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Abstract

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THE ROLE OF THE PROPER VOLUME OF MOLECULES IN THE THEORY OF COLLISIONAL BROADENING OF SPECTRAL LINES IN GASES

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1. The collisional width of spectral lines $1/T_2 = 1/T_f + 1/T_1$ is made up of broadenings caused by an adiabatic perturbation of the frequency $(1/T_f)$ and by the partial nonadiabaticity of collisions, which limits the lifetime by radiationless transitions $(1/T_1)$. If the perturbation by a collision is weak, then for calculating both components of the broadening one may apply perturbation methods, widely used for these purposes in the theory of magnetic resonance:

$$\frac{1}{T_f} = 2W_f = \int_0^\infty M_a(t)\,dt; \qquad \frac{1}{T_1} = 2W_1 = \int_0^\infty M_n(t)e^{i\omega_0 t}\,dt, \qquad (1)$$

where $M_a(t)$ and $M_n(t)$ are the correlation functions of the adiabatic and nonadiabatic perturbations; ω_0 is the transition frequency; W_f and W_1 have the usual meaning of the transition probabilities under the action of the random process (1). A rigorous calculation shows that $M_a(t)$, for example, is equal to

$$M_a(t) = \overline{\Delta\omega(\tau)\Delta\omega(\tau+t)} =$$

$$= C_n^2 \iint_{\rho v} dW(p,v) \int_{-\infty}^{\infty} d\tau \times \left\{\left[\rho^2 + v^2\tau^2\right]\left[\rho^2 + v^2(\tau - t)^2\right]\right\}^{-n/2}, \qquad (2)$$

provided only that the flights of the perturbing particles are regarded as rectilinear, and that the shift caused by them obeys the law $\Delta\omega = C_{nR}^{-n}$, $R = \sqrt{\rho^2 + v^2(\tau - t)^2}$ (ρ is the impact parameter; v is the relative velocity; τ is the moment of maximum approach). The definition of $M_n(t)$ differs from (2) only by a numerical factor taking into account the fraction of nonadiabaticity.

It is known, however, that the usual theory of collisional broadening ([2]) estimates the adiabatic contribution to the width more rigorously:

$$\frac{1}{T_f} = 2\pi N\bar{v}\int_\rho \rho\, d\rho \int_v dW(v)\left[1-\cos\frac{A_{nC}n}{v\rho^{n-1}}\right] \tag{3}$$

(here $A_n = \sqrt{\pi}\,\Gamma((n-1)/2)/\Gamma(n/2)$). Since this formula remains valid for perturbations of any strength, it must contain, in particular, also the results obtained with the aid of (1), (2), i.e., reduce to $2W_f$ for weak perturbations.

Formula (3), as well as (2), is valid under the assumption of rectilinear flights. Nevertheless, the integration over ρ is always extended from 0 to ∞ ([2,3]), i.e., in essence the molecules are regarded as point masses for which any approach is possible. At this price a certain simplification of the calculation is achieved, but a number of substantial difficulties then arise: 1) $M_a(0) \equiv D$, i.e., the dispersion of the perturbations, becomes ∞, and its correlation time

$$t_c = \frac{1}{D}\int_0^\infty M_a(t)\, dt$$

becomes 0; 2) $1/T_f$, $1/T_1$,

defined in (1), also tend to infinity; 3) $1/T_f$, as defined from (3), under no conditions reduces to $2W_f$, as it would if the region of weak perturbations did not exist at all. Thus, within the framework of the point-molecule model it is impossible either to determine the correlation characteristics of the acting perturbation (noise), or to use perturbation theory to estimate the line width. It is evident that these difficulties are connected not with shortcomings of the method, but with the imperfection of the model: taking into account, in one form or another, the proper volume of the molecules makes it possible to eliminate them completely.

