LINE SHAPE OF V-DOUBLING TRANSITION

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A correlation theory is developed for the shape of the spectra of a two-level system subjected to a sudden amplitude-phase modulation as a result of collisions. With Λ-doubling as an example, it is shown that the spectrum of such a system consists of a resonance line and involves losses of the Debye type. The resonance line is found to average out with increasing pressure, and the loss spectrum becomes narrow near zero frequency.

As is well known, Λ-doubling of rotational levels of diatomic molecules is due to the splitting of the degenerate electron term as a result of a different non-adiabatic coupling of each of them with other electronic states[1]. Describing the rotation of the molecules classically (this is done only to simplify the reasoning), the two considered components of the electronic term of the molecule, rotating with a given angular momentum **K**, can be classified as positive and negative in accordance with the change of the sign of the function upon reflection in a fixed plane of rotation of the nuclei (case of coupling "b" after Hund). On the other hand, if the influence of the spin is significant and it is necessary to deal actually with splitting of the $^2\Pi_{1/2}$ term (case of coupling "a"), then both components differ in the factors +1 or −1, which result from the wave function upon reflection.

There are two mechanisms of line broadening in the Λ-doubling transition. First, the finite lifetime of each doublet is connected with the fact that the momentum K is changed by the molecule collisions in the gas. Inasmuch as the frequency of the Λ-transition depends on K[1], in collisions in which the rotational state of the partners changes, the frequency $\omega(K)$ of the Λ-transition shifts by an amount on the order of $\delta\omega \sim \omega(K)/K$. The second cause of the broadening of the Λ-transition is due to the fact that the collisions lead to a reorientation of **K** without a change of the splitting $\omega(K)$. As a result, the positive and negative components are intermixed in each collision, whereas between the collisions the non-stationary wave function of the doublet is represented in the form of a time-oscillating superposition of a positive and a negative state. This cause of broadening may turn out to be much more effective than the first cause, since the cross sections of the collisions that lead to reorientation of **K** usually are much larger than the cross sections of the inelastic collisions.

Let us assume that only the second broadening cause is significant and that each collision with effective cross section σ leads to a uniform distribution of the projections of **K**. We assume also that the collision time τ_c, during which the rotation of **K** takes place, is small compared with the free-path time $\tau_0 = [N\sigma\bar{v}]^{-1}$, as is usually the case in impact theory for strong collisions.

In the language of the gyroscopic model[2] this denotes that the field vector suddenly changes its orientation, $1/\tau_0$ times per second, into some other orientation which is realized with a probability $d\Omega/4\pi$ without any connection with the preceding orientation. Thus, the change of the field is a Markov process without correlation with a very simple (uniform) distribution of the angles in any instant of time. Each reorientation causes an according change in the plane of precession of the effective spin representing the Λ-doublet. This imparts a diffusion character to the precession (in spite of the constancy of the precession frequencies), and leads to a spatially-isotropic relaxation of all the components of the effective spin, causing broadening of the line of the transition to Λ-doubling.

We derive below the relaxation equations governing this process, and calculate on their basis, in the approximation of the correlation theory, the form of the frequency dependence of the dispersion, which determines the absorption spectrum in the Λ-transition.

1. RELAXATION

Inasmuch as the Hamiltonian of the Λ-doublet corresponds only to two states, and its eigenfunctions differ in symmetry with respect to the plane normal to **K**, it can be written in the following form:

$$\hat{H} = \frac{\omega_0}{2}\frac{\sigma\hat{K}}{K} = \frac{\omega_0}{2}\begin{Vmatrix} \cos\vartheta & \sin\vartheta e^{i\varphi} \\ \sin\vartheta e^{-i\varphi} & -\cos\vartheta \end{Vmatrix}, \tag{1.1}$$

where ϑ and φ denote the orientations of **K** in a fixed coordinate system, and $\hat{\sigma}$ are Pauli matrices.

