SPECTRAL LINE MIXING AND LINE WING SHAPE: A CRITICAL REVIEW

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The spectral intervals in which the absorption is due to the line wings are important for atmospheric optics applications. In this connection, the currently popular concept of the essential role played by line mixing in shaping the spectral line wing contour is discussed it is shown that the arguments offered by some authors to support this idea are unconvincing.

1. INTRODUCTION

The effect referred to as spectral line mixing or quantum state interference is well known in spectroscopy. Major contributions to the development of the relevant theory were made by Fano[1] and Zwanzig[2] followed by other authors[3–14] (for experimental studies see Refs. 15–17). It is important that these authors considered the frequency detuning $\Delta\omega = |\omega - \omega_0| \ll \gamma$, where γ is the line half-width, ω is the field frequency, and ω_0 is the quantum transition frequency (the spectral line center).

However, papers[18–33] have recently appeared that claim that this effect is a decisive factor for shaping the vibrational-rotational spectral line wings in gases. In fact, this implies an actual revision of the problem. A critical analysis of this approach and am explanation of its methodical inconsistency is the subject of the present work. We may add that in the ”resonance age” certain subtleties inherent in the problem have been the cause of misconceptions and apparent paradoxes. Brilliant discussions of examples of this kind can be found in Refs. 34–36.

The significance of the problem is predetermined by the well-known remarkable role of the band and line wings in atmospheric optics and its applications.[37]

2. TERMS AND DEFINITIONS

We will discuss the ”conventional” fore of the absorption coefflcient[1,7,8,38–40]

$$\kappa(\omega) \sim \frac{1}{\pi}\,\mathrm{Re}\int\limits_0^\infty dt\; e^{i\omega t}\,\mathrm{Tr}\,\rho\left(S^{-1}(t)MS(t)M\right)_{av}. \tag{1}$$

The quotation marks will be removed in § 8. We also mean to say that Eq. (1) is the most standard solution of the most standard problem of the probability of single-photon processes.

Here M is the dipole moment operator of an ”active” (interacting with the field) molecule with Hamiltonian H_0 and density matrix ρ (Tr is the trace); $(\ldots)_{av}$ denotes averaging over the perturbing molecules and centers-of-mass motions; S is the evolution operator of the entire system; t is time. The line center $\omega_{nm} = ((H_0)_n - (H_0)_m)/\hbar$, and $(H_0)_n$ is the eigenvalue of H_0 with quantum number n. It follows from Eq. (1) that

$$\kappa(\omega) = \sum_{nm} \kappa_{nm}\left(\Delta\omega_{nm}\right), \qquad \Delta\omega_{nm} = \omega - \omega_{nm} \quad , \tag{2}$$

and we may refer to κ_{nm} as the absorption coefficient of the line resulting from the quantum transition $m - n$. It should be noted that the summation over the lines in Eq. (2) occurs whether the interference contribution is great or small, the latter affecting only the form of κ_{nm}.

Equation (1) is beautifully simplified by general procedures[1] and the semiclassical representation method.[3]

Evaluating $\int\limits_0^\infty dt(\ldots)$ of the operator functions yields[10]:

$$\kappa(\omega) \sim -(1/\pi)\ \mathrm{Im}\mathrm{Tr}M\left(\omega - \hat{L}_0 - \hat{\Phi}\right)^{-1}\rho M. \tag{3}$$

The symbol $\wedge$ denotes the superoperators; $y = \hat{F}x$ with the usual operators x and y implies the following expression for their matrix elements:

$$y_{nm} = \sum_{n'm'} F_{nm,n'm'}\,x_{n'm'} \tag{4}$$

The set of numbers $F_{n,m,n'm'}$ determines $\hat{F}$. In Eq. (3) $\hat{L}_0 x = 1/\hbar[H_0, x]$ and $\hat{\Phi}$ is the relaxation superoperator. Its explicit form is rather cumbersome (see Ref. 1) and we will comment on some general points.

If $\hat{\phi}$ is diagonal ($\phi_{nm,n'm'} = \phi_{nm}\delta_{nn}\delta_{mm'}$), the inversion of the resolvent in Eq. (3) is trivial:

$$\kappa_{nm} = \tilde{S}_{nm} f_{nm}(\Delta\omega_{nm}).$$

Here the line intensity $\tilde{S}_{nm}$ depends solely on the characteristics of the transition $m \to n$; f_{nm} is the dispersion contour with linewidth $\mathrm{Re}\Phi_{nm}$ and line shift $\mathrm{Im}\Phi_{nm}$. The situation is found to change drastically for

$$\Phi_{nm,n'm'} \neq 0; \qquad n, m \neq n', m'. \tag{5}$$

Deviations from f_{nm} occur even in the vicinity of ω_{nm}; $\tilde{S}_{nm}$ is replaced by intensity combinations (interference!), i.e., the "isolation" of the terms in Eq. (2) no longer exists. Therefore, the claim is made that Eq. (5) is the condition for line mixing that emphasizes its quantum origin.

Another important point is the dependence of $\phi_{nm,n'm'}$ on ω. Hence, f_{nm} is by no means the conventional dispersion contour with constant half-width and center shift. It does have a conventional form $f_n^{(d)}$ but only near the line center where $\omega = \omega_{nm}$.

In the projection operator method[2] $\kappa(\omega) \sim (1/\pi)\,\mathrm{Tr}Mg$, and g is the formal solution of the kinetic equation. (There are a lot of kinetic equations that have been derived heuristically, though, as a rule, they are valid for the resonant case):

$$-\rho M - i\omega g = (1/i)\,\hat{L}_0 g + \hat{\Gamma} g \tag{6}$$

where $\hat{\Gamma}(\omega)$ is the relaxation superoperator

$$\hat{\Gamma}(\omega) = -\int_0^\infty dt\, e^{i\omega t}\Big[\hat{L}'(1-\hat{P})\, e^{-it(1-\hat{P})\hat{L}} \times (1-\hat{P})\,\hat{L}'\tilde{\rho}\Big]_{av} \tag{7}$$

$$\hat{L}'x = (1/\hbar)\,[U, x]$$

$\hat{P}$ is the projection operator; $\hat{L}x = (1/\hbar)\cdot[\tilde{H}, x]$; $\tilde{H}$ is the total Hamiltonian; U is the Coulomb energy of the intermolecular interaction; and in $(\ldots)_{av}$ the density matrix of the "buffer" (perturbing) molecule is written explicitly. Using the transformation of integral (7) as in Ref. 1 and the recipes of dealing with resolvent operators given in Ref. 7 it can be rigorously proved that

$$\hat{\Phi} = i\hat{\Gamma} \tag{9}$$

with all the ensuing consequences.

