

Collision broadening in two-photon spectroscopy

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Collision-broadening theory is used to obtain a general expression for the steady-state rate of two-photon simultaneous absorption as a function of their sum energies and momenta in gases, under conditions where both homogeneous (collision) and inhomogeneous (Doppler) broadening take place. Effects of molecular motion on the line-broadening parameters are discussed, as well as extensions to bands of overlapping lines, inclusion of radiative damping, saturation effects, effect of intermediate resonating levels (consecutive absorption), and time-resolved experiments.

I. INTRODUCTION

High-resolution two-photon optical spectroscopy¹ was used recently as a means of studying atomic and molecular spectra free of Doppler broadening.²⁻⁸ The method developed from an old idea of Goppert-Meyer,⁹ and followed earlier experiments at radio frequencies^{10(a)} and in the optical region.^{10(b)} Under proper conditions, the simultaneous absorption of two photons of equal frequencies and opposite momenta leads to the population of an excited molecular level, followed by resonance fluorescence, with a resonance line shape (as a function of the frequency sum) which is independent of the Doppler effect. It is thus possible to study fine features of atomic structure and possibly also the structure of small molecules at high resolution, while the shape of ordinary absorption spectra is dominated by Doppler broadening.

One aspect of this method is the possibility of studying homogeneous line-broadening phenomena at pressures and temperatures, and in spectral ranges, in which Doppler broadening usually exceeds all other homogeneous broadening mechanisms (collision, radiation, and power broadening and shifts). This method is complementary in many ways to the method of Lamb-dip spectroscopy¹¹⁻¹³ (as a steady-state spectroscopic technique), and to the methods of maser beams, optical nutation, quantum beats, and photon echoes (as transient techniques),¹⁴ as Doppler-free methods of obtaining information about homogeneous damping mechanisms.

We shall present below an adaptation of the theory of spectral line shapes in gases to two-photon absorption, paying particular attention to collision

broadening. In many cases, two-photon absorption is monitored by the measurement of one-photon resonance fluorescence as the major channel of decay of the excited system. The process can be described as resonance scattering into a one-photon continuum of a two-photon system impinging on a homogeneous and stationary molecular-gas sample. We shall concentrate here on the calculation of the excitation rates by two photons irrespective of the decay mode of the excited system. The theory is simplified under the condition³ that there exists no intermediate molecular level at resonance with one of the photons (simultaneous absorption). How little should we avoid the intermediate level depends on a properly defined correlation time introduced in Sec. IV (where consecutive two-photon absorption is discussed).

The only way in which the simultaneous-resonance two-photon absorption significantly depends on the radiation frequencies is contained (as shown below) in a resonance-line-shape function of the frequency sum. This function is the Fourier transform (at the frequency sum) of a molecular autocorrelation function, as in the linear-response theory of one-photon absorption.^{15,16} Unlike the one-photon case, however, the dynamical variable involved in the time correlations is not the molecular dipole moment but an operator intimately related to the molecular polarizability. This operator has a matrix element combining the initial and final states of the two-photon absorption process, and its selection rules are similar to those of the polarizability operator. The general characteristics of the correlation function (rotational-invariance considerations, etc.) are therefore common to two-photon absorption¹⁷ and to Raman spectra,¹⁸

with the most notable exception that Raman line shapes depend on the frequency difference, whereas two-photon absorption depends on the frequency sum.

In Sec. II, the theory of two-photon absorption by a single molecule is reformulated, introducing radiative damping in a nonperturbative fashion. The theory is then extended for the case of a collision-broadened isolated molecular transition under dilute-gas (impact) conditions. Starting from the Brownian-particle model, in which the line-broadening parameters are independent of the molecular velocities, the theory is later generalized to velocity-dependent effects. Extensions are further discussed covering the following topics: (a) Transition from Doppler-free to Doppler-dominated line shape by variation of the frequency difference; (b) bands of overlapping lines and effects of relaxation; (c) combined radiative and collisional damping; (d) power-broadening (saturation) effects resulting from application of strong fields; (e) transition from simultaneous to consecutive two-photon absorption via an intermediate resonant state; and (f) time-resolved fluorescence resulting from short-pulse two-photon absorption is investigated in some detail.

II. ISOLATED MOLECULE

As was already mentioned in the Introduction, the theory of two-photon-absorption line shapes involves time correlations of off-diagonal elements of a molecular-dynamical variable (T_2 -type correlations). We start with the ordinary (dyadic) formalism of scattering theory to describe the isolated-molecule response. The tetradic formalism for scattering amplitudes^{16,19,20} will be introduced in Sec. III as a convenient means for the introduction of collisions. Consider a single molecule undergoing two-photon absorption from a lower molecular level $|g\rangle$ to an isolated level $|s\rangle$. The radiation field before the absorption is represented by two beams ($i=1,2$) with n_i photons of angular frequency ω_i , momentum \vec{k}_i , and polarization λ_i in each one.