Equations. Since the reorientation of the vector **K** is a Markov process without correlation, the equations for the density matrix can be obtained from[3] with allowance for the concrete form of the Hamiltonian (1.1), in which the random quantities are the angular variables:

$$\dot{\rho}(t,\vartheta,\varphi) = -i[\hat{H}(\vartheta,\varphi), \rho(t,\vartheta,\varphi)] - \frac{\rho(t,\vartheta,\varphi) - \bar{\rho}(t)}{\tau_0}, \tag{1.2}$$

$$\bar{\rho}(t) = \int_0^{2\pi}\int_0^{\pi} \rho(t,\vartheta,\varphi)\frac{\sin\vartheta\, d\vartheta\, d\varphi}{4\pi}. \tag{1.3}$$

Using the collecting indices $\alpha, \beta = 11, 12, 21, 22$, we represent (1.2) in the form

$$\dot{\rho}_\alpha(t,\vartheta,\varphi) = G_{\alpha\beta}(\vartheta,\varphi)\rho_\beta(t,\vartheta,\varphi) + \frac{\bar{\rho}_\alpha(t)}{\tau_0}, \tag{1.4}$$

where $G_{\alpha\beta}$ is a fourth-order matrix, the determina-

tion of which follows from a comparison of (1.4) with (1.2) with allowance for (1.1). Its explicit form will be made clear subsequently.

Solution. Recognizing that at $t = \infty$ there exists a stationary solution of (1.4),

$$\rho_\alpha(\infty) = \tau_0^{-1} G_{\alpha\beta}^{-1} \bar{\rho}_\beta(\infty) = \tau_0^{-1} \sum_\alpha {}^1/_2 G_{\beta\alpha}^*, \tag{1.5}$$

let us find the Fourier transform of the quantity $\bar{\rho}(t) - \bar{\rho}(\infty)$, defined by the relation

$$\bar{\Phi}(\omega) = \int_0^\infty [\bar{\rho}(t) - \bar{\rho}(\infty)] e^{-i\omega t} dt. \tag{1.6}$$

Obviously, an analogous Fourier transformation can be introduced also for the partial density matrices connected with the matrices averaged over ϑ and φ by relation (1.3). Therefore, taking the Fourier transform of Eq. (1.4) directly, and solving this equation with respect to $\Phi(\omega, \vartheta, \varphi)$, we get

$$\Phi(\omega, \vartheta, \varphi) = -[\hat{G} - i\omega\hat{E}]^{-1} \left\{ \rho(0) - \bar{\rho}(\infty) + \frac{1}{\tau_0} \bar{\Phi}(\omega) \right\}, \tag{1.7}$$

where $\hat{E}$ is a unit matrix: $\delta_{\alpha\beta}$. Averaging of this expression with respect to ϑ and φ will affect only the quantity on the right

$$\int_0^{2\pi} d\varphi \int_0^\pi [\hat{G} - i\omega\hat{E}]^{-1} \frac{\sin\vartheta\, d\vartheta}{4\pi} = \hat{Q}, \tag{1.8}$$

so that by solving the resultant equation with respect to $\bar{\Phi}(\omega)$ we obtain finally

$$\bar{\Phi}(\omega) = \hat{B}(\omega)[\rho(0) - \bar{\rho}(\infty)], \tag{1.9}$$

where

$$\hat{B} = \tau_0 \left[\left(\hat{E} + \frac{1}{\tau_0} \hat{Q} \right)^{-1} - \hat{E} \right] \tag{1.10}$$

in close analogy with the result of[4].

Averaging. The concrete form of the matrix $\hat{G} - i\omega\hat{E}$, which enters in (1.8), is

$$\hat{G} - i\omega\hat{E} = \begin{Vmatrix} -s & i\omega_0 \sin\vartheta e^{-i\varphi} & -\frac{i\omega_0}{2}\sin\vartheta e^{i\varphi} & 0 \\ \frac{i\omega_0}{2}\sin\vartheta e^{i\varphi} & i\omega_0\cos\vartheta - s & 0 & -\frac{i\omega_0}{2}\sin\vartheta e^{i\varphi} \\ -\frac{i\omega_0}{2}\sin\vartheta e^{-i\varphi} & 0 & -i\omega_0\cos\vartheta - s & \frac{i\omega_0}{2}\sin\vartheta e^{-i\varphi} \\ 0 & -\frac{i\omega_0}{2}\sin\vartheta e^{-i\varphi} & 0 & -s \end{Vmatrix} \tag{1.11}$$