It is a fundamental fact (we would like to call it "Fano's theorem") that because of Eq. (9) $\hat{\Phi}$ as well as $\hat{\Gamma}$ depends only on the T matrix. Figure 1 is reminiscent of its definition. The dynamic problem of colliding molecules appears to be eliminated (for example, there is no need to compute the "loops" in Fig. 1) because "stationary" procedures for computing T that are closely related to its asymptotic sense are known.[44–46]

However, on the other hand, any attempt to calculate Φ in a straightforward way using Eqs. (9) and (7) (for example, upon introducing the classical center-of-mass motion, which is evidently a simplification) would immediately thrust us back to the dynamic problem since $\exp(-it)\cdot(1-\hat{P})\hat{L}$ is, in fact, $S(t)$ from Eq. (1), and $T \sim S(\infty)$. Natural questions then arise: what is Eq. (6) for? Why then in spite of Fano's theorem is the dynamic approach adopted instead of the asymptotic problem for T when considering the line wings?

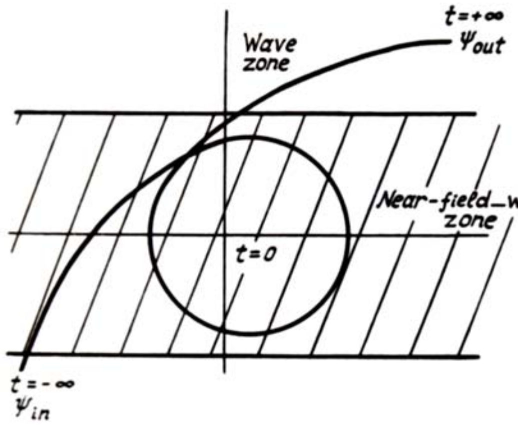

FIG. 1. Trajectory of relative center-of-mass motion of two molecules interacting via the Coulomb energy U. ψ_{in} and ψ_{out} are the wave functions of the initial and final states of the system. $\psi_{out} = T\psi_{in}$, where T is the scattering matrix.

The solution of this riddle is related to a unique peculiarity of scattering theory,[47,48] viz. the feasibility of retrieving the "near- field" (the total solution) from the "wave zone" (the asymptotic solution), see Fig. 1. The structure

$$\hat{\Phi} = \hat{\Phi}^{(1)} + \hat{\Phi}^{(2)} \tag{10}$$

adequately reveals this fact. Here $\hat{\Phi}^{(1)}$ (see Eq. (11)) is indeed T, and $\hat{\Phi}^{(2)}$ represents the above-mentioned "near-field-wave zone" relation-ship; $\hat{\Phi}^{(2)}$ is a rather complicated contour integral of the function containing the solution of the Lippman-Schwinger equation, i.e., $\hat{\Phi}^{(2)}$ is also expressed in terms of T.

Further, the matrix elements of $\hat{\Phi}$ are proportional to $(\Delta\omega)^2$, i.e., $\hat{\Phi}^{(2)}$ predominates at large frequency detunings. This case implies the "near field," and it is simpler to deal with Eq. (7) than to take a roundabout way through the "wave zone" and the integral of $\hat{\Phi}^{(2)}$. In the limit $\Delta\omega - 0$, $\hat{\Phi}^{(2)}$ in Eq. (10) can be neglected and at resonance the following relation, popular in many "resonance" calculations, is valid:

$$\hat{\Phi}^{(1)} \sim T \otimes T, \quad \Phi^{(1)}_{nm,n'm'} = \mathrm{const} \tag{11}$$

with respect to $\Delta\omega_{nm}$.

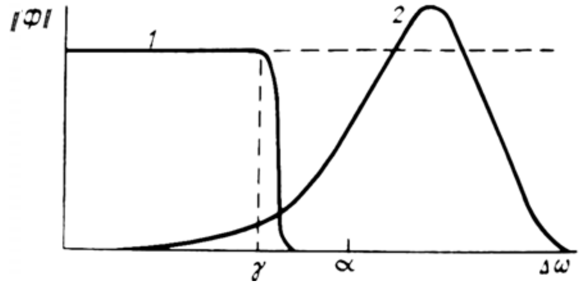

FIG. 2. Matrix elements of the relaxation superoperator $\hat{\Phi}$ *vs frequency detuning* $\Delta\omega$. *1* — $\|\Phi^{(1)}\|$, *2* — $\|\Phi^{(2)}\|$, $\hat{\Phi} = i\hat{\Gamma}$, $\|\ldots\|$ *is the norm operator,* γ *is the line half-width,* α *is the lower limit of applicability for analytical perturbation theory. The plateau of curve 1 corresponds to the constant from Eq. (11).*

A more thorough analysis leads to the curves shown in Fig. 2. It is most simple to use the semi-classical representation for $\hat{\Gamma}^{(1)}$ $(= -i\hat{\Phi}^{(1)})$ and $\hat{\Gamma}^{(2)}$ $(= -i\hat{\Phi}^{(2)})$ from Ref. 40. As a result it becomes clear that the roles of the terms in Eq. (10) are entirely different: $\hat{\Phi}^{(2)}$ and $\hat{\Gamma}^{(1)}$ are responsible for the line center, while $\hat{\Phi}^{(2)}$ and $\hat{\Gamma}^{(2)}$ govern the line wings. The question is which curves are implied rather than what is the asymptotic limit of each curve. Therefore, the methods and criteria valid for the line center cannot be extended to include the line wings.

Unfortunately, the authors who have dealt with the general aspects of the subject sometimes prefer heuristic considerations to exact results similar to those mentioned above. For example, passing from T to the dynamic problem or the necessity of calculating the nondiagonal elements $\Phi_{nm,n'm'}$, which are purely technical problems from the standpoint of Eqs. (3)–(9). nearly grow into "physical concepts".

We believe that it is the heuristic approach which is behind the inadequacy of the arguments in favor of ascribing a great significance to line mixing In the explanation of the line wing shape. For the sake of convenience these arguments will be divided into groups though in Refs. 18–33 they can be found in different combinations.

