Non-Markovian binary theory of interference between spectral lines

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The pressure-induced transformation of a multicomponent spectrum is discussed. A non-Markovian kinetic equation is obtained for the evolution of the dipole moment operator of an active molecule in the binary approximation. The relative motion of the colliding particles is discussed classically. The transition to the kinetic equation of the Markovian theory (MT) is demonstrated. Two variants of the theory are compared with the formalism of the familiar impact theory. The simple example of two interacting transitions (lines separated by δ in the spectrum) is used to show that the differences between the descriptions of the spectrum provided by the three theories can be neglected in the nonadiabatic limit $\delta\tau_c \ll 1$, where τ_c is the collision time. In the intermediate situation corresponding to $\delta\tau_c \sim 1$, the non-Markovian theory alone provides the correct description of the non-Lorentzian wings of the lines, their shifts and widths, and the appearance of forbidden transitions. Under highly nonadiabatic conditions, for which $\delta\tau_c \gg 1$, only the secularized form of MT can be used, which is then identical with the impact theory.

INTRODUCTION

It is well known that collisions between particles in a gas not only broaden and shift the individual lines in the multicomponent spectrum but, in general, also give rise to interference between the lines. When the splitting δ of the components of the spectrum is small in comparison with τ_c^{-1} (where τ_c is the collision time), the broadening of the spectrum is nonadiabatic in character, and interference manifests itself as a spectral transfer or migration of frequency (polarization) between the components. The rate of transfer is proportional to the collision frequency τ_0^{-1}, which increases with increasing gas pressure. When it becomes greater than δ, the structure is found to collapse, and partial or complete compression of the spectrum by pressure becomes possible. This effect has been examined in detail within the so-called impact theory,[1–3] in which collisions are looked upon as instantaneous interaction events, so that, for all $t > \tau_c = 0$, the relaxation of the density matrix, or of the dipole moment of the system, is described by differential kinetic equations. The result of a collision is represented in these equations by the time-independent operator $\hat{P}$, which acts in the space of the lines and whose off-diagonal elements characterize the rate of spectral transfer.

The above picture of nonadiabatic transformation of spectra is now generally accepted. It explains the pressure-averaging of the hyperfine structure of NMR and ESR spectra,[4] the fine structure of atomic spectra,[5] and the rotational structure of the vibrational spectra of molecules.[6] In many of these applications of the impact theory, the line splitting δ rises from 10^7 to 10^{12} s^{-1} while remaining less than $\tau_c^{-1} \sim 10^{13}$ s^{-1}. However, recent work[7,8] has extended this theory to vibrational spectroscopy where $\delta \geqslant \tau_c^{-1}$ is not infrequent. This type of direct extrapolation of the simple interference picture to the region where collision broadening is qualitatively different (adiabatic) is, at the very least, unjustified.

From the point of view of impact theory, this extrapolation is unacceptable because spectral transfer is excluded by this theory when the broadening becomes adiabatic ($\delta\tau_c \gg 1$). On the other hand, impact theory itself is hardly valid in this region. Since it ignores the development of the process during the collision time (for $t < \tau_c$), it cannot describe the distant wings of lines separated from resonance by the amount $|\Delta\omega| > \tau_c^{-1}$ (Refs. 9 and 10), i.e., it cannot describe the interference between spectral components separated by $\delta > \tau_c^{-1}$ from one another.[11] The problem of this interference and its consequences can be solved only within the framework of a more general, binary, non-Markovian theory capable of describing the development of this process both between and during collisions.

The conclusion that there is no adiabatic spectral transfer has recently been disputed[12] from the standpoint of the more general theory. Some grounds for this are provided by the analysis of the Markovian variant of this theory, which is obtained from it by taking a particular limit, and is regarded valid for $t \gg \tau_c$. Comparison of this with impact theory, valid in the same range, shows that there is a formal identity between them in all respects except for the definition of the operator $\hat{P}$. The nonsecular part of this operator, which is responsible for transfer and vanishes in impact theory in the limit of adiabatic broadening, remains in MT to the same extent as the secular part. It is not obvious, however, whether it follows generally that MT can be obtained from the non-Markovian theory if it is intended to use it subsequently to calculate the distant periphery of spectral components.

To elucidate this question, and to compare adiabatic and nonadiabatic transformations of the spectrum, we undertake below a revision of existing ideas on line interference by considering the example of the well-studied four-level model. The results can be briefly summarized as follows. The non-Markovian theory can alone describe the spectrum in all its details, including the appearance of forbidden (sti-

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mulated by collisions) components. The two asymptotic theories provide only an approximate description of the shape of the spectrum, but the impact theory is indicated by these results to be preferable to MT, and we provide a formal kinetic and physical explanation of this.