The transition rate to the excited level (and hence the resonance-fluorescence rate, assuming a unity quantum yield for one-photon dipole emission, neglecting other radiative and nonradiative processes) is given by the resonant part of the decay rate of the initial state under the interaction with the radiation fields.²¹ Consider, therefore, the total attenuation rate Γ_{gg} which, by the optical theorem, is related to the Lippmann-Schwinger T matrix as follows²²:

$$\Gamma_{gg} = -(2/\hbar) \text{Im} \langle \bar{g} | T(E) | \bar{g} \rangle. \quad (1)$$

Here

$$T(E) = V + VG(E)V \quad (2)$$

and

$$G(E) = (E - H + i\epsilon)^{-1}, \quad (3)$$

H being the full radiation-plus-matter Hamiltonian, including the interaction V with the radiation field. Also, $|\bar{g}\rangle$ is a shorthand for the product state of the bare molecule and photons,

$$|\bar{g}\rangle = |g, n_1, n_2\rangle, \quad (4)$$

and E_g is the total energy eigenvalue in this state,

$$E_g = \epsilon_g + n_1 \hbar \omega_1 + n_2 \hbar \omega_2. \quad (5)$$

In order to spell out the particular resonant contributions owing to scattering through the excited state $|s\rangle$, let us introduce appropriate projection and level-shift operators.^{23,24} For the sake of simplicity, we shall deal first with the case where ω_1 and ω_2 are sufficiently far apart so that only $\omega_1 + \omega_2$ (and not $2\omega_1$ or $2\omega_2$) is near resonance with $\omega_{sg} = \hbar^{-1}(\epsilon_s - \epsilon_g)$. Also, let us not ignore, for the time being, inhomogeneous-broadening and degeneracy effects. The resonant states are then spanned by the one-dimensional projection operator

$$P = |\bar{s}\rangle \langle \bar{s}|, \quad (6)$$

whose complement is

$$Q = 1 - P, \quad (7)$$

where

$$|\bar{s}\rangle = |s, n_1 - 1, n_2 - 1\rangle. \quad (8)$$

The corresponding level-shift operator is²³

$$R = V + VQG_{QQ}QV, \quad (9)$$

where V is the interaction with the radiation and

$$G_{QQ} = (EQ - QHQ + i\epsilon)^{-1}. \quad (10)$$

Using these definitions we can write

$$T = R + RPGPR, \quad (11)$$

where the second term leads to the resonant contribution Γ_{gg}^{res} . The first term (R) will give only a practically constant background to the resonance line shape. The resonance contribution is

$$\Gamma_{gg}^{res} = -(2/\hbar) \text{Im} \langle \bar{g} | R | \bar{s} \rangle \langle \bar{s} | G | \bar{s} \rangle \langle \bar{s} | R | \bar{g} \rangle. \quad (12)$$

The propagator $\langle \bar{s} | G | \bar{s} \rangle$ includes further interactions with the radiation field through virtual emission and absorption of photons. Here we have to distinguish between corrections depending on n_1 and n_2 , which constitute nonlinear saturation effects, and spontaneous-emission terms which provide for the radiation damping of the propaga-

tor. Considering, for example, the latter only (the earlier corrections cause saturation or power broadening), we can then write

$$\langle s|G|s\rangle = 1/(\omega_1 + \omega_2 - \omega_{sg} - D_s + \frac{1}{2}i\Gamma_s) \equiv g_s(\omega_1 + \omega_2), \quad (13)$$

where $\omega_{sq} = \hbar^{-1}(\epsilon_s - \epsilon_g)$ is the bare molecular resonance frequency, and D_s and Γ_s are, respectively, the radiative shift and width,²⁵ given by $D_s - \frac{1}{2}i\Gamma_s = \langle s|R|s\rangle$. These are generally functions of $\omega = \omega_1 + \omega_2$.