3. ANALYTICAL PERTURBATION THEORY. FIRST CROUP OF ARGUMENTS

The following relations are very popular in the line mixing-line wing problem: [19,20,22–30]

$$\kappa(\omega) = \sum_{nm} \frac{\tilde{S}_{nm}}{\pi} \frac{\gamma_{nm} + (\omega - \omega_{nm}) A_{nm}}{(\omega - \omega_{nm} - \beta_{nm})^2 + \gamma_{nm}^2}; \tag{12}$$

$$A_{nm} = 2 \sum_{n'm' \neq nm} \frac{M_{n'm'}}{M_{nm}} \frac{\mathrm{Re}\, \Phi_{nm,n'm'}}{\omega_{nm} - \omega_{n'm'}},$$

where γ_{nm}, β_{nm} are the line-width and the line center.

Two points are worth emphasizing. First, Eq. (12) is derived in first-order analytical perturbation theory when the resolvent operator is inverted.[49,50] Second, the dependence of $\hat{\Phi}$ on ω is ignored (condition (11) is used), in other words $\hat{\Phi} - \hat{\Phi}^{(1)}$ (see Eq. (10), and A_{nm} = const as in Eq. (11)).

Now condition (5) allows us to regard Eq. (12) as the evidence that interference is a line wing effect. Indeed, $A_{nm} \neq 0$ only by virtue of Eq. (5); furthermore, the line contour is dispersive ($f_{nm}^{(d)}$) in the line center, and the deviations from $f_{nm}^{(d)}$ increase with frequency detuning. Moreover, the terms in Eq. (12) become negative sooner or later. I. e., the interference comes to play a dramatic role: separate lines (see the discussion of Eq. (2)) contribute to a decrease of $\kappa(\omega)$ rather than increasing it (!?). Note that, as follows from Eqs. (1) and (2), $\kappa_{nm} > 0$.[40]

The discussion of Eq. (12) should start with the remark that the validity conditions for the analytical perturbation theory[51,52] applied to the operator inversion in Eq. (3) lead to the point $\alpha > \gamma$ in Fig. 2. It is necessary that the condition $\Delta\omega > \alpha$ be fulfilled and no other lines be centered within the line-width. A barely passing glance at Fig. 2 will suffice to see the obvious incompatibility of the first and second points mentioned after Eq. (12) which are claimed to justify the importance of line mixing.

The structure of Eq. (12) is certainly quite evident and some authors (see, e. g., Refs. 28 and 30) speak about the collision approximation (11) in the perturbation theory for inverting the resolvent. However, the problem is that these things are incongruous: the collision approximation is associated with resonance (see Ref. 35 for a comprehensive treatment) and implies a special calculating technique[3,7,9–14] for $\kappa(\omega)$ in Eq. (3).

The analytical perturbation theory is undoubtedly valid for $\Delta\omega > \alpha > \gamma$, yet it follows from the above that we are to use Eq. (2) in Fig. 2 instead of Eq. (1). Therefore, the following substitutions are to be made in Eq. (12): γ_{nm} — and $\Phi^{(2)}_{nm,nm}$, $\Phi_{nm,n'm'} \to \Phi^{(2)}_{nm,n'm'}$ in A_{nm}. Then referring to the role of line mixing the "new" γ and A will have to be compared. As shown in Ref. 40 for the case of large $\Delta\omega$, it is necessary to estimate the parameter η.

$$\eta = \frac{\sigma R}{t^{*} s v} \tag{13}$$

The notation of Eq. (13) is elucidated by Fig. 3; $v = |\bar{v}| \cong 2\hbar\omega_0 / M$, M is the reduced mass; ω_0 (in s^{-1}) is the level separation for the "active" molecule; $R = (\mu/\omega_0)^{1/a}$; $U(R)/\hbar = \mu/R^a$ is the expression for the quantum potential (with parameters μ and a), t^* is the duration of the collision, σ is the inelastic scattering $(A - B)$ cross section, $s = \pi r^2$; and r is the molecular "radius."

The "nonresonant interference" (the term emphasizes the transition from Eq. (1) to Eq. (2) in Fig. 2) is essential for $\eta \gg 1$, and vice versa. To be sure, the condition $\Delta\omega \gg \gamma$ is to be examined first. The estimates show that $\eta \ll 1$ is "almost always" the case, at least for atmospheric gases and the experimental data available. In other words, the interference cannot be critical for the wing shape. To be precise, we have to add "at low pressures P": since $\gamma \sim p$ the increase of P (for example in going to liquids) at a given $\Delta\omega$ would mean a reversion to the resonance case. A possible exception is the Q-branch lines (see the measurements in Refs. 20, 23–25, 58).

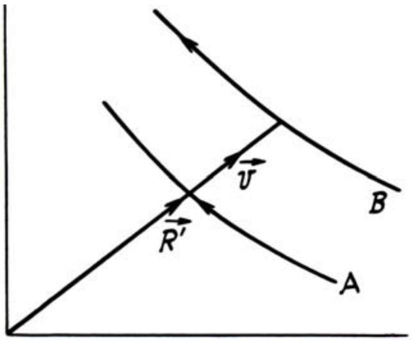

FIG. 3. Diagram of the relative motion of center of mass. The velocity of the "jump" **v** *has only a radial component.*

4. THE "LARGE FREQUENCY DETUNING ASYMPTOTICS AND SOME EXAMPLES

The far line wings have been considered in detail elsewhere.[39,40,53] Investigated there was the asymptotic behavior of functions of type (2) in Fig. 2. The nontrivial temperature and frequency dependence of the absorption coefficient and the physics involved were also discussed. It was shown[40,53–57] that the theory was capable of interpreting the experimental data and predicted certain new effects inherent in the line wings. Some of them were detected in experiments. Those results left no place for line mixing as an appreciable effect in the line wing problem. Now we will comment on some relevant examples.

In the "large $\Delta\omega$" asymptotic limit the interference correction reduces[40] to the substitution of $\tilde{S}_{nm}(1+\chi_{nm})$ by $\tilde{S}_{nm}$, which yields $\chi^{*}_{nm} = A_{nm}(\omega-\omega_{nm})\gamma_{nm}$ in Eq. (12) after reducing it to the analogous form. This value can be readily estimated, for example, using the data of Ref. 29. Figure 4 is of great significance here. As the figure shows, there are important quantitative differences here with a very similar qualitative behavior. The latter merely reflects the fact that the values A_{nm} and χ_{nm} result from the perturbation theory, but on going from curve (1) to curve (2) in Fig. 2 the small parameter (13) comes to the fore.