1. NON-MARKOVIAN GAS-KINETIC EQUATION

The criterion for the validity of the binary approximation in gases and gaseous mixtures is $\tau_c/\tau_0 \ll 1$. When this is satisfied, the kinetic equation for the density matrix can be obtained by the very general method developed in Ref. 13. It allows a non-Markovian formulation of the theory, which retains first-order corrections in the parameter τ_c/τ_0. This theory was developed in Ref. 14, but was applied to liquid solutions in which particles approached one another in hops or by interdiffusion. Gas analogs of this theory have been known for a considerable time[15] but, for our purposes, it will be convenient to derive the gas-kinetic equation in a form familiar in encounter theory,[14] in which the approach of particles to one another is looked upon as a process that is independent of their interaction $V(r)$, i.e., the separation between the particles $r(t)$ is considered to be a given or random function of time. In impact theory, this corresponds to the approximation of rectilinear trajectories, which differ only by initial velocities and impact parameters.

Let $\mathbf{d}(t)$ by the Heisenberg operator responsible for the absorption of light, for example, the dipole moment of an active molecule. It obeys the Schrödinger equation which takes into account only the interaction with the nearest partner for a particular instance of a collision:

$$\dot{\mathbf{d}}_s(t) = i[H_0, \mathbf{d}_s(t)] + i[V(s+t), \mathbf{d}_s(t)]. \tag{1.1}$$

Since any collision begins at $-\infty$ and ends at $+\infty$, its main characteristic is the time s between the beginning of observations ($t = 0$) and the instant of closest approach (maximum interaction). We now proceed to the interaction picture

$$\tilde{\mathbf{d}}_s(t) = e^{-iH_0 t}\mathbf{d}_s(t)\, e^{iH_0 t},$$

and introduce the evolution operator $\hat{R}(s,t,t')$, defined by

$$\tilde{\mathbf{d}}_s(t) = \hat{R}(s,\ t,\ t')\tilde{\mathbf{d}}_s(t') = U(s,\ t,\ t')\tilde{\mathbf{d}}_s(t')\, U^+(s,\ t,\ t'), \tag{1.2}$$

where

$$U(s,t,t') = T\exp\left[i\int_{t_0}^{t} e^{-iH_0\tau} V(s+\tau)\, e^{iH_0\tau} d\tau \right], \tag{1.3}$$

and T is the chronological operator.

According to formula (2.6) in Ref. 14, the non-Markovian kinetic equation for the quantity $\tilde{\mathbf{d}}(t)$ averaged over all the collisions is

$$\dot{\tilde{\mathbf{d}}}(t) = N\left\{ i\,[e^{-iH_0 t}\langle V(s+t)\rangle e^{iH_0 t},\ \tilde{\mathbf{d}}(t)] - \int_0^t dt' \left\langle \frac{d^2}{dt\, dt'}\, \hat{R}(s,\ t,\ t') \right\rangle \tilde{\mathbf{d}}(t') \right\}, \tag{1.4}$$

where N is the density of perturbing particles.[1)] The averaging $\langle \ldots \rangle$ in (1.4) involves integration over the initial positions of the particle on the trajectory and summation over all the parameters defining the trajectory. After some rearrangement, the final gas-kinetic equation assumes the form

$$\dot{\mathbf{d}}(t) = i[H_0, \mathbf{d}(t)] + \left\{ iN\int_{-\infty}^{+\infty} ds\,[\langle V(s)\rangle, \mathbf{d}(t)] - \int_0^{\infty} d\tau\, \hat{\Gamma}(\tau)\, e^{iH_0\tau}\mathbf{d}(t-\tau)\, e^{-iH_0\tau} \right\}. \tag{1.5}$$

The kernel of this equation

$$\hat{\Gamma}_{ik,lm}(\tau) = N\left\langle \int_{-\infty}^{+\infty} ds\, e^{i(\omega_{il}+\omega_{mk})s} \left\{ \frac{\partial^2}{\partial s\, \partial s'} U_{il}(s,s')\, U_{mk}^{+}(s,s') \right\}_{s'=s-\tau} \right\rangle \tag{1.6}$$

has already been averaged over s, and the angle brackets imply only averaging over the collision parameters:

$$\langle \ldots \rangle = \int_0^{\infty} 2\pi\, bdb \int_0^{\infty} vf(v)\, dv\, (\ldots),$$

just as in the usual impact operator. However, in contrast to the impact theory, (1.5) is an integro-differential equation and $\hat{\Gamma}(\tau)$ contains information on the evolution of the system over times comparable with and less than τ_c. In (1.6), $U(t,t') = U(0,t,t')$ and the definition of the operator U given by (1.3) differs from the generally accepted definition of the evolution operator in the interaction picture by the fact that i has been replaced with $-i$.