The factor $\langle \bar{g}|R|\bar{s}\rangle$ can be considerably simplified if we assume that the denominator in G_{QQ} is far away from resonance.³ Let all intermediate states $|r\rangle$ through which the molecule undergoes the transition from g to s be far from resonance. That is, $|\omega_{rg} - \omega_i|$ is large compared with a characteristic correlation (or memory) time τ_c ($\tau_c = \Gamma_s^{-1}d\Gamma_s/d\omega$ in the case of radiation damping). We can then neglect the interactions in the resolvent G_{QQ} , writing

$$\langle \bar{g}|R|\bar{s}\rangle \approx \sum_{i=1,2} \sum_r \langle \bar{g}|V|\bar{r}_i\rangle \frac{1}{E_{\bar{g}} - E_{\bar{r}_i}} \langle \bar{r}_i|V|\bar{s}\rangle, \quad (14)$$

where

$$|\bar{r}_1\rangle = |r, n_1 - 1, n_2\rangle, \quad |\bar{r}_2\rangle = |r, n_1, n_2 - 1\rangle. \quad (15)$$

Assume now the dipole approximation for the interaction with the field,

$$V = - \sum_{i=1,2} \mu^{\lambda_i} \mathcal{E}^{\lambda_i}(\vec{k}_i, \omega_i), \quad (16)$$

μ^{λ_i} being the dipole-moment component along the polarization of the i th beam and \mathcal{E}^{λ_i} being the electric-field operator. Using a box normalization of the radiation fields in a volume L^3 we have²⁵

$$\langle n_i|\mathcal{E}|n_i - 1\rangle = -i(\hbar\omega_i n_i/2L^3)^{1/2} \quad (17)$$

in the dipole approximation. Hence

$$\langle \bar{g}|R|\bar{s}\rangle = (\hbar/2L^3)[\alpha_{gs}^{(+)}{}^{12}(\omega_1) + \alpha_{gs}^{(+)}{}^{21}(\omega_2)] \times (\omega_1\omega_2 n_1 n_2)^{1/2}, \quad (18)$$

where

$$\langle g|\alpha^{(+)}{}^{ij}|s\rangle = -\hbar^{-1} \sum_r \frac{\mu_{gr}^{\lambda_i} \mu_{rs}^{\lambda_j}}{\omega_i - \omega_{rg}}. \quad (19)$$

Equation (19) resembles a matrix element of the polarizability tensor α^{ij} , with the exception that α^{ij} includes a mirror image of $\alpha^{(+)}$ reflected on the imaginary ω axis,

$$\begin{aligned} \alpha^{ij}(\omega) &= \alpha^{(+)}{}^{ij}(\omega) + \alpha^{(-)}{}^{ij}(\omega) \\ &= \alpha^{(+)}{}^{ij}(\omega) + \alpha^{(+)}{}^{ij}(-\omega^*). \end{aligned} \quad (20)$$

The coefficient $\alpha^{(+)}(\omega_1) + \alpha^{(+)}(\omega_2)$ is obtained instead of (20) since the process here involves absorption of two photons, whereas the Kramers-Heisenberg expression for the polarizability results from emission and absorption. The extension to complex ω is required if we want to replace ω by $\omega + i\epsilon$ as we approach resonance with ω_{rg} .

As the difference $\omega_1 - \omega_2$ decreases, we have to face the possibility that $2\omega_1$ and $2\omega_2$ will also be near resonance, in addition to $\omega_1 + \omega_2$. In this case the projection operator P should be extended to three dimensions including, in addition to (6), also

$$|\bar{s}'\rangle = |s, n_1 - 2, n_2\rangle, \quad |\bar{s}''\rangle = |s, n_1, n_2 - 2\rangle. \quad (21)$$

To each of the latter final states corresponds only one intermediate state, $|\bar{r}_1\rangle$ or $|\bar{r}_2\rangle$, respectively, for a given molecular state r . The resonance line shape will therefore consist of the sum

$$\begin{aligned} \Gamma_{gg}^{\text{res}} &= -\frac{\hbar}{2L^3} \text{Im} \sum_{i,j=1,2} \omega_i \omega_j n_i (n_j - \delta_{ij}) |\langle e|\beta^{ij}|g\rangle|^2 \\ &\quad \times g_s(\omega_1 + \omega_2), \end{aligned} \quad (22)$$

where we have introduced the symmetrized tensor

$$\begin{aligned} \beta^{ii} &= \alpha^{(+)}{}^{ii}(\omega_i), \\ \beta^{ij} &= (1/\sqrt{2})[\alpha^{(+)}{}^{ij}(\omega_i) + \alpha^{(+)}{}^{ji}(\omega_j)], \end{aligned} \quad (23)$$

where $i \neq j$.