$$s = 1/\tau_0 + i\omega. \tag{1.12}$$

Inverting the matrix (1.11) and averaging it in (1.8) we get

$$\hat{E} + \frac{\hat{Q}}{\tau_0} = \begin{Vmatrix} a-b & 0 & 0 & -b \\ 0 & a & 0 & 0 \\ 0 & 0 & a & 0 \\ -b & 0 & 0 & a-b \end{Vmatrix}, \tag{1.13}$$

$$a = \frac{s(s^2+\omega_0^2) - (s^2 + {}^1/_3\omega_0^2)/\tau_0}{s(s^2+\omega_0^2)}, \quad b = \frac{\omega_0^2}{3\tau_0 s(s^2+\omega_0^2)}. \tag{1.14}$$

Inverting this matrix and using it in (1.10), we obtain untimately:

$$\hat{B} = \tau_0 \begin{Vmatrix} \frac{a-b}{a(a-2b)} - 1 & 0 & 0 & \frac{b}{a(a-2b)} \\ 0 & \frac{1-a}{a} & 0 & 0 \\ 0 & 0 & \frac{1-a}{a} & 0 \\ \frac{b}{a(a-2b)} & 0 & 0 & \frac{a-b}{a(a-2b)} - 1 \end{Vmatrix}. \tag{1.15}$$

This matrix determines completely the kinetics of the relaxation for arbitrary conditions: the latter is obviously none other than the inverse Fourier transform of (1.9).

Gyroscopic description. If from the very outset we introduce the notation of the gyroscopic model: $X_1 = \rho_{11} - \rho_{22}$, $X_2 = \rho_{12}$, $X_3 = \rho_{21}$,

$$\rho = {}^1/_2 + \sum_{i=1}^3 X_i \hat{\sigma}_i, \tag{1.16}$$

then the problem simplifies noticeably. This is connected with the conservation of the normalization of the density matrix ($\rho_{11} + \rho_{22} = 1$) which reduces the rank of all the matrices to three. For the three-component vector X_i we obtain in lieu of (1.9)

$$\bar{\Phi}_i(\omega) = \int_0^\infty \bar{X}_i(t) e^{-i\omega t} dt = B_{ik} X_k(0). \tag{1.17}$$

Here B_{ik} is a diagonal matrix:

$$B_{ik} = c(\omega)\delta_{ik}, \tag{1.18}$$

in which

$$c(\omega) = \tau_0 \frac{1-a}{a} = \frac{s^2 + {}^1/_3\omega_0^2}{s(s^2+\omega_0^2) - (s^2 + {}^1/_3\omega_0^2)/3)/\tau_0}. \tag{1.19}$$

Thus, the relaxation of all the components of the effective spin occurs in perfect uniformity. This was to be expected, in view of the complete spatial isotropy of the problem.

2. CORRELATION THEORY

Absorption. A general formula for the absorbed power of the alternating field at $\rho_0 = ({}^1/_2)$ ($\omega \ll kT$) can be expressed concretely in the following manner:

$$N = \frac{\omega^2 n_0 E^2}{2kT} \int_0^\infty \mathrm{Sp} \left[\rho_0 \frac{\hat{\bar{D}}(\tau)\hat{D}(0) + \hat{D}(0)\hat{\bar{D}}(\tau)}{2} \right] \cos\omega\tau\, d\tau \tag{2.1}$$

$$= \frac{\omega^2 n_0 E_0^2}{4kT} \mathrm{Re} \int_0^\infty \bar{D}_\alpha(\tau) e^{i\omega\tau} d\tau D_\alpha^*(0),$$

where n_0 is the equilibrium population difference of the Λ doublet, $\hat{D}$ is the operator of the dipole moment of the transition, and E_0 is the amplitude of the absorbed monochromatic wave of frequency ω.