2. ABSORPTION SPECTRUM

According to the fluctuation-dissipation theorem, the absorption of light at frequency ω is described by[17]

$$I(\omega) = \Phi(\omega)\,\mathrm{Re}\int_0^{\infty} dt\, e^{-i\omega t}\,\mathrm{Sp}(\rho_0 \mathbf{d}\mathbf{d}(t)), \qquad \Phi(\omega) = \frac{4\pi\omega}{3\hbar c} N_0 \left\{ 1 - \exp\left[-\frac{\hbar\omega}{kT} \right] \right\}, \tag{2.1}$$

where ρ_0 is the equilibrium density matrix. Only the spectral function

$$\mathscr{F}(\omega) = I(\omega)/\Phi(\omega) = \mathrm{Re}\,\mathrm{Sp}(\rho_0 \mathbf{d}\mathbf{d}(\omega)),$$

expressed in terms of the Laplace transform of the observed function

$$\mathbf{d}(\omega) = \int_0^{\infty} e^{-i\omega t}\mathbf{d}(t)\, dt$$

need be calculated. If we use (1.5) to calculate it, we find that

$$\mathscr{F}(\omega) = \mathrm{Re}\sum_{iklm} \rho_i^0 \mathbf{d}_{ik}[\hat{G}^{-1}(\omega)]_{ik,lm}\mathbf{d}_{lm}, \tag{2.2}$$

where

$$G_{ik,\,lm} = \hat{R}_{ik,\,lm}(\omega) + i(\omega - \omega_{lm} - \Delta\omega_{lm})\,\delta_{il}\delta_{mk}, \tag{2.3}$$

$$\hat{R}_{ik,lm}(\omega) = \int_0^{\infty} d\tau\, \hat{\Gamma}_{ik,lm}(\tau)\exp[i(\omega_{lm}-\omega)\tau], \tag{2.4a}$$

$$\Delta\omega_{lm}=N\int_{-\infty}^{+\infty} ds\langle V_{ll}(s)-V_{mm}(s)\rangle. \qquad (2.4b)$$

The evaluation of the spectrum is thus reduced to the inversion of the matrix $\hat{G}(\omega)$ and its convolution according to the recipe given by (2.2).

The impact analog of the operator $\hat{R}(\omega)$ does not depend on frequency and its off-diagonal elements are interpreted as the rates of spectral transfer between the corresponding lines in the multicomponent spectrum. In the non-Markovian theory, the off-diagonal elements of $\hat{R}(\omega)$ cannot be looked upon as the rates of transfer because they depend on the continuous variable ω which, in general, is not equal to the eigenfrequencies of the system. To compare impact theory with the non-Markovian theory, we must begin by freeing ourselves of the frequency dependence $\hat{R}(\omega)$, i.e., pass to the so-called Markov limit.

In the literature there is complete unanimity on how this transition can be carried out correctly.[12–14,18] It is considered that the transition to the interaction picture in accordance with the formula

$$\mathbf{d}(t-\tau)=\exp[iH_0(t-\tau)]\tilde{\mathbf{d}}(t-\tau)\exp[-iH_0(t-\tau)] \qquad (2.5)$$

completely removes fast motion with eigenfrequencies H_0 from $\tilde{\mathbf{d}}(t-\tau)$, leaving behind only slow attenuation on the scale of the mean free time τ_0. Because of this, $\tilde{\mathbf{d}}(t)$ can be taken out from under the integral sign in (1.5), since the other cofactor $\hat{\Gamma}(\tau)$ is attenuated much more rapidly, i.e., in a time $\tau_c \ll \tau_0$. If these ideas can be regarded as undisputed, we are equally entitled to use the following equation instead of (1.5):

$$\dot{\mathbf{d}}(t)=i[H_0,\mathbf{d}(t)]+\left\{iN\int_{-\infty}^{+\infty} ds[\langle V(s)\rangle,\mathbf{d}(t)]-\int_0^t d\tau\,\hat{\Gamma}(\tau)\mathbf{d}(t)\right\}. \qquad (2.6)$$

This is still a non-Markovian equation, but its solutions have an exponential asymptotic form, and it is sufficient to extend the integration over τ to $+\infty$ in order to describe it. This leads to the basic equation of the Markovian theory with the time-independent relaxation operator

$$\hat{\Gamma}(0)=\int_0^\infty \hat{\Gamma}(\tau)\,d\tau.$$

When this is used to find $\mathbf{d}(\omega)$ and to calculate the spectrum, the latter can differ from (2.2) only by the different definition of the matrix $\hat{G}$:

$$\hat{G}_{ik,\,lm}=\hat{\Gamma}_{ik,\,lm}(0)+i(\omega-\omega_{lm}-\Delta\omega_{lm})\delta_{il}\delta_{mk}. \qquad (2.7)$$

It is precisely this matrix that must be compared with its impact analog, since their frequency dependence is the same.

