T/T^*$ is the average frequency of the Q branch, $\Gamma = (\overline{\omega}_Q \tau_J)^{-1}$ $a = [1 - (2i/\Gamma)]^{1/2}$, $x = \omega/\overline{\omega}_Q$ $p = [ix - (1 - a)\Gamma]/2a\Gamma$, and ${}_2F_1$ and $\Gamma(p)$ are respectively a hypergeometric and a gamma function.[12]

At high densities we have $\Gamma \gg 1$ and by simplifying (4) we obtain a simple

Lorentz line

$$F^{\rm CARS}(\omega) \sim \frac{1}{(\omega - \bar{\omega}_Q)^2 + (\Delta\omega_{1/2})^2} \qquad (5)$$

with half-width

$$\Delta\omega_{1/2} = \frac{1}{2}\,\bar{\omega}_Q^2\,\tau_J. \qquad (6)$$

Comparing (6) with the known perturbation-theory result[13,14] we find that the noise correlation time is $\tau_c = \tau_{J/2}$ if the rotational relaxation is effected by weak collisions, whereas in the case of strong collisions $\tau_c = \tau_J$ (see Ref. 5). Since the time of the rotational relaxation admits of independent measurement either with the aid of the broadening of the individual J component of the O or S branch, or with the aid of NMR data on spin-rotational relaxation,[15] it follows that a combination of such experiments can in principle determine in each concrete case which of the two models is closer to reality.

In the opposite limiting case of low densities $(\Gamma)^{1/2} \ll 1$ we get $[(1-a)/(1+a)]^2 \sim 1$ and the series can be replaced by an integral. This yields for the shape of the spectrum the approximate expression

$$F^{\rm CARS}(\omega) \sim e^{-2(x-\sqrt{\Gamma})}|Ei\,[x - \sqrt{\Gamma} - i\sqrt{\Gamma}(1-\sqrt{\Gamma})]|^2 \qquad (7)$$

where Ei is the integral exponential function.

As $\Gamma \to 0$ we have

$$F^{\rm CARS}(\omega) \to e^{-2x}\,Ei^2(x) \qquad (8)$$

and it is infinite at zero frequency, so that effectively its half-width vanishes at $\Gamma = 0$. This makes mandatory an initial spectrum-broadening stage, which is clearly seen in the dependence of the half-width of the spectrum on the density (see Fig. 1) and was

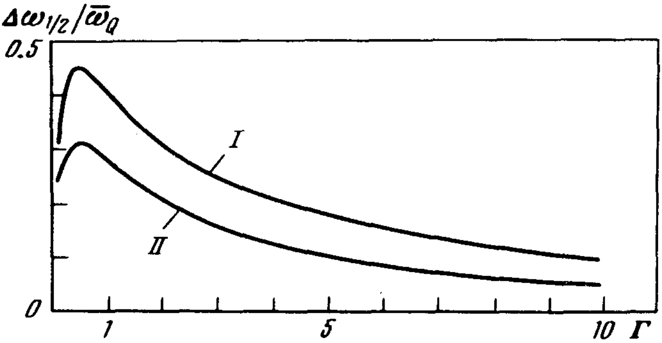

FIG. 1. Dependence of the half-width of the CARS spectrum on the density: I—strong collisions, II—weak collisions.

recently experimentally observed by the active-spectroscopy method in both the gas[7] and the liquid[8] phases.

The transformation of the contour at intermediate densities is shown for both models in Fig. 2. As seen from the figure, the increase of the density shifts the peak of the spectrum towards the central frequency $\bar{\omega}_Q$ of the Q branch and simultaneously symmetrizes the initial static contour.

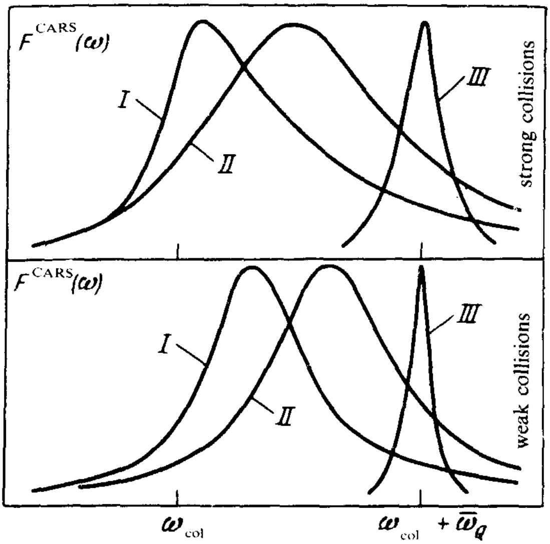

FIG. 2. Change of the shape of the CARS spectrum with increasing density: I–$\Gamma = 0.1$; II–$\Gamma = 0.5$; III–$\Gamma = 10$.

We note that for ordinary Raman-scattering spectra at low densities the line shift takes place without a change in the half-width.[16] This long-known[1] effect of "non-broadening" of the Q branch has by now been confirmed for a large number of systems. The possibility of obtaining, within the framework of the same relatively simple model, qualitative agreement with different experiments serves as some evidence of the adequacy of the model.

Knowing the pressure at which the half-width of the CARS line goes through the maximum[7] identified by us with that shown in Fig. 1, we obtain the corresponding collision cross section $\sigma = 2.02$ Å^2.

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