The change of the dipole moment under the influence of the Markov noise obeys the equations

$$\frac{d\hat{D}}{dt} = i[\hat{H}\hat{D}] - \frac{\hat{D} - \hat{\bar{D}}}{\tau_0}, \tag{2.2}$$

$$\hat{\bar{D}} = \int_0^{2\pi} d\varphi \int_0^\pi d\vartheta \hat{D}(\vartheta, \varphi) \frac{\sin\vartheta}{4\pi}, \tag{2.3}$$

which can be readily derived by the same method as (1.2) and (1.3). However, by virtue of the obvious difference between these equations, we obtain in place of (1.4)

$$\frac{dD_\alpha}{dt} = G_{\beta\alpha}^* D_\beta + \frac{\bar{D}_\alpha}{\tau_0}. \tag{2.4}$$

Since $\hat{\bar{D}}(\infty) = 0$, the Fourier transform of (2.4), which is perfectly analogous to that just taken, gives a result similar to (1.9):

$$\int_0^\infty \bar{D}_\alpha(t) e^{i\omega t} dt = A_{\alpha\beta} D_\beta(0), \tag{2.5}$$

where

$$A_{\alpha\beta}=\tau_0\left\{\left[\delta_{\alpha\beta}+\frac{1}{\tau_0}\overline{(G_{\beta\alpha}^{*}+i\omega\delta_{\alpha\beta})^{-1}}\right]^{-1}-\delta_{\alpha\beta}\right\}=B_{\beta\alpha}^{*}. \quad (2.6)$$

Thus, a general relation exists between matrices $\hat{A}$ and $\hat{B}$, namely $\hat{A}=\hat{B}^{+}$. Substituting (2.5) and (2.6) in (2.1) we obtain finally

$$N=\frac{\omega^2 n_0 E_0^2}{4kT}\operatorname{Re}A_{\alpha\beta}D_\beta(0)D_\alpha^{*}(0)=\frac{\omega^2 n_0 E_0^2}{4kT}\operatorname{Re}B_{\alpha\beta}D_\alpha^{*}(0)D_\beta(0). \quad (2.7)$$

This general formula is the Markov analog of the corresponding result obtained in the impact approximation in[5]. The difference between them reduces mainly to the different definition of the matrix $\hat{A}$. Averaging over the Markov variables (ϑ and φ), denoted by the bar in (2.6), replaces the averaging over the impact parameters of the collision.

Dispersion. Inasmuch as in our problem it is necessary to deal with long-wave spectroscopy ($\omega \ll kT$), we can describe the effect just as successfully by using the imaginary part of the susceptibility. This is sometimes even more convenient in that it makes it possible to describe more naturally and distinctly--in terms of dispersion theory—not only the resonance absorption but also the Debye losses in the low-frequency region.

Using the definition of the susceptibility in terms of the absorption[6] and the estimate of N obtained in (2.7), we get

$$\chi''=\frac{2N}{\omega E_0^2}=\frac{\omega n_0}{2kT}\operatorname{Re}B_{\alpha\beta}D_\alpha^{*}(0)D_\beta(0). \quad (2.8)$$

Taking into consideration the explicit form of (1.15), we get therefore

$$\chi''\approx\frac{\omega n_0}{2kT}[\operatorname{Re}B_{11,11}(|D_{11}|^2+|D_{12}|^2)+\operatorname{Re}B_{11,22}\cdot 2\operatorname{Re}D_{11}^{*}D_{22}+2\operatorname{Re}B_{12,12}|D_{12}|^2]. \quad (2.9)$$

In the absorption of the electric component of the alternating field at the Λ transition, only the off-diagonal elements of the moment are different from zero, namely $D_{12}=D_{21}^{*}$, while $D_{11}=D_{22}=0$. Therefore

$$\chi''=\frac{\omega n_0|D_{12}|^2}{kT}\operatorname{Re}B_{12,12}=\frac{\omega n_0|D_{12}|^2}{kT}\operatorname{Re}c(\omega), \quad (2.10)$$

where $c(\omega)$ is defined in (1.19). On the other hand, if we bear in mind the model problem of a spin-$\frac{1}{2}$ particle in a random reorienting magnetic field of constant magnitude, then $D_{11}=D_{22}=|D_{12}|/\sqrt{2}=\gamma/2$, as is always the case in the absorption of the magnetic component of the wave. However, even in this case, as can be readily verified by direct utilization of (1.15), we have

$$\chi''=\frac{\omega n_0\gamma^2}{2kT}\left[\frac{1}{2}\operatorname{Re}(B_{11,11}-B_{11,22})+\operatorname{Re}B_{12,12}\right]=\frac{3\omega n_0\gamma^2}{4kT}\operatorname{Re}c(\omega). \quad (2.11)$$