Actually, according to impact theory,[1–3,10,11]

$$\hat{G}_{ik,\,lm}=\hat{P}_{ik,\,lm}+i(\omega-\omega_{lm})\delta_{il}\delta_{mk}, \qquad (2.8)$$

where

$$\hat{P}_{ik,\,lm}=N\langle\delta_{il}\delta_{mk}-S_{il}^{*}S_{km}\rangle=\hat{\gamma}_{ik,\,lm}-i\Delta\omega_{lm}\delta_{il}\delta_{mk} \qquad (2.9)$$

is calculated in the S-matrix formalism with $S=U(+\infty,-\infty)$. The impact theory and MT will be identical for $\hat{\Gamma}(0)=\hat{\gamma}$. However, this is not the case in general. The two theories become identical when the factor $\exp[i(\omega_{il}+\omega_{mk})s]$ in (1.6) is omitted, assuming[11] that it is close to unity. The integrals with respect to s and τ are then trivial, and the evolution matrices becomes S-matrices. This reduction of $\Gamma(0)$ to γ is justified if $(\omega_{il}+\omega_{mk})\tau_c \ll 1$. The situation is different when this inequality is reversed. According to (1.6), the secular parts of $\hat{\Gamma}(0)$ and γ are then identical, as before, but their off-diagonal elements are differently defined in MT and in impact theory. To elucidate this difference and to explore its consequences, we shall examine the spectra of a simple system that has already been used to illustrate line interference. We shall have to explain the changes that occur as we pass from nonadiabatic to adiabatic broadening, the extent to which the non-Markovian description of the phenomenon is more complete, and which asymptotic theory is in better agreement with it.

3. FOUR-LEVEL SYSTEM. PERTURBATION THEORY

Consider the four-level idealization of the actual spectrum of a system, assuming that the splitting of the upper and lower doublets is small in comparison with the separation between them (Fig. 1). We shall investigate the spectrum consisting of four high-frequency transitions between the doublets, two of which are allowed and two forbidden by selection rules for a free system.

The shape of the spectrum is determined by the operator $\hat{R}(\omega)$, which we shall calculate from perturbation theory, assuming that the nonzero matrix elements are

$$V_{12}(t)=V_{34}(t)=V(t), \quad \operatorname{Im}V(t)=0. \qquad (3.1)$$

This implies that the perturbations of both low-frequency transitions occur in phase and have the same time dependence. In this important special case, all the results become much simpler. In second-order perturbation theory, everything is expressed in terms of the correlation function

$$K(\tau)\overline{V^2}=K(\tau)\int_{-\infty}^{+\infty} dt\langle V^2(t)\rangle=\int_{-\infty}^{+\infty} dt\langle V(t)V(t-\tau)\rangle, \qquad (3.2)$$

where $\overline{V}^2$ is the variance of the perturbation. The operator $\hat{R}(\omega)$, calculated from (1.6) and (2.4) in this approximation, has the following form in the basis of the lines $\{ik,lm\}=\{41,32\}$:

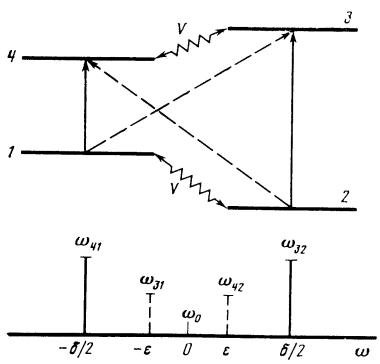

FIG. 1. The four-level system. The frequency is measured from $\omega_0 = 1/2(\omega_{41}+\omega_{32})$—the central frequency.

$$\hat{R}(\omega)=R(\omega)\begin{bmatrix}1 & -1\\ -1 & 1\end{bmatrix},\quad R(\omega)=R'(\omega)+iR''(\omega),\qquad (3.3)$$

where

$$R(\omega)=\overline{V^2}[F(\omega-\varepsilon)+F(\omega+\varepsilon)],\quad F(\omega)=\int_0^\infty d\tau K(\tau)e^{-i\omega\tau}. \qquad (3.4)$$