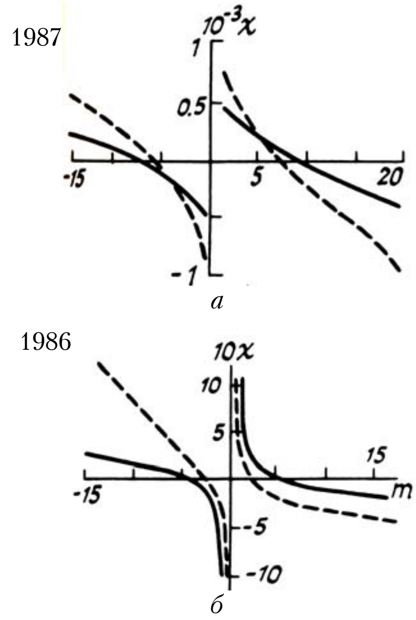

FIG. 4. Parameters taking into account interference in the case of CO, $\kappa = \sum_{1} S_1(1+\chi_1)f^1$, *m is the rotational quantum number:*
a) value of χ_1 *from Ref. 29;* $f \sim f^{(d)}$, $T = 292$ K, $T = 173$ K *(solid line);*
b) values of χ_1 *from Ref. 40.* $f \sim f_{wing}$; $T = 300$ K *(solid line),* $T = 100$ K *(dashed line).*

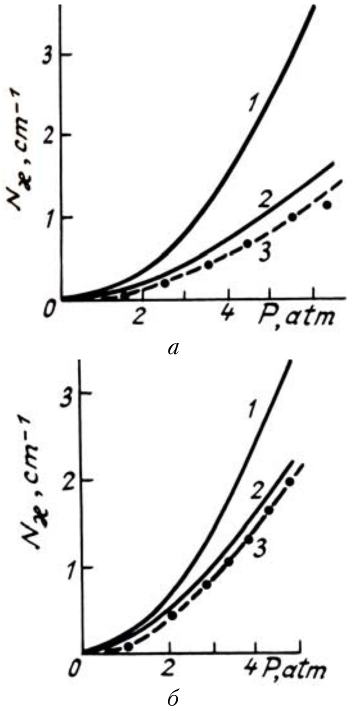

FIG. 5. Absorption coefficient of CO_2 *broadened by for* 2387.62 cm^{-1} *at different temperatures and pressures; points —experiment*[26], 1988*; 1 —* $\kappa^{(d)}$*: 1 — calculation*[26]*; 3 — calculation according to line wing theory with line shape from Ref.* 74, 1982. *a)* $T = 296$ K*; b)* $T = 370$ K.

The data in Fig. 5 are regarded by the authors of Ref. 26 as a considerable success of Eq. (12) as compared to the dispersive contour ($A_{nm} = 0$ in Eq. (12)). However, curve (3) shows that the "large $\Delta\omega$" asymptotics is more successful in calculating the absorption coefficient.

Figure 6 is also evidence of this fact. The line mixing scheme fails to reproduce the experimental data even by varying the parameters of the intermolecular interaction in the Gibbs function. At the same time the calculation by the formulas from Ref. 40 is rather convincing and, what is most important, there appears a potential with parameters obtained from thermodynamic measurements.

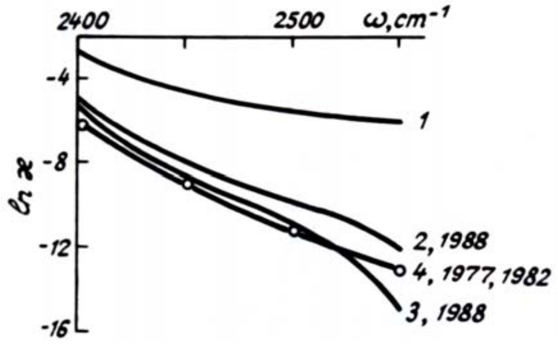

FIG. 6. CO_2–Ar *absorption coefficient in the wing of the* 4.3 μm *– band of* CO_2 *at* $T = 296$ K. *Points—experiment, 1 – dispersion line shape, 2 and 3 – calculation*[30] *with different potentials, 4 – calculation*[74] *according to the line wing theory.*

Still more significant is Fig. 7, where the points correspond to spectral microwindows, i. e., intervals between the lines. Curves 1 and 2 were obtained within the framework of a consistent treatment of line mixing as a decisive factor. Importantly, the curves turned out to be universal, i.e., independent of the perturbing species. But the experimental data by no means confirm that prognosis. Curve (3) constructed using Eq. (12) has the wrong asymptotic limit: instead of the natural (and experimentally verified)

$$\chi_\infty = \lim_{\Delta\omega_{nm}\to\infty} \kappa/\kappa^{(d)} = 0$$

the authors of Ref. 29 obtained $\chi_\infty = 0.1$, calculating the resolvent by Eq. (11) and employing rather a rough procedure[59] for T. It becomes obvious after Section 3 that the nonsense $\chi_\infty \neq 0$ results from the extrapolation of $\Phi^{(1)}$ to the forbidden zone in Fig. 2.

The classical part of the problem dominates in the "large $\Delta\omega$ " asymptotic limit: the line wing is formed as a result of collisions of the molecules as small distances, where the Gibbs exponent is different from unity. The same conclusions were arrived at in Refs. 60 and 61, which is expressly evidenced by Fig. 8 but with initial expression (3).

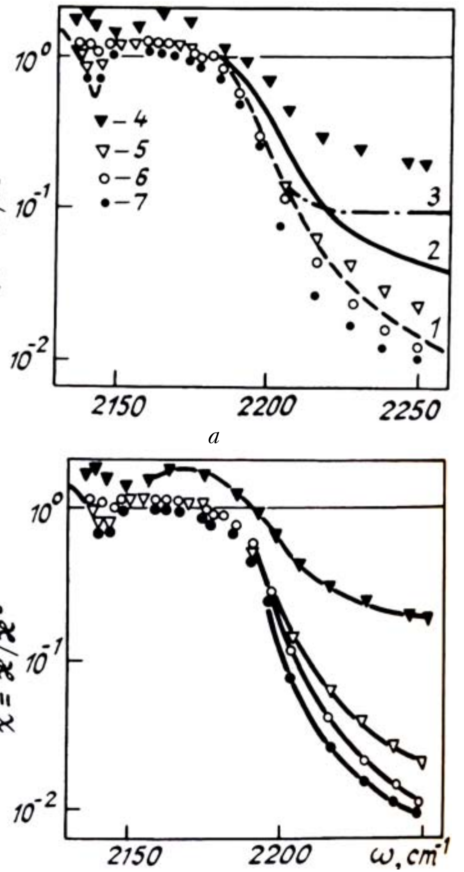

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FIG. 7. Deviation of the CO_2 *absorption coefficient from that calculated with dispersion line shape for different per tubing gases at* $T = 78$ K. *Experiment*[18]*: 4 –* CO–N_2, *5 –* CO–H_2, *6 –* CO–NBe, *6 –* CO– He*;*
a) 1, 2 – calculation[18] *with varying degrees of account of interference; 3 – calculation*[29] *using perturbation theory to account for interference: b) curves – calculation by line wing theory.*[40,57]