In terms of the beam intensities $I_i = cL^{-3}\hbar\omega_i n_i$ (assuming $n_i \gg 1$),

$$\Gamma_{gg}^{\text{res}} = \frac{1}{2\hbar c^2} \sum_{i,j=1,2} I_i I_j |\langle s|\beta^{ij}|g\rangle|^2 [-\text{Im}g_s(\omega_1 + \omega_2)]. \quad (24)$$

Under the condition of no intermediate resonant level (simultaneous absorption), the resonance line shape is given by $g_s(\omega_1 + \omega_2)$, which depends of the frequency sum, and its bandwidth (in the absence of collisions) is governed by the radiative width.

We have so far avoided the problem of space degeneracy.¹⁷ Both states g and s can be degenerate, and (assuming the radiative-damping process is isotropic) (24) splits into separate contributions belonging to different bases of the irreducible representations of the rotation group. Let j_s and m_s be the quantum numbers for the total angular momentum and its z projection in the level s , etc. The irreducible bases are formed by the vector-subtraction scheme^{26,27}

$$\{ |g\rangle\langle s| \}_M^{(K)} = \sum_{m_g m_s} (-1)^{j_s - m_s} c(j_g, j_s, K; m_g, -m_s, M) \\ \times |g m_g\rangle\langle s m_s|. \quad (25)$$

The symmetric tensor β can be split into the two irreducible tensors $\beta^{(0)}$ and $\beta^{(2)}$ only. We therefore have

$$\Gamma_{gg}^{\text{res}} = \frac{1}{2\hbar c^2} \sum_{K=0,2} \sum_{i,j=1,2} I_i I_j W_{ij}^{(K)} |\langle s || \beta^{(K)} || g \rangle|^2 \\ \times [-\text{Im}g^{(K)}(\omega_1 + \omega_2)], \quad (26)$$

where $\langle s || \beta^{(K)} || g \rangle$ is the reduced matrix element of the tensor $\beta^{(K)}$, and (using the terminology of Fano and Racah²⁶)

$$W_{ij}^{(K)} = [e_i^{(1)} \times e_j^{(1)}]^{(K)} \cdot [e_i^{(1)} \times e_j^{(1)}]^{(K)} \quad (27)$$

is a geometric factor determined by the unit vectors \vec{e}_i and \vec{e}_j that specify the polarizations λ_i and λ_j . By a proper choice of polarizations one can separate the terms $K=0$ and $K=2$. This, for example, has been used to separate the $g_s(\omega_1 + \omega_2)$ contribution from the $g_s(2\omega_1)$ and $g_s(2\omega_2)$ contributions.³

The Doppler shift can be easily incorporated here if the molecular levels are extended to include the translational degrees of freedom. The discrete level (and its corresponding projection operator) is replaced by a continuum of translational states.¹⁹ The frequency difference $\omega_i + \omega_j - \omega_{sg}$ in $g_s(\omega_i + \omega_j)$ is replaced by

$$\omega_i + \omega_j - \omega_{sg} - \frac{p_s^2}{2m} + \frac{p_g^2}{2m} \\ \approx \omega_i + \omega_j - \omega_{sg} - (\vec{k}_i + \vec{k}_j) \cdot \frac{\vec{p}_g}{m}, \quad (28)$$

where, by momentum conservation,

$$\vec{p}_s = \vec{p}_g + \vec{k}_i + \vec{k}_j, \quad (29)$$

\vec{p}_a being the translational momentum in level a , and where m is the mass of the molecule and k_i and k_j are the wave vectors of the photons ω_i and ω_j , respectively. In (28) we have assumed $k \ll p$, and thus (neglecting a recoil energy) we obtained a Doppler-shifted resonance frequency $\omega + (\vec{k}_i + \vec{k}_j) \cdot \vec{p}_g/m$. The expression for Γ_{gg}^{res} (assuming there is no velocity dependence of the radiative shift and width) is finally obtained by averaging over a proper (usually canonical) distribution of the initial momentum \vec{p}_g . The Doppler shift vanishes, and the momentum averaging becomes redundant, as $\vec{k}_1 + \vec{k}_2$ approaches zero.