A more specific representation of the real and imaginary parts of $F(\omega)$ can be obtained by considering the example of the function[19]

$$K(\tau)=(2\tau_c/\pi)^2[\tau^2+(2\tau_c/\pi)^2]^{-1},$$

which corresponds to the long-range interaction $\sim r^{-2}$, which, in turn, justifies the application of perturbation theory. We then have

$$F(\omega)=\tau_c\left\{e^{-|x|}+\frac{i}{\pi}[e^x\,\mathrm{Ei}(-x)-e^{-x}\,\mathrm{Ei}^*(x)]\right\},$$

$$x=\frac{2\omega\tau_c}{\pi}. \qquad (3.5)$$

The real and imaginary parts of this expression are shown in Fig. 2. The imaginary part of $F(\tau)$ has the following asymptotic behavior:

$$\mathrm{Im}\,F(\omega)=\begin{cases}(4/\pi^2)\omega\tau_c^2\ln|\omega\tau_c|, & \omega\tau_c\ll 1 \qquad (3.6a)\\ -1/\omega, & \omega\tau_c\gg 1 \qquad (3.6b)\end{cases}$$

We note that the high-frequency asymptotic behavior described by (3.6b) is independent of the choice of the function $K(\tau)$.

To go over to MT, we must determine the matrix $\hat{\Gamma}(0)$ in (2.7). This matrix is not in simple correspondence with the frequency-dependent operator (3.3) of the non-Markovian theory. The latter operator can be transformed into it through an element-by-element transformation, the recipe for which is clear from (2.4a): $\hat{\Gamma}_{ik,lm}(0)=\hat{R}_{ik,lm}(\omega_{lm})$. The final result is

$$\hat{\Gamma}(0)=\Gamma\begin{bmatrix}1 & -1\\ -1 & 1\end{bmatrix}+i\Delta\begin{bmatrix}1 & 1\\ -1 & -1\end{bmatrix}, \qquad (3.7)$$

where

$$\Gamma=\overline{V^2}[\mathrm{Re}\,F(\varepsilon-\delta/2)+\mathrm{Re}\,F(\varepsilon+\delta/2)]={}^1/_2(W_{34}+W_{12}), \qquad (3.8)$$

$$\Delta=V^2[\mathrm{Im}\,F(\varepsilon-\delta/2)-\mathrm{Im}\,F(\varepsilon+\delta/2)], \qquad (3.9)$$

and

$$W_{12}=\overline{V^2}\int_{-\infty}^{+\infty}d\tau K(\tau)e^{-i\omega_{12}\tau},\quad W_{34}=\overline{V^2}\int_{-\infty}^{+\infty}d\tau K(\tau)e^{-i\omega_{34}\tau}$$

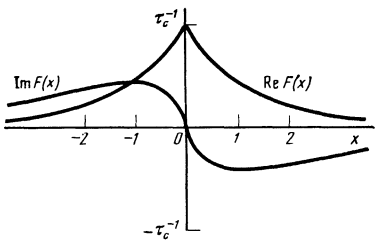

FIG. 2. Real and imaginary parts of the function $F(x)$, where $x=2\omega\tau_c/\pi$.

can be interpreted as the probability of a transition between the levels in the bottom and top doublets, respectively.

It is readily verified that, for nonadiabatic broadening, for which

$$\delta\tau_c\ll 1,\quad \varepsilon\tau_c\ll 1, \qquad (3.10)$$

the non-Markovian theory, the impact theory, and MT yield the same result if we neglect the frequency dependence of $F(\omega)$ and put $F(\omega)=F(0)$. We then have $W_{12}=W_{34}=W_0$ and

$$\hat{\Gamma}(0)=\hat{\gamma}=W_0\begin{bmatrix}1 & -1\\ -1 & 1\end{bmatrix}, \qquad (3.11)$$

where W_0 is the probability of frequency transfer between the lines. This formulation of the problem is customary for low-frequency magnetic spectroscopy and its solution, first obtained by McConnell,[20] was subsequently frequently reproduced in another context[1-3,19] until it found an application in vibrational spectroscopy.[7,8] However, it is in this last case that the conditions for nonadiabatic broadening (3.10) may be violated, and we must now investigate the consequences of this.

4. INTERFERENCE BETWEEN LINES IN ADIABATIC COLLISIONS

When at least one of the inequalities (3.10) is violated, the frequency dependence $F(\omega)$ begins to play a significant role. In the non-Markovian theory, the spectrum then acquires both allowed lines (at frequencies $\pm\delta/2$) and forbidden components at frequencies $\pm\varepsilon$, whose relative integrated intensity is proportional to τ_c/τ_0 (Ref. 21). The appearance of these components is due to the kinetic description of the system during the collision time, when the optical selection rules are lifted due to interaction between the particles. This is the principal difference and advantage of the non-Markovian theory as compared with its asymptotic variants. Moreover, the non-Markovian theory gives the correct description of the wings of allowed lines: $\mathscr{F}(\omega)\propto\omega^{-4}e^{-\omega\tau_c}$.