Therefore, generalizing these results, we can express χ'' as a universal function of the dimensionless parameters $z=1/\omega_0\tau_0$ and $x=\omega/\omega_0$:

$$\chi''=\lambda\frac{xz(z^2+x^2+1/3)}{4z^2(1/3-x^2)^2+x^2(1+z^2-x^2)^2}, \quad (2.12)$$

in which the difference between (2.10) and (2.11) is reflected only by the difference in the form of the constant λ, namely $\lambda=2n_0|D_{12}|^2/3kT$ in the first case and $\lambda=n_0\gamma^2/2kT$ in the second.

3. TRANSFORMATION OF THE SPECTRUM BY PRESSURE

It is of interest to investigate the form of the absorption spectrum in the limiting cases of small ($z \ll 1$) and large ($z \gg 1$) pressures.

Rarefield gas. For small pressures, the simplified expression for $\chi''(x, z)$ assumes a particularly simple form for the frequency region close to resonance ($x = 1$) and close to zero frequency ($x = 0$). In the former case we obtain the usual Lorentz contour

$$\chi_L''(x,z)=\frac{\lambda}{2}\frac{{}^2/_3 z}{(\Delta x)^2+({}^2/_3 z)^2};\quad z\ll 1,\quad \Delta x=|x-1|\ll 1, \quad (3.1a)$$

and in the second case the Debye contour

$$\chi_D''(x,z)=\frac{\lambda}{2}\frac{({}^2/_3 z)\cdot x}{x^2+({}^2/_3 z)^2};\quad z\ll 1,\quad x\ll 1. \quad (3.1b)$$

On the whole, the picture of the distribution of intensities corresponds to a superposition of a Lorentz contour and Debye contour (see the figure), both of which are characterized by the same relaxation rate ${}^2/_3\tau_0$. The coefficient ${}^2/_3$ is due to the fact that one of the three spatial orientations of K is parallel to the generalized spin and is therefore ineffective: instead of precession, which ensures the diffusion, it causes only the rotation of the spin about its own axis.

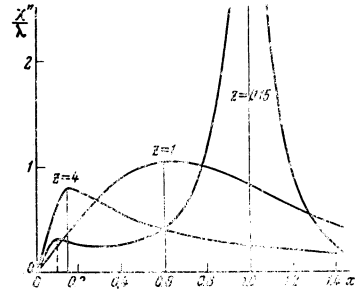
The unusual appearance of the Debye contour is explained as follows by the character of the process under consideration. In the classical approximation, the absorption in Λ doubling can be visualized as absorption of an oscillating dipole (with frequency ω_0) directed along the vector **K**. The electric field component directed along **K** is absorbed by the dipole, if its frequency is close to ω_0. The field components normal to **K** do not interact with the dipole oscillations and are absorbed only at frequencies close to the reciprocal time of the orientation relaxation $1/\tau_0$.

It is seen from (3.1a) and (3.1b) that $\chi_L'' \gg \chi_D''$, as a result of which the maximum of the resonance curve goes off the figure.

Dense gas. With increasing pressure, the maxima in the regions $x \sim z$ and $x \sim 1$ become comparable in magnitude, and subsequently the absorption maximum goes over into the region of low frequencies. Expression (2.12) then reduces to the following:

$$\chi''=\lambda\frac{zx}{({}^2/_3)^2+(xz)^2};\quad z\gg 1,\quad x\ll 1, \quad (3.2)$$

which leads to a lengthening of the relaxation time



Frequency dependence of the susceptibility at three different values of z.

$[(2/3)\omega^2\tau_0]^{-1}$ and to a narrowing of the line loss.

This is precisely the limiting case described by perturbation theory when applied to a problem that is formally analogous to that considered by Gordon[7]. It must be borne in mind, however, that for Λ transitions the effect of narrowing can be masked by broadening due to the finite lifetime of the doublet (see above). Therefore, an investigation of the region of large pressures should be carried out, generally speaking, with allowance for collisions that change both the orientation of **K** and its absolute magnitude.

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