We would like to draw the reader's attention to the dates cited in Figs. 4, 6, and 8. Probably they can be regarded as a variation of the theme: "The new is the long forgotten old". Another illustration is Fig. 9. and in Refs. 39 and 75 the calculated points were obtained nearly *ab initio*. It should be added that the authors of some recent papers (e.g., Refs. 28–30, 60, and 61) have re-derived the relations from Ref. 39, and some conclusions concerning the role of the intermolecular interaction potential in the line wing problem forming the ideological content of Refs. 39 and 40, were made once again in Refs. 18, 31, 32, 60, 61.

Continuing on this theme, note that in a recent paper Hartmann reliably approximates his measurements in the 4.3 μm band of CO_2 by the empirical line shape from Ref. 62, and the latter contour agrees fairly well with the "large $\Delta\omega$" asymptotic limit (see Refs. 54 and 55). The measurements in Ref. 27 were made for large pressures ($P \sim 1$–77 atm), and it turns out that the discrepancies between the measured values and the calculations based on Eq. (12), themselves not small (up to an order of magnitude), tend to increase with increasing P. This fact is at least worth heeding because the entire concept of line mixing states quite the opposite.

Recently, attempts have been made to go beyond the limits of Eq. (12), to take into consideration the frequency dependence of the relaxation, to use asymptotic ideas. However, they cannot possibly be considered to be successful when compared to the already developed "large $\Delta\omega$ " asymptotics. (Some details of Refs. 20, 60, and 61 have been mentioned above).

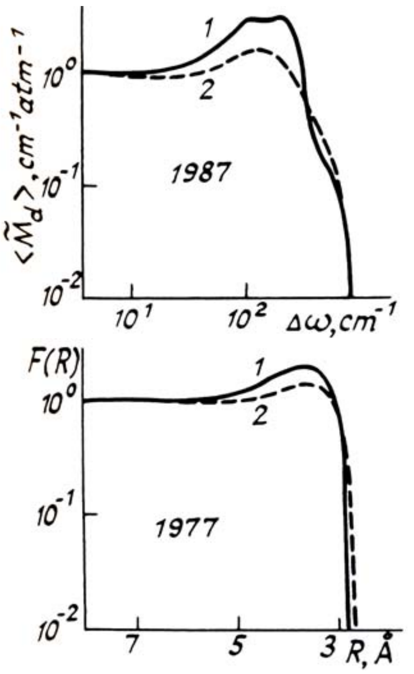

FIG. 8. Broadening parameter $\langle \hat{M}d \rangle$[61] *and function* $F(R)$[40] ($\Delta\omega \sim R^{-a}$) *determining the temperature and pressure dependences of the* H_2O *absorption coefficient in the case of self-broadening; 1 –* $T = 296$ K, *2 –* $T = 430$ K.

The central point in Ref. 28 was the "solution" $g = \exp(\tau/i\hbar) \cdot U(t_0)$ for the evolution operator g of the Schrödinger equation for two colliding molecules; $U(t_0)$ is the potential at the time t_0, which is to be interpreted as "the time center of the collision". Direct substitution readily shows how far this solution is from the truth, and references to the structure of the relations where g appears will not save the day. It is clear, for example, that large $\Delta\omega$*s* create prerequisites for an asymptotic evaluation of the integral in Eq. (11), but the stationary point will correspond to the law of conservation of energy for the photon absorption and will therefore depend on $\Delta\omega$. Hence the arbitrary t_0 cannot be used instead of the stationary value as is done in Ref. 28.

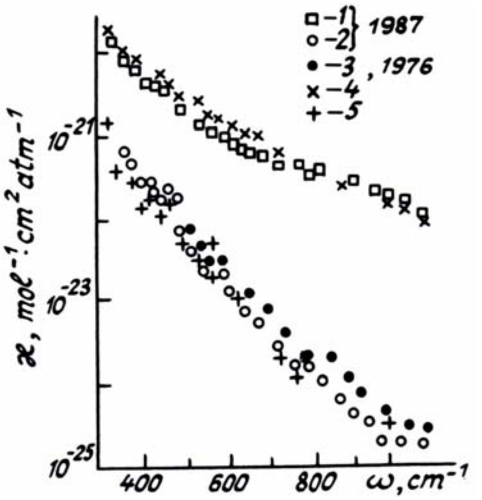

FIG. 9. Experimental H_2O *absorption coefficient obtained by Burch (see Ref.* 61*):* x – H_2O– H_2O, + – H_2O–N_2. *Calculation:*[61] □ – H_2O–H_2O, ° – H_2O–N_2; • – *calculation for the case of* H_2O–N_2 *by the line wing theory*[75]. $T = 296$ K.

The approach of Refs. 60 and 61 also seems close to the "large $\Delta\omega$" asymptotic approach, viz., the nondiagonal elements of $\hat{\Phi}$ are ignored ($\Delta\omega \gg \gamma$) under the resolvent inversions; to tell the truth, the author of Refs. 60 and 61 confines himself to general considerations and a parameter of type (13) does not appear. However, this attempt to extend this idea to the calculation of the matrix elements Φ cannot be recognized as successful. Actually, $\mathrm{Im} \lim\limits_{\varepsilon\to\infty} \hat{L}'(\omega - \hat{L} + i\varepsilon) \cdot \hat{L}'$ (see Eqs. (7) and (8) for notation) will become a numerical δ-function only in the total Hamiltonian eigenfunction representation. The substitution of the eigenvalues of U for the argument, as is done in Refs. 60 and 61, naturally eliminates the Schrödinger equation problem, but this action is not any better them the "solution" in Ref. 28. It is worthwhile to note that an indispensable condition for (3) is the factorization of the density matrix, and its straightforward procedure[60,61] even with violation of hermiticity must be substantiated.