Let us begin with the situation where $\varepsilon\tau_c\gg 1$ and $\delta\tau_c\ll 1$, as before (Fig. 3a). This is the characteristic situation for vibrational spectroscopy. If the allowed lines are due to cold and hot vibrational transitions, they can take part in exchange as a result of collisions that excite and deactivate the low-frequency mode,[8] where the splitting δ of these lines can be as small as desired. Since, in this case, collisions are adiabatic, the probabilities (3.8) that they will induce transitions are exponentially small. However, apart from this, there are no other significant changes. The quantity

$$\Delta=-\overline{V^2}\delta/\varepsilon^2 \qquad (4.1)$$

is negligible in comparison with δ which, in turn, is so small in comparison with ε that the presence of satellites on the periphery of the spectrum can be neglected, and we can confine our attention to the asymptotic description of the collapse of allowed lines, in which we can use either the impact theory or MT with equal success.

It is interesting to examine the case where both inequalities in (3.10) are reversed, and one of the doublets becomes

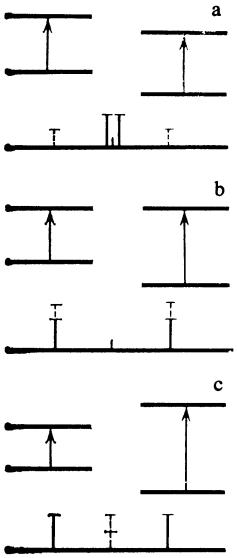

FIG. 3. Different types of four-level system: a) $\delta\tau_c \ll 1$, $\varepsilon\tau_c \gg 1$; b) $\varepsilon = \delta/2$, $\varepsilon\tau_c \gg 1$; c) $\varepsilon = 0$, $\delta\tau_c \gg 1$.

degenerate, i.e., $\varepsilon = \delta/2$ (Fig. 3b). Transitions within this doublet are nonadiabatic with maximum probability $W_{34} = 2\overline{V^2}\tau_c = W_0$, which is exponentially greater than the small probability W_{12} in the other doublet, so that the latter can be simply neglected. We are thus dealing with mixed broadening, which is simultaneously (although in different channels) adiabatic and nonadiabatic. However, judging by (3.8), this has no effect on MT if we do not take into account the change in the absolute magnitude of the probability as compared with (3.11):

$$\operatorname{Re}\hat{\Gamma}(0) = \frac{W_0}{2}\begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}. \tag{4.2}$$

We note that, if we were to turn off the 1-2 transition, not by increasing the detuning ω_{12} but simply putting $V_{12} = 0$, then MT would give (4.3) and not (4.2). The physically equivalent situations ($W_{12} \equiv 0$ or $W_{12} \approx 0$) are described by MT in a qualitatively different manner. On the contrary, in impact theory, the absence of transitions in the split doublet signifies that the corresponding element S_{12} is zero, which immediately leads to the secularization of $\hat{P}$ in (2.9), so that

$$\operatorname{Re}\hat{\gamma} = \frac{W_0}{2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}. \tag{4.3}$$

The consequence of this difference is that, in MT, the spectrum has been subjected to collapse and compression by pressure, whereas, in impact theory, it has been subjected to monotonic broadening alone. Unfortunately, there is no clear criterion for discriminating against either of these theories, since the region of collapse for $\delta\tau_c \gg 1$ lies outside the range of validity of the binary approximation ($\tau_c \ll \tau_0$). Without going outside these limits, we can analyze only the well-resolved spectrum: $\delta \gg \tau_c^{-1} \gg \tau_0^{-1}$. Let us put $\rho_1^0 = \rho_2^0 = 1/2$, $\mathbf{d}_{14} = \mathbf{d}_{23} = 1$, so that, using (3.3) and (2.2), we obtain the following expression for the spectrum in the non-Markov theory:

$$\mathcal{F}(\omega) = \frac{R'(\omega)\delta^2}{2[\delta^2/4 - \omega^2 - 2\omega R''(\omega)]^2 + 8\omega^2 R'^2(\omega)}. \tag{4.4}$$

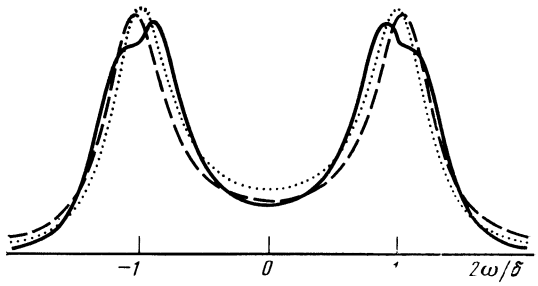

FIG. 4. The spectral function $\mathcal{F}(\omega)$, calculated in second-order perturbation theory for the system shown in Fig. 3b. The parameters are: $\delta\tau_c = \pi$, $\overline{V^2}\tau_c^2 = \pi/8$. Non-Markovian theory—solid curve, impact theory—dashed curve, MT—broken curve.