III. COLLISION BROADENING

Consider now the collision-damped molecular system. The expression for the absorption and

scattering of radiation has to be modified in two ways. First, the single-molecule operator μ^{λ_i} in (16) should be replaced by the many-body operator

$$M^i(\vec{k}) = \sum_{A=1}^N \mu_A^{\lambda_i} e^{i\vec{k} \cdot \vec{R}_A} \quad (30)$$

pertaining to N molecules, with positions \vec{R}_A ($A=1, \dots, N$), assuming the dimensions of the molecules are small compared with the wavelength of the radiation. Second, the Hamiltonian H_0 for the single molecule should be replaced by the many-body molecular Hamiltonian H_m , which includes the intermolecular potentials. Assume that the molecular levels g , r , and s are well separated, and collisional couplings between them are negligible. Nevertheless, each of them (together with other close-lying molecular levels) are smeared into a continuum of eigenvalues of H . Consider momentarily a complete set of eigenvalues of H . If the collisional coupling of g and s mentioned above is sufficiently weak, we can still define continuum subsets of eigenstates of H associated with each molecular level. Let P_g and P_s be, respectively, the projection operators for the subsets labelled g and s , and let the individual states in each set be labelled γ and σ , respectively, with the energies ϵ_γ and ϵ_σ forming continua. Also, suppose a distribution $\rho(E_\gamma)$ of initial states is specified. The resonance attenuation of the initial set of states is then given by

$$\Gamma_{gg}^r = -\frac{2}{\hbar} \sum_{\gamma\sigma} \rho(E_\gamma) \langle \tilde{\gamma} | P_g R P_s | \tilde{\sigma} \rangle \\ \times \frac{1}{E_\gamma - E_\sigma + i\epsilon} \langle \tilde{\sigma} | P_s R P_g | \tilde{\gamma} \rangle, \quad (31)$$

where $E_\gamma = \epsilon_\gamma + n_1 \hbar \omega_1 + n_2 \hbar \omega_2$, etc., and the generalized summation over γ and σ includes integrations over the energies ϵ_γ and ϵ_σ . We further neglect effects of the interaction on ρ , assuming it is separable,

$$\rho(E_\gamma) \approx \rho(\epsilon_\gamma) |n_1 n_2\rangle \langle n_1 n_2| \quad (32)$$

(i.e., it represents a pure state of bare photons).

The expression (31) for Γ_{gg}^{res} can be easily extended to an arbitrary complete set of wave functions. Introducing tetradic Liouvillian notation¹⁶

$$LX = \hbar^{-1} [H, X] \quad (33)$$

(where X is an arbitrary dyadic operator),

$$\Gamma_{gg}^{\text{res}} = -\frac{2}{\hbar^2} \text{tr} \{ \rho P_g R P_s [1/(-L + i\epsilon)] P_s R P_g \}. \quad (34)$$

Here L operates on the dyadic operator $P_s R P_g$.

This operator forms a vector in Liouville space which can be denoted $R_{sg}|sg\rangle$ in the double-bracket notation of Liouville-space vectors.^{19,28}

Assume, again, that the resolvent G_{QQ} in R is far from resonance. It is then possible to neglect the interactions and leave only the independent-molecule contributions to the Hamiltonian in G_{QQ} . We can then rewrite R , replacing β^{ij} by the sum of one-molecule operators

$$B^{ij}(\vec{k}_1 + \vec{k}_2) = \sum_{A=1}^N \beta_A^{ij} e^{i(\vec{k}_i + \vec{k}_j) \cdot \vec{R}_A}. \quad (35)$$

The plus and minus signs pertain to emission ($P_g R P_s$) and to absorption ($P_s R P_g$), respectively.

The Liouvillian L can in general combine terms with different molecular labels in $P_g R P_s$ and $P_s R P_g$ (resonance exchange of excitation by collisions¹⁶). The situation is simplified in foreign-gas broadening, where this becomes very unlikely, since interactions between absorbing molecules are neglected. In this case one can replace the sum over A by a single term, adding a factor N to Γ_{gg}^{res} . The extension to self-broadening, where resonance exchange can occur, produces a change only in the line-broadening parameters,¹⁹ adding a contribution to the linewidth.

We are thus led to the conclusion that if no intermediate level is at resonance with the field the operator $P_s R P_g$ defines a basis of single-molecule excitations on which L operates. This basis is specified by the internal states g and s and by the number of photons absorbed in each field mode. The translational states are unspecified, subject to the momentum-conservation condition (29) which results from the exponential factor in (35). If β^{ij} is independent of translational degrees of freedom, then $P_s R P_g$ is proportional to the sum over momentum states (using a discrete "box-quantized" set) of one-molecule operators

$$\sum_{\vec{p}_g} |\vec{s}, \vec{p}_g + \vec{k}_i + \vec{k}_j\rangle \langle \vec{g}, \vec{p}_g|. \quad (36)$$