5. SUM RULES. SECOND GROUP OF ARGUMENTS

Let us return to the discussion of the arguments underlying the line mixing-line wings concept. Another group of arguments is associated with sum rules, i.e., with the relations of the type (see Eqs. (7), (9), and (4))

$$\sum_{n'm'} f_{n'm'} \Gamma_{n'm',nm} = \sum_{n'm'} \Gamma_{nm,n'm'} f_{n'm'} = 0,$$

$$\text{or} \quad \hat{\Gamma} \quad \hat{\Gamma}^{+}. \tag{14}$$

Here, f is an operator which is by no means arbitrary, and * denotes the Hermitian conjugate

The central idea looks very attractive: Eqs. (14) are claimed to be equations for the matrix elements of $\hat\Gamma$ (or $\hat\Phi$, see Eqs. (9)), and those needed to complete the system are constructed on the basis of model considerations (see Refs. 18, 28–32, 63). Thus the most complicated calculational problem of the relaxation superoperator is avoided.

Some specific expressions of type (14) have been found for the resonance case.[29,36] Bearing in mind, however, the idea formulated above, we need to be interested in more general questions, such as whether Eq. (14) actually exists. If "yes", then what does it mean?

If in search of the answer we return to the exact equation (7) with $\hat L'$ on the left, look at Eq. (8), take into account that U is only a function of its arguments, it becomes clear that there is a condition equivalent to Eq. (14) (see Eq. (4)):

$$\hat\Gamma^{+} x = 0, \quad x \in \tilde W , \tag{15}$$

Here $\tilde W$ is the subspace of ordinary functions (the multiplication operators) in the operator space. In the language of linear algebra Eq. (15) implies that $\tilde W$ is the kernel of the linear transformation $\hat\Gamma^{+}$ (Eq. (14) is this kind of transformation). It is well known in linear algebra[64,65] that the linear transformation can be retrieved from the orthogonal complement to the kernel. The existence of the kernel can only suggest the idea of a convenient basis, but the kernel is trivial in our case. Actually, it is at this point where an underwater rock is hidden: Eq. (14) cannot be interpreted as an equation for $\Gamma_{nm,n'm'}$. Eqs. (14) and (15) must be fulfilled automatically no matter how $\hat\Gamma$ (model, numerical, etc.) is constructed. For example, this is similar to the case of the scattering matrix whose unitarity has to always be verified when developing the calculating technique for T. However, the unitarity conditions themselves do not appear as additional equations.[66]

The above implies that upon writing $\hat\Gamma \,\square\, \hat L'\hat A$ one can think of a model for $\hat A$. But one cannot exclude $\hat L'$ and adjust the parameters of $\hat A$ to satisfy Eq. (14). In essence, recalling the derivation of Eq. (15), the triviality of the question becomes readily understood. Indeed, what can be said about unknown function ψ from the known f, if we only have the "equation" $\psi f = f\psi$? Just nothing. But Eq. (14) is the very equation of that type in implicit form.

Generally speaking, the structure of Eq. (7) with the operator $\hat L'$ on the left is far from fortuitous – it ensures the normalization of the density matrix. There are variants where $\hat L'$ is on the right, which provides "projection" onto the dynamic subsystem.[2,67]

6. SUBTLETIES OF THE KINETIC EQUATIONS. THIRD GROUP OF ARGUMENTS

The essence of the arguments in Refs. 18, 31 and 32 lies in the conviction that the significance of line mixing can be declared at a theorem level, provided one proceeds from Eq. (2) to the equation for the superoperators. It is certainly to be added that there seems to be nothing to prevent the transformation of such conclusions into an "extremist" statement about the importance of interference "under any conditions". (Then the two-level approximation so popular in nonlinear spectroscopy will prove to be an out law).

If we digress from mathematical details that are immaterial at this point, the idea will be as follows. Suppose we succeed in writing the equation

$$\frac{\partial Q}{\partial t} + \frac{1}{i\hbar}\hat L_0 Q + \int_0^t \hat\Gamma(t, \tau)\, Q(\tau) = 0 \tag{16}$$

for the operator (!) Q (for example, g in Eq. (6) is the Fourier transform of Q). Assume also that we notice the existence of $\hat\Lambda$ in the expression

$$Q = \hat\Lambda M . \tag{17}$$

Then it appears quite natural, by virtue of Eqs. (16) and (17), to attempt to construct an equation for $\hat\Lambda(t)$

$$\frac{\partial \hat\Lambda}{\partial t} + \frac{1}{i\hbar}\hat\Lambda \hat L_0 + \int_0^t d\tau\, \hat\Lambda(\tau)\, \hat N(t - \tau) \tag{18}$$

with an appropriate relaxation operator $\hat N$. As stated in Refs. 18, 31, 32, it is Eq. (18) which allows Eq. (5), $f_{nm}^{(d)}$, Eq. (14), etc. to be used efficiently.

Generally speaking, passing from Eq. (16) to Eq. (18) via Eq. (17) is a step of principle. In the language of functional analysis we cam speak of a higher "level of abstraction" of the problem. (Say, the transition from equations with functions to operator equations, e.g., to the evolution operator in quantum mechanics, or from operator equations to superoperator equations). Certainly, one should follow the relevant rules.[68,69] These read: the transition from Eq. (16) to Eq. (18) is possible if and only if the domain of definition and the range of values for Λ coincide; i.e., $\hat\Lambda, \hat\Lambda^2, \hat\Lambda^3, \ldots$ must have the same domain of definition.

The case under study can be explained as follows. To find the domain of definition for $\hat F$ in Eq. (4) we have to select all xs for which the sum exists. Region I in Fig. 10 results, with a shaded part that is self-mapped. The remaining x are transformed by Eq. (4)

into region II. Here the sum (4) already diverges and a suitable method of generalized summation has to be resorted to.[70] Then similar considerations yield region III and we have to use a more generalized summation for which the procedure employed to obtain region II is a particular case. Figure 10 assumes that region III is self-mapped. Surely, all the procedures are but a trivial realization of the analytic continuation principle[71] in constructing mathematical objects.

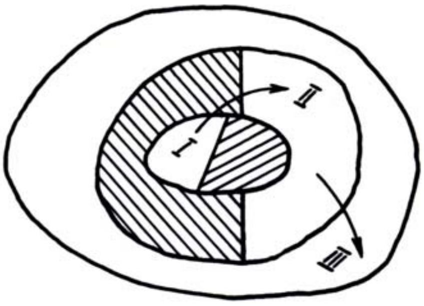

FIG. 10. Range of function for F. I — domain of ordinary summation; II, III — domains of generalized summation.