2. The simplest way to take into account the proper dimensions of the molecules is to cut off the interaction potential at impact parameters smaller than the van der Waals diameter ρ_0 ($\Delta\omega = C_{nR}^{-n}$ for $\rho > \rho_0$ and $\Delta\omega = C_n[\rho_0^2 + v^2(t-\tau)^2]^{-n/2}$ for $\rho \leqslant \rho_0$). The representation of rectilinear motion is then fully retained, although the molecules are modeled by hard spheres rather than by point masses. In this case τ_c acquires the meaning of a collision time ($\tau_c \approx \rho_0/\bar{v}$), the noise dispersion turns out to be finite, and

$$2W_f = D\tau_c = 4N\frac{n-1}{n-2}\frac{A_n^2 C_n^2}{\rho_0^{2n-4}}\frac{1}{\bar{v}}. \tag{4}$$

The use in (3) of the cut-off potential reveals the existence of two possibilities. For $\bar{v} \ll v_0 \equiv A_{nC}n/\rho_0^{n-1}$, the introduction of ρ_0 proves inessential, and the usual result of the point model remains valid: $1/T_f \sim \bar{v}^{(n-3)/(n-1)}$ ($n > 3$) —the line width increases with increasing temperature. However, in the high-temperature region ($\bar{v} \gg v_0$) the same formula gives an entirely different result—

identical with (4), i.e., the line narrows as $1/\bar{v}$. The boundary between the region of line broadening and narrowing ($\bar{v} \approx v_0$) shifts into the high-temperature region as $\rho_0 \to 0$, and therefore within the point model ($\rho_0 = 0$) the region of weak interaction proves unattainable. The real existence of this region is demonstrated by the fact that magnetic-resonance lines in a gas prove to be strongly narrowed: the dipole-dipole interaction—the main source of broadening in condensed media—is completely averaged out by thermal motion.

3. The hard-sphere model is apparently a satisfactory approximation in those cases where the rigidity of the molecule and the line broadening are due to different potentials. Such, for example, is the situation when the spin or the electron whose transitions emit the given line is located inside the molecule and is shielded by peripheral atoms, which absorb the impacts of the incident particles. The situation may be different in the case of atomic collisions, when one and the same potential (for example, the van der Waals potential) is the cause both of scattering and of the frequency perturbation. Experience shows that, for inert gases, the repulsive potential up to very high energies varies as $C_n^* R^{-n}$. As the energy of the colliding particles increases, closer approach of the atoms becomes possible and, simultaneously, the maximum value of the frequency shift increases.* Within this model of elastic atoms the dependence of the limiting approach ρ_0 on velocity is determined by the balance condition

$$C_n^*/\rho_0^n = m\bar{v}^2/2. \tag{5}$$

Using (5) and (4), we obtain: $2W_f \sim \bar{v}^{(3n-8)/n}$ ($n > 3$). Thus, in contrast to the hard-sphere model, the line width increases with temperature even in the region of applicability of perturbation theory.

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* We express our gratitude to Zh. Nikitin, who pointed out this possibility to us.

This fact is explained by the increase of the dispersion of the perturbation D with temperature, whereas in the preceding case it remained constant.

4. From elementary physical considerations it is clear that the condition for the applicability of perturbation theory to the calculation of W_f is the smallness of the phase shift during the collision process: $\int \Delta\omega\, dt \ll 1$. But in this form—without averaging over all possible flybys—it cannot be used as a criterion of the weakness of the perturbation. One can, however, verify that this criterion, expressed in terms of the correlation characteristics of the noise and identical to the condition $\bar{v} \gg v_0$, has the form

$$W_f \tau_0 \ll 1 \quad \text{or} \quad D\tau_0\tau_c \ll 1, \tag{6}$$

where $\tau_0 = \left({}^1/_4\pi\rho_0^2 N\bar{v}\right)^{-1}$ is the mean free time. In atomic spectroscopy the perturbation is strong, since under ordinary conditions $W_f \approx 10^{12}$ sec^{-1} $\gg 1/\tau_0 \approx 10^8$ sec^{-1}, and, consequently, inequality (6) is not satisfied. This situation persists up to very high temperatures, and therefore the point model gives a satisfactory estimate of the adiabatic line width.

The situation is different with the nonadiabatic transition probability W_1, which, as can be seen from (1), is no greater than $W_f(\omega_0\tau_c)^{-2} \approx 10^7$ sec^{-1}. The condition for the applicability of perturbation theory, $W_1\tau_0 \ll 1$, is satisfied in this case. Thus, formula (1) can serve as a basis for calculating the magnitude of W_1, but in doing so it is necessary, in one form or another, to take into account the finite sizes of the molecules.

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Note: Figure translations are in progress. See original paper for figures.