It is immediately clear that the intensity of the center is exponentially small because $R'(0) = 2\overline{V^2}\operatorname{Re}F(\varepsilon) \propto \exp(-\delta\tau_c/\pi)$. Neither asymptotic theory can, in principle, cover this central region of the spectrum, which lies at a distance greater than $1/\tau_c$ from the two resonances (Fig. 4). From this point of view, the differences between the asymptotic theories are of fundamental rather than practical character, because the retention of the nonsecular terms in (4.2) takes us outside the range of validity of MT.

All these conclusions are only strengthened as we pass on to the next situation in which $\varepsilon = 0$ and $\delta\tau_c \gg 1$ (Fig. 3c). This arises when two-quantum vibrational-rotational transitions, which simulate the mirror components of the P- and R-branches of the IR spectrum of a diatomic molecule, are allowed. Forbidden lines then belong to the Q-branch and lie at the center of the spectrum. When the vibrational-rotational coupling is neglected, their frequencies are equal and the spectrum transforms into a triplet with a forbidden, doubly degenerate line at the center. To describe it, we must turn to the non-Markov theory which, when the second order in the interaction V is taken into account, redefines (3.4) so that

$$R'(\omega) + iR''(\omega) = 2\overline{V^2}F(\omega). \tag{4.5}$$

Substituting this in (4.4), we find that the central portion of the peak duplicates the shape of $\operatorname{Re}F(\omega)$ and then decays exponentially on either side with a decay constant τ_c^{-1} (Fig. 5). The intensity at the center is

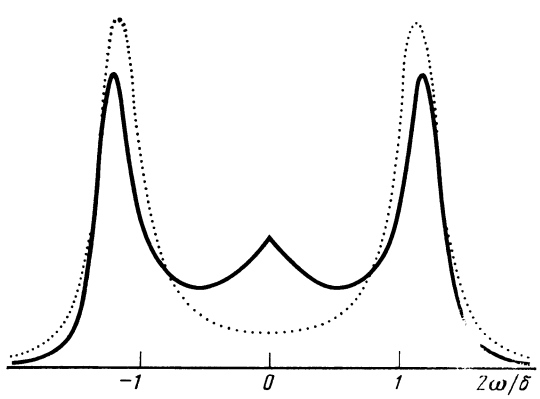

FIG. 5. Spectral function $\mathcal{F}(\omega)$, calculated in second-order perturbation theory for the system shown in Fig. 3c. The parameters are the same as in Fig. 4. Non-Markovian theory—solid line, MT—dotted line.

$$\mathcal{F}(0)=8\overline{V}^2\,\mathrm{Re}\,F(0)/\delta^2 \qquad (4.6)$$

and increases linearly with the collision frequency because $\overline{V}^2\sim v^2\tau_c/\tau_0$ (v is a parameter characterizing the strength of the coupling).

The integrated intensity of the forbidden line, $\mathcal{F}(0)/\tau_c$, is smaller by the factor (v^2/δ^2) (τ_c/τ_0) than that of the allowed components. If the coupling were strong, the difference between the intensities would decrease to τ_c/τ_0. The relative intensity would then be equal to the fraction of time spent by the molecule in the collision. The selection rules for a free rotator, which forbid the Q-band, are suspended during this time. The interaction produces an orienting field capable of transforming the motion of the molecule into small-amplitude vibrations whose spectral manifestation is the Stark splitting of the spectrum with the strong Q-band at its center.[22] In the binary theory, this structure is looked upon as the "induced spectrum that exists only during the time of the collision." However, in a liquid, $\tau_c\geqslant\tau_0$ and it is precisely this previously forbidden Q-band that acquires an intensity comparable with or even exceeding the intensity of the other lines. At any rate, the transformation of the IR spectrum of HCl in buffer gases as their pressure increases is of this kind.[21-23] It can only be treated by the non-Markovian theory, whether it be the perturbation theory[21] or the binary theory examined here. It is important to emphasize that, in adiabatic collisions, the for forbidden line is sharper and therefore better defined in the spectrum than in the case of the discontinuous and fundamentally nonadiabatic perturbations examined in Refs. 21 and 23.