In the physical problem of the absorption coefficient there appear, of course, functions $\psi(t) = S(t)\psi_n$ (ψ_n are the eigenfunctions of H_0). The chain $\psi(t) - S - Q$ leads to Eq. (16), and, should we construct a sequence similar to Fig. 10, it would terminate as early as region I. For unitary S, the functions $\Psi_n(t)$ form the same space of quadrat leally integrable functions as Ψ_n. Therefore, Eq. (16) can be obtained by direct differentiation of the definition for Q.

It is assumed in Refs. 18, 31, 32 that the same is true for $\hat{\Lambda}$ from Eq. (17). However, for $\hat{\Lambda}$ one has to construct a "matreshka" of Fig. 10 because the structure of $\hat{\Lambda}$ falls to provide the convergence of sum $\hat{\Lambda}^2 x$, even if $\hat{\Lambda}x$ converges. Therefore it is necessary to proceed to the generalized summation, i.e., a proper redefinition of $\hat{\Lambda}$. But then, in differentiating with respect to t, additional terms appear in Eq. (18) that radically change the form of the equation.

The fact that the mathematical structure of equations of type (18) in Refs. 18, 31, 32 is at least questionable is evidenced by the following case: there are $\hat{L}'s$ on the right and on the left of $\hat{N}$. Multiplying Eq. (18) by the basis function $\Psi^{(j)} \in \tilde{W}$ and applying Eq. (15) yields a system of equations for $\Lambda_{nm,n'm'}$ which is independent of relaxation(?!). Of still greater significance is the following fact: the solution of Eq. (18) is the resolvent that does not coincide (?!) with the exact result (3).

7. NUMERICAL COMPARISONS. FOURTH GROUP OF ARGUMENTS

We will assume that the reader has come to believe in all the foregoing mathematical "games." But then a question is sure to arise that stresses the paradoxical nature of the situation: why do the criticized views lead to formulas, which, granted, only in certain cases, fit the experimental data, but do it more than Just passably (paradox 1).

The variant of Ref. 18 is most noteworthy. It contains the simplest model description of relaxation (see the discussion of Eq. (14)) and gives the following expression for χ (see Fig. 7 for the definition)

$$\chi(\omega) = \frac{\sum\limits_{nm} \tilde{S}^0_{nm}/(\Delta\omega_{nm})^2 - \left[\sum\limits_{nm} \tilde{S}^0_{nm}/\Delta\omega_{nm}\right]^2}{\sum\limits_{nm} S^0_{nm}(1 - S^0_{nm})/\Delta\omega^2_{nm}}. \quad (19)$$

Here $\tilde{S}^0_{nm} = \tilde{S}_{nm} \Big/ \sum\limits_{nm} S_{nm}$, $\Delta\omega_{nm} = \omega - \omega_{nm}$. Another variant is based on Eqs. (12) for χ with a model or numerical construction of Φ (making use of Eq. (11)).[19,25–29,63] Again it is established that the calculations give a fairly satisfactory fit to the experimental data and coincide with the results obtained from Eq. (19). Interestingly, these results are but slightly dependent on the way T is calculated in (11). This is "paradox-2" and in the opinion of the authors of Refs. 19, 28, and 29 also works on the side of the following version: line mixing is such a critical factor that it is sufficient to account for it any way possible. We will discuss only the coincidence of Eq. (12) with Eq. (19) and "paradox-2," leaving the resolution of the main question till Section 9.

To begin with, it should be noted that spectral microwindows of CO_2 and CO are meant. Direct evaluations show that it is possible to confine ourselves to only two lines in immediate proximity to ω. Certainly, realistic elements of matrix T should be used — these mean the transition probability. The molecular collisions are capable of initiating a transition only between closely separated rotational states. Of course, the unitarity of T yields

$$T^+T = T^{-1}T = 1. \quad (20)$$

Finally, all the examples refer to linear molecules and imply the quantum problem of the rigid rotor. The rest is a matter of computations. In the abovementioned circumstances Eqs. (19) and (12) lead to the same result. Therefore in § 9 we will deal only with Eq. (19).

The role of Eqs. (20) is most noteworthy. These equations play the part of "sum rules" and, as such, make it possible to express the combinations of nondiagonal T_{nm} in (11) through the line half-width. The results of the calculation of T are thereby smoothed out, which explains "paradox-2".

8. RELATIONS BETWEEN ABSORPTION COEFFICIENTS OF SEPARATE LINES

First let us return to relation (1). Rather subtle considerations show that it does not satisfy "first principles". To avoid the trouble while deriving the expression for the absorption coefficient, the long-wave approximation for the centers of mass has to be abandoned. Then

$$\kappa(\omega) \sim (1/\pi)\ \mathrm{Re}\int_0^\infty dt\ e^{i\omega t}\ \mathrm{Tr}\ \rho\left(S_{(}^{-1} M\Pi SD\Pi^{+1}\right)_{av} \quad (21)$$

where $G\Pi = \exp\left(i\frac{\omega}{c}\vec{\kappa}_0\vec{r}\right)$, $\vec{\kappa}_0$ is Poynting's vector of the external field, normalized to unit magnitude, and the coordinates of $\vec{r}$ are the center-of-mass coordinates of the "active" molecule.

The formal consequence of Eq. (21) is expressions of the form

$$\sum_{nm}(\omega - \omega_{nm})^l \cdot \kappa_{nm}(\omega) = B_l, \quad l = 1, 2\ldots \quad (22)$$

with the terms from Eq. (2) and known B_1; in particular

$$B_1 = (\omega/Mc)\ \mathrm{Re}\int_0^\infty dt\ e^{i\omega t}\ \mathrm{Tr}\ \rho\left(S^{-1} M\Pi S\Pi^{+} M\ \vec{p}\ \vec{k}_0\right)_{av} \quad (23)$$

where $\vec{p}$ is the center-of-mass momentum operator. Actually, it is Eqs. (22) that should be referred to as "the sum rules" rather than the trivial Eqs. (14) since the commutation of U and M is important in deriving Eqs. (22). This very equation is an effective application of $[U, M] = 0$.

Quantity (23) is calculated in a straightforward manner, and

$$\sum_{nm}(\omega - \omega_{nm})\,\kappa_{nm}(\omega) = \sum_{nm}\frac{\xi_{nm}}{\gamma_{nm}}(\omega - \omega_{nm})f_{nm}^{(d)}(\omega) \quad (24)$$

with

$$\xi_{nm} \neq 0\ , \quad (25)$$

depending on the values contained in Π.