The terms in this sum can be used as vectors in Liouville space spanning a subspace with fixed initial and final one-molecule internal states.¹⁹ The radiative degrees of freedom can be simply removed by using the identity

$$L |\vec{s}\rangle \langle \vec{g}| = [-L + (\omega_i + \omega_j) + L_m] |\vec{s}\rangle \langle \vec{g}| \quad (37)$$

if we neglect in L the interaction between molecules and radiation (L_m being the molecular Liouvillian corresponding to H_m), assuming that collision-broadening exceeds the radiative damping. We can therefore replace $(-L + i\epsilon)^{-1}$ by $(\omega_i + \omega_j - L_m + i\epsilon)^{-1}$, leaving R an operator on the molecular degrees of freedom only, and removing the tilde

signs (\sim) from (36). The analysis from now on proceeds as in the theory of collision broadening of one-photon absorption spectra.¹⁹ The subspace on which L_m operates is spanned by the operators

$$|s, \vec{p}_g + \vec{k}_i + \vec{k}_j\rangle \langle g, \vec{p}_g| \quad (38)$$

with variable \vec{p}_g .

Let us associate with this subspace a projection operator P_{sg} . We should note here that this subspace belongs to the $(\vec{k}_i + \vec{k}_j)$ th invariant subspace of the translation group in Liouville space.

The molecular Liouvillian L_m contains all intermolecular interactions, in addition to the free-molecule Liouvillian L_0 which is constructed from energy differences of the isolated molecule. These interactions couple the basis defined by P_{sg} with its complement,²⁹ defined by $Q_{sg} = 1 - P_{sg}$.

The situation is particularly simple when all velocity effects (Doppler shifts, velocity dependence of scattering amplitudes, etc.) can be neglected. This situation is realized in the so-called Brownian-particle model, describing a heavy molecule imbedded in a gas of a light perturber.^{19,30} In this case we can ignore translational degrees of freedom altogether and confine the projection operator to the one-dimensional space spanned by $|s\rangle \langle g|$.

Using the density operator ρ as a metric to define scalar products in Liouville space,¹⁹ we can use the Zwanzig-Fano method of projection operators to reduce $(\omega_i + \omega_j - L + i\epsilon)^{-1}$ into a one-molecule operator.^{16,19} In the case of the one-dimensional operator we simply get

$$P_{sg}(\omega_i + \omega_j - L + i\epsilon)^{-1} P_{sg} = (\omega_i + \omega_j - \omega_{sg} - \delta_{sg} + i\gamma_{sg})^{-1}, \quad (39)$$

where δ_{sg} and γ_{sg} are the line shift and width, respectively. In dilute gases, where binary collisions prevail, these parameters are proportional to the number density of the perturbing gas. Over a spectral range

$$\Delta\omega \lesssim \tau^{-1}, \quad (40)$$

where τ is a characteristic correlation time of the collision (the "duration" of the collision), δ and γ are practically constant, independent of $\omega_i + \omega_j$ (the "impact" approximation).^{19,28} At ordinary pressures and temperatures $\gamma\tau \gg 1$, and therefore the Lorentz function (39) constitutes a good approximation to the resonance line shape. In dilute gases, the distribution of collisions is isotropic. Hence it can be shown that δ_{sg} and γ_{sg} are rotationally invariant and therefore confined to the irreducible representation of the rotation group.²⁷ Therefore in the case of space degeneracy the line-shape expression splits up into independent

contributions of the different irreducible representations ($K=0$ and 2), as in (26), each one having its single shift $\delta_{sg}^{(K)}$ and width $\gamma_{sg}^{(K)}$ parameters. The calculation of the $K=2$ parameters, for example, is made precisely in the same manner as those of Raman spectra.¹⁸

The theory has to be modified in order to incorporate velocity effects. The one-dimensional set $|s\rangle\langle g|$ is replaced by the continuum (38) with variable \vec{p}_g (or the quasicontinuum, if box quantization is used). The single resonance frequency ω_{sg} is then replaced by the diagonal matrix (or kernel, in the continuum limit) of Doppler-shifted resonance frequencies,

$$\Omega_{\vec{p}_g'; \vec{p}_g}(\vec{k}_i + \vec{k}_j) = [\omega_{sg} + (\vec{k}_i + \vec{k}_j) \cdot \vec{p}_g/m] \delta_{\vec{p}_g'; \vec{p}_g}. \quad (41)$$