In conclusion, we draw attention to the special case where one of the two interfering lines is forbidden right from the outset (for example, $\mathbf{d}_{23}=0$). According to (3.3) and (2.2), in this case,

$$\mathcal{F}(\omega)=\frac{R'(\omega)\,(\omega-\delta/2)^2}{2[\delta^2/4+R''^2(\omega)-(\omega+R''(\omega))^2]^2+8\omega^2R'^2(\omega)}. \qquad (4.7)$$

We have already expressed the view that, because of the transfer between allowed and forbidden components, the latter become partly allowed and may appear in the spectrum.[2,24] In actual fact, this is not so: the forbidden line manifests itself as a valley in the wing of the allowed line. In particular, it is clear that, at the center of the valley, the absorption intensity is $\mathcal{F}_{\min}=0$. The same result is obtained in the nonadiabatic impact theory as well. If, instead of it, we use MT, it turns out that

$$\mathcal{F}(\omega)=\frac{\Gamma((\omega-\delta/2-\Delta)^2-\Delta^2)}{2[(\delta/2+\Delta)^2-\omega^2-\Delta^2]^2+8\omega^2\Gamma^2}, \qquad (4.8)$$

which leads to the physically meaningless result $\mathcal{F}_{\min}=\mathcal{F}(\omega_{32}+\Delta)<0$.

5. CONCLUSION

We have verified that the transition from MT to the non-Markovian theory leads to the unexpected appearance of line interference, a better description of the periphery of the spectrum, and, finally, to negative intensity at the valley minimum on the forbidden component. In our view, these difficulties originate in the unjustified removal of $\tilde{\mathbf{d}}(t-\tau)$, defined in (2.5), from under the integral sign in (1.5). This procedure converts the non-Markovian kinetic equation to (.26), which has a Markovian asymptotic behavior. It is justified only when $\tilde{\mathbf{d}}(t)$ varies slowly on the scale of τ_c. However, it is readily verified that this is not the case in the presence of interference.

To demonstrate this *a posteriori*, we use the Markovian version of (2.6) in its general form, and determine the behavior of $\mathbf{d}(t)$. For two interfering lines, we have

$$\frac{d}{dt}\begin{bmatrix}\mathbf{d}_{14}(t)\\ \mathbf{d}_{23}(t)\end{bmatrix}=\begin{bmatrix}i\delta/2-\gamma & \gamma'\\ \gamma' & -i\delta/2-\gamma\end{bmatrix}\begin{bmatrix}\mathbf{d}_{14}(t)\\ \mathbf{d}_{23}(t)\end{bmatrix}. \qquad (5.1)$$

Assuming that $\gamma,\gamma'\ll\delta$, we write the solution of (4.1) in the interaction picture:

$$\tilde{\mathbf{d}}_{14}(t)=\left[\mathbf{d}_{14}(0)-i\mathbf{d}_{23}(0)\,\frac{\gamma'}{\delta}\right]e^{-\gamma t}+i\mathbf{d}_{23}(0)\,\frac{\gamma'}{\delta}\,e^{-\gamma t-i\delta t},$$
$$\tilde{\mathbf{d}}_{23}(t)=-i\mathbf{d}_{14}(0)\,\frac{\gamma'}{\delta}\,e^{-\gamma t+i\delta t}+\left[\mathbf{d}_{23}(0)+i\mathbf{d}_{14}(0)\,\frac{\gamma'}{\delta}\right]e^{-\gamma t}. \qquad (5.2)$$

As can be seen, $\tilde{\mathbf{d}}(t)$ contains terms that oscillate with the frequency of the line splitting δ which, in the adiabatic situation, is much greater than τ_c^{-1}. Consequently, it is precisely in the adiabatic limit that we make the mistake of passing from (1.5) to (2.6). On the other hand, when there is no interference, ($\gamma'=0$), the procedure for taking out $\tilde{\mathbf{d}}(t-\tau)$ is undisputed, and the kinetic equation is equally valid in the form of either (1.5) or (2.6).

The following recommendations can be based on the above discussion: (1) only the secular form of MT can be legitimately used in the case of adiabatic broadening (this has already been pointed out in Ref. 13, (2) the integral form of the non-Markovian theory must be used in any detailed description of the spectra that includes the periphery of the resonances and forbidden lines, and (3) impact theory is the preferred choice for the simplified description of the spectra.

[1)] A more general derivation of an equation analogous to (1.4), which uses only the binary nature of the interaction in tenuous gases, is given in Ref. 16.

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