The importance of Eqs. (22) and (24) for the questions at hand becomes clear as the result of one Important circumstance. For small frequency detunings Eqs. (1) and (21) are practically indistinguishable. However, setting $\Pi = 1$ in relation (21) from the very beginning and re-deriving Eqs. (22) gives the relation $B_1 = 0$, which contradicts result (25). This "noncommutativity" emphasizes the fundamental importance of relation (21) and its consequences (22) and (24).

It should be noted that $f_{nm}^{(d)}$ is obtained in Eq. (24) for any variant — with the assumed interference or without it. In essence, $(\omega - \omega_{nm})\gamma_{nm}^{-1}f_{nm}^{(d)}$ are terms from the refractive index, and their appearance is far from accidental: Re in Eq. (23) turns into Im because of $\vec{R}$, whereas the absorption coefficient and the refractive index are the imaginary and real parts of the complex permittivity.

Finally, according to the model of Ref. 40, for small frequency detunings $\xi = (2\pi l/\lambda)\tau^{-1}$, where λ is the wavelength of the light, l is the distance at which the relaxation of an "active" molecule occurs after the absorption of a quantum, and τ is the time when the molecule ceases to remember its initial velocity. For the same small $\Delta\omega$, within the framework of the strong collision model (see Ref. 72) τ is equal to the time between collisions and is proportional to γ^{-1}. Therefore,

$$\xi/\gamma \cong 2\pi l/\lambda, \quad \Delta\omega = O(\gamma) \quad (26)$$

The foregoing discussion is illustrated by Fig. 11: the left-hand side of Eq. (24) and the refractive index are calculated in a straightforward way. The computed values are fairly consistent with conditions (26), provided the quantities ξ_{nm} are replaced by some average value.

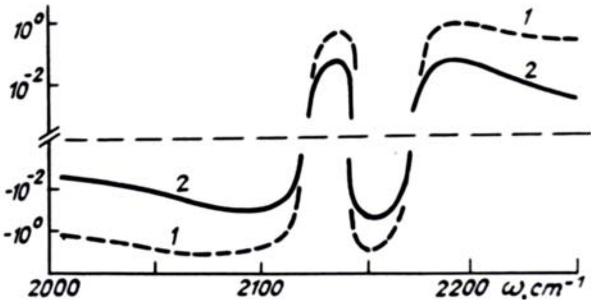

FIG. 11. Refractive index (curve 1) and left-hand side of Eq. (24) (curve 2) for the self-broadened CO *molecule. The curves connect points calculated in the intervals between lines.*

9. FOURTH CROUP OF ARGUMENTS. CONTINUATION

Let us return to the question that arose at the beginning of § 7. The answer (or the resolution of "paradox-1") will be the derivation of Eq. (19) from Eqs. (21) and (24). It should be born in mind that we mean here only the ability of Eq. (19) (or (12)) to fit the experimental values. The appearance of Eq. (19) specifically from relation (21) emphasizes the importance of the physical aspects involved in relation (21).

The calculations themselves are relatively trivial. Let $\kappa_{nm} = f_{nm}^{(c)} + \varphi_{nm}$, regarding φ_{nm} as a manifestation of the spectral dependence of the diagonal matrix elements of the relaxation operator at $\Delta\omega \simeq \gamma$. The second of relations (26) implies that $(\xi/\gamma)\Delta\omega \ll 1$. Having approximately defined the average frequency detuning $(\omega - \omega_{nm})_{av}$ by equating $(\omega - \omega_{nm})_{av} \sum \tilde{S}^0_{nm}(\omega - \omega_{nm})^{-1}$ to Eq. (24). we will actually derive Eq. (19). Of course Eq. (24) defines only $\sum\limits_{nm} \varphi_{nm}$ and says nothing as to the contour of a separate line.

CONCLUSION

The above considerations should not be interpreted by any means as the nonrecognition of line mixing as such. The excellent papers here cited here demonstrate the existence of the effect and its subtleties under the resonance interaction.

However, the laws governing the behavior of the line center cannot be directly extrapolated to the line wings, for these regions are separated by so extensive a "watershed" that we have to speak, in essence, about quite different physical problems. The qualitative prerequisites which must be taken into account are well known.[5,6,53]

The interpretation of the resonance interaction ($\omega \simeq \omega_0$, Fig. 12) proceeds from the assertion that it is "switched on" on a segment of the "free path", driving the molecule into an excited state, i.e., optical nutation takes place[73] around n_3 or n_4 (Fig. 12). In this case, each collision is optically active (i. e., accompanied by the absorption of a quantum). This restores the equilibrium (makes the molecule return to its lower state n_1 or n_2, see Fig. (12)) disturbed by the field between collisions. There would be no problems with a two-level system, but for the case of Fig. 12 collisions may "mix up' closely spaced levels. Naturally, a "short memory" becomes essential, i.e., a seguence of ψ_n in a succession of collisions. The meaning of the synonym "the interference of quantum states" and what is meant by the indispensability of resonance, especially the purely quantum character of the effect, are clear.

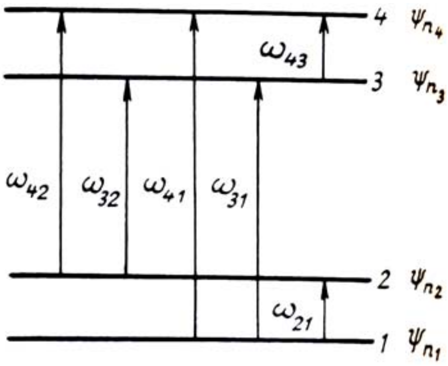

FIG. 12. Energy level diagram of a molecule the Hamiltonian H_0. ψ_{nj} *are the eigenfunctions of* H_0 *and* n_j *are the corresponding eigenstates;* ω_{41}, ω_{31}, ω_{42}, $\omega_{32} \simeq \omega$; ω_{43}, $\omega_{21} \ll \omega_0$.

However, at fairly large frequency detunings, the interaction of an active molecule with the field occurs only during a collision (the nutation amplitude ~ $1/\Delta\omega$). The molecule gets rid of the absorbed energy through a series of subsequent, already optically inactive collisions — such a stage of the evolution can be called a "drift". Actually, the transformation from relation (1) to relation (21) is formally related to them: "the drift time" appears in the expression for ξ (see Eq. (26)).

These circumstances make the importance of a "short memory" problematic — after all, the quantum states of an active molecule are statistically independent for optically active collisions separated by a drift (but it is they and only they that contribute to the absorption coefficient). These features explain the meaning of parameter (13) and its evaluation.

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