A. I. Burshteĭn. *Collapse and narrowing of spectra during condensation of gases.* In the adiabatic collision theory, all spectral lines are subject to a broadening which is linear in the gas density, and the broadening of each line occurs in a manner independent of the behavior of other lines. If the broadening is nonadiabatic, certain components of the spectrum interfere (exchange frequencies) and thus undergo a collapse (or coalescence) with increasing density. It is as a result of this collapse that the Stark, Zeeman, and hyperfine structures are averaged over, and a homogeneously broadened line appears at the center of gravity of the spectrum.[1] Of particular interest is the case of extremal collapse, after

which the spectrum becomes progressively narrower with increasing density. An extremal collapse on an optical transition is possible[2] if the structure of the initial term (i) is identical to that of the final term (f) and if the two terms are perturbed identically by collisions:

$$S_{ii'} = S_{ff'}. \tag{1}$$

The collision operator $P_{if,i'f'} = \langle \delta_{ii'}\delta_{ff'} - S_{ii'}S^*_{ff'}\rangle$, which is bilinear in the S matrices, in this case has a zero eigenvalue which corresponds to the width of an infinitely narrowed line.

The narrowing conditions, which essentially never prevail in atomic spectroscopy, do prevail quite often in molecular spectroscopy. The IR spectra of linear molecules, which have a rich rotational structure of P and R branches in a low-density gas, collapse to an isolated Q line as the density is raised. This line contracts as the system undergoes a further condensation. In the semi-classical theory for this transformation it is assumed that the nonadiabatic collisions manage to change only the rotational angular momentum of the molecule, **J**—not the orientation of the molecule. This process of "J-diffusion"[3] modulates the frequency and polarization of the rotation without interrupting its phase; the effect is equivalent to condition (1). Accordingly, after the collapse of the IR spectra and the anisotropic Raman spectra, their widths $1/\tau_{\theta 1}$ and $1/\tau_{\theta 2}$ decrease monotonically with increasing density (collision rates $1/\tau_J$). This fact is expressed by the Hubbard relation $\tau_{\theta l}\tau_J = l(l+1)I/kT$, where l is the moment of inertia of the molecule. This fact is a spectral manifestation of the condensation process, which transforms free rotation into rotational diffusion. This process and the accompanying collapse are described most generally by the Keelson-Storer model of rotational relaxation, which incorporates all other strong and weak collisions as limiting cases.[4]

The collapse of the spectra of isotropic Raman scattering is also extremal.[5] In such spectra the spectral exchange is induced by a modulation of the rotational energy at a rate $1/\tau_E = (1+\gamma)/\tau_J$ $(0 \leqslant \gamma < 1)$. The phase of the scattered radiation is not interrupted even if the molecule rotates in the course of collisions. After the collapse of this spectrum, its narrowing is opposed only by a shift of the vibrational phase, which is usually small in diatomic molecules. It thus becomes possible to describe the contraction of the spectrum of nitrogen from a tenuous gas to a cryogenic liquid semiclassically (Fig. 1).[6] Except for the singularity at the critical point, the experimental data deviate from the theoretical corridor whose boundaries correspond to strong ($\gamma = 0$) and weak ($\gamma = 1$) collisions only after the vibrational loss of phase coherence (which increases linearly with the collision rate, $1/\tau_v$) becomes greater than the width of the average rotational structure, $\overline{\omega_Q^2}\tau_E$ ($\overline{\omega_Q^2}$ is the frequency dispersion in the Q band). By studying the width of the collapsed spectrum,

$$\Delta\omega_{1/2} = \frac{\overline{\omega_Q^2}\tau_J}{1+\gamma} + \frac{1}{\tau_v}$$

as a function of the gas pressure and (in a liquid) as a function of τ_J, measured by NMR methods, it becomes possible to distinguish the rotational and vibrational components of the broadening of the Q band. This method,[6] which has found applications in both linear[7] and CARS spectroscopy,[8] has now become the primary source of information on the relaxation rates of the rotational energy and the adiabatic loss of phase coherence in gases.

The quantum-mechanical theory of the collapse of the Q band[9] yields expressions for these rates in terms of the scattering phase shifts, and calculations can be carried out from these expressions. This theory explains the large cross sections for rotational relaxation and the anomalous temperature dependence of these cross sections which was found in Ref. 10. The theory also confirms that the loss of vibrational phase coherence of simple molecules is only slight; i.e., it can be calculated by perturbation theory. In liquid solutions, however, the situation is different. The diffusion scale times for the encounters of interacting particles are longer than the collision times, and a strong interaction between them is not ruled out. The encounter theory[11] shows that during an either pronounced or slight loss of phase coherence the central part of the spectrum is Lorentzian, but its width increases instead of decreasing with the rate of encounters. This conclusion holds for solutions of any type:

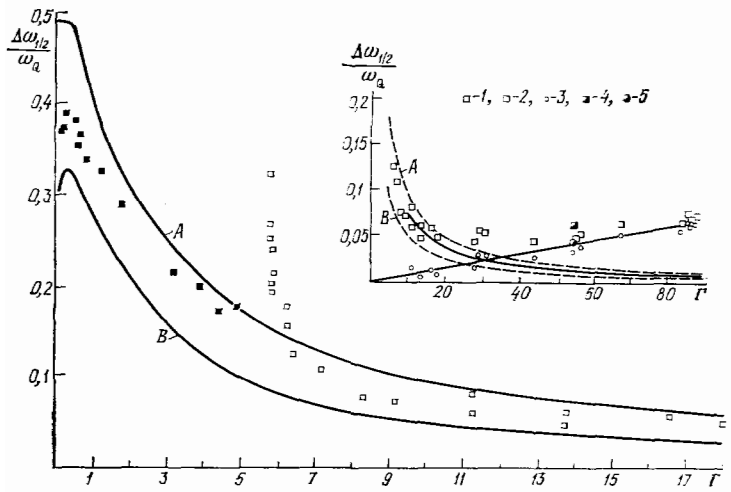

FIG. 1. Half-width of the spectrum of isotropic Raman scattering as a function of rate ($\Gamma = 1/\omega_Q\tau_J$) of collisions which change the rotational angular momentum (in units of ω_Q). 1—Raman scattering in a gas; 2,3—Raman scattering in a liquid; 4,5—CARS in liquid. The circles show the rate of the loss of phase coherence found by subtracting the rotational component from $\Delta\omega_{1/2}$ (Refs. 4 and 6).

gaseous, liquid, or solid. Their static (statistical) spectra are such that any motion which results in a spectral exchange initially causes a broadening and only later causes a narrowing of the spectrum.[12] If perturbation theory is used outside its range of applicability, in the region of "motion-induced broadening," the rate of this broadening may be seriously overestimated. If errors are to be avoided, it is necessary to analyze the shape of the non-Lorentzian wings of the spectrum, which carries information on what is happening to the spectrum: a narrowing or a broadening. The theory of frequency modulation shows that[13] there is a structural feature at the far periphery of the spectrum which is accessible to experimental observation[14] and which makes it possible to distinguish between these situations of a qualitative level.

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