The shift and width parameters are replaced by the nondiagonal Hermitian matrices (or kernels)

$$\Delta_{\vec{p}_g'; \vec{p}_g}(\vec{k}_i + \vec{k}_j), \quad \Gamma_{\vec{p}_g'; \vec{p}_g}(\vec{k}_i + \vec{k}_j) \quad (42)$$

representing the particular effect of the scattering from \vec{p}_g to \vec{p}_g' by collisions. The shape of these matrices is generally quite complicated and can be simplified under specific models.³⁰ General expressions can be given to these matrix elements in terms of the binary-collision Lippmann-Schwinger T matrix.¹⁹ The resonance line shape is then given (for a single K term) by (24) with $g_s(\omega_i + \omega_j)$ replaced by the sum

$$\langle g_s(\omega_i + \omega_j) \rangle = \frac{N}{L^3} \sum_{\vec{p}_g, \vec{p}_g'} \rho_{\vec{p}_g} [(\omega_i + \omega_j)I - \Omega - \Delta + i\Gamma]_{\vec{p}_g'; \vec{p}_g}^{-1}, \quad (43)$$

where $[\dots]_{\vec{p}_g'; \vec{p}_g}^{-1}$ denotes the matrix element of the inverse matrix and I is the unit operator. $\rho_{\vec{p}_g}$ is the distribution of initial momenta. The volume (L^3) factor within the summation sign disappears in the continuum limit ($L^3 \rightarrow \infty$, $N/L^3 = \text{const}$) where the sum over \vec{p}_g and \vec{p}_g' turns into an integration.³¹

IV. DISCUSSION

The theory formulated above can be used to study various physical phenomena concerning collision broadening, with or without the interference of the nonhomogeneous Doppler broadening. Furthermore, some of the assumptions made along the derivation of the theory can be relaxed, enabling its extension to other physically interesting situations. We shall briefly discuss here some of the applications and extensions:

(a) *Velocity effects.* Two-photon absorption can be used (in the same manner Lamb-dip spectroscopy is used¹¹) to study effects of translational motions on collision broadening under conditions of temperature, pressure, or spectral range in

which the Doppler broadening ordinarily obscures all other broadening mechanisms.

By choosing $\vec{k}_i + \vec{k}_j = 0$, the Doppler shift is completely removed. However, the expressions for the Δ and Γ matrix elements still remain \vec{p} dependent, and the resulting line shape is generally not Lorentzian, except in very special situations (as in the Brownian-particle model mentioned above).

The removal of the condition $\vec{k} = \vec{k}_i + \vec{k}_j = 0$ introduces a new interesting possibility. By increasing \vec{k} , the relative magnitude of the Doppler width, compared with the collision broadening, can be varied at fixed density and temperature. The interplay between the two (inhomogeneous and homogeneous) broadening mechanisms can thus be brought to light. For example, the mixing of the different Doppler modes by nonforward scattering ($\vec{p}_g' \neq \vec{p}_g$) can be studied in cases where the elastic-scattering cross sections are large in comparison to the collision-broadening cross section.³²

(b) *Bands of overlapping lines.* The theory as formulated above can be readily extended to the case where g and s are embedded in bands of close-lying levels (e.g., vibrational-rotational levels of a single electronic configuration). If the resonance-absorption process is nonselective, not restricting the absorption to a single pair g, s , we must consider the absorption from the band of levels $g \in \mathcal{K}_g$ to the band $s \in \mathcal{K}_s$, where \mathcal{K}_g and \mathcal{K}_s are the subspaces (in Hilbert space) covered by the two bands. In this case, the projection operator P_{sg} should be replaced by the sum

$$P = \sum_{g \in \mathcal{K}_g} \sum_{s \in \mathcal{K}_s} P_{sg}. \quad (44)$$

The line shift and width are then associated with matrices Δ and Γ defined on this subspace. They remain matrices, and not numbers, even if all velocity effects can be dropped out (as in the Brownian-particle model), and the line shape will generally not be a sum of Lorentzians. Equation (39) is replaced then by the sum

$$\sum_{sgs'g'} \rho_g \beta_{sg}^{ij} \beta_{s'g'}^{ij*} [(\omega_i + \omega_j)I - \Omega - \Delta + i\Gamma]_{sg; s'g'}^{-1}, \quad (45)$$

where $\Omega_{sg; s'g'} = \omega_{sg} \delta_{ss'} \delta_{gg'}$ is the diagonal (tetradic) matrix of resonance frequencies and Δ and Γ are generally nondiagonal tetradic matrices. The diagonal elements are the shift and width of individual lines and the off-diagonal elements $\Gamma_{sg; s'g'}$ are cross-relaxation rates, which depend on inelastic scattering involving the transitions $g \rightarrow g'$ and $s \rightarrow s'$ (i.e., intraband energy transfer). The generalization to velocity-dependent relaxation follows by inspection of (43) and (45). The various elements of Δ and Γ remain frequency independent

if all the band frequencies ω_{sg} stay confined to an interval $\Delta\omega \lesssim \tau^{-1}$ [the impact approximation; see Eq. (40) above].

(c) *Combined radiative and collision broadening.* To the intermolecular interactions contained in the Liouvillian we can add the radiative interactions that lead to radiative damping, as in the isolated-molecule case [Eq. (13)]. The resulting line-shift and width parameters are then composed of radiative (pressure independent) and collisional (pressure-dependent) contributions with (possibly) interference effects. The question of whether and when we may simply add the two contributions independently or not has not been sufficiently clarified as yet. Doppler-free spectroscopy can provide us with conditions where the two broadening mechanisms are comparable in magnitude and the pressure dependence of the combined effect can be elucidated. These questions are particularly intriguing in the case of resonance broadening.³³

(d) *Saturation effects.* In the preceding example we have discussed only spontaneous-emission effects leading to radiative damping. These involve matrix elements of the interaction V independent of the occupation numbers n_i and n_j of the applied beams. Nonlinear optical phenomena, such as saturation, involve higher orders of the applied-field-dependent interactions. An approximation under which these phenomena are conveniently studied is the external-field approximation in which the applied field is treated as a time-dependent c -number field, leaving only internal radiation fields in the second-quantized form. The justification of such an approach for laser coherent fields has been demonstrated recently.³⁴

Under the external-field approximation, saturation phenomena can be formally studied, to arbitrary orders of the applied fields. A simple diagrammatic method for dealing with such calculations has been developed recently.³⁵ The resulting line shape will include a power-dependent saturation broadening and shift.

(e) *Transition from simultaneous to consecutive two-photon absorption.* The condition requiring the intermediate states $|r\rangle$ to be far from resonance with any of the two field modes may not be always sustained. In such cases, the simple relation of R to the one-molecule operator does not hold. The resolvent G_{QQ} in R then includes many-body collision effects, bringing out a complicated non-Hermitian ω -dependent expression. If (as in the case of levels s and g) r is sufficiently close to resonance,

$$|\omega_{rg} - \omega_i| \lesssim \tau^{-1}, \quad (46)$$

we can invoke the impact approximation also in the calculation of G_{QQ} . It can be shown that the product $P_g R P_s G P_s R P_g$ then factorizes into a product of three Green's functions, each defined on the one-molecule basis, as is PGP . This result can be interpreted as a succession of radiative processes. Fluctuations in the thermal bath in which the molecule is imbedded decay within the correlation (or memory) time^{36,37} which can be defined as

$$\tau = \frac{1}{\Gamma} \frac{d\Gamma}{d\omega}, \quad (47)$$

where Γ measures the strength of the coupling to the bath. In the binary-collision limit, this is the duration of collisions. Since $\Delta\omega^{-1}$ (where here $\Delta\omega = \omega_{rg} - \omega$) is a lower limit for the time it takes to absorb a photon off resonance, fluctuations in the bath are too rapid to be discerned by the radiation, and therefore each photon separately sees a "dressed" (i.e., collision-broadened) molecule under the mean influence of the thermal bath ("consecutive absorption"). In the other extreme, both photons interact before the bath fluctuations have time to damp. We then must treat the absorption of the two photons as a single event, from the point of view of the dressed molecule ("simultaneous absorption").

Following this line of thought, a theory can be developed for consecutive two-photon absorption similar to the theory of resonance Raman scattering.³⁸⁻⁴⁰

(f) *Time-resolved photon scattering.* So far, only steady-state situations have been considered. The formalism can be extended to the study of time-resolved fluorescence which follows two-photon absorption from a short-lived pulse, containing the two field modes. An experimental study of the corresponding one-photon problem has been carried out by Williams *et al.*⁴¹ They observed a gradual transition from characteristic resonance fluorescence to direct scattering (that adiabatically follows the pulse profile) as the incident radiation is tuned off resonance with the molecular transition. The range of frequencies over which this occurs is determined by the Doppler width, but the characteristics of this behavior are very sensitively pressure dependent. A theoretical analysis of both the isolated-molecule case⁴² and the collision-broadened case⁴³ has been carried out recently. The time-dependent resonance excitation probability was found to be given (for the single-photon transition $g \rightarrow s$) as⁴³

$$P_g^{(1)}(t) = -2 \operatorname{Re} \langle \bar{s} | V | \bar{g} \rangle^2 \int d\tau d\tau' \theta(t-\tau) \theta(t-\tau') \varphi(\tau) \varphi^*(\tau') \langle ss | G_1(t-\tau) | ss \rangle \langle sg | G_2(t-\tau') | sg \rangle. \quad (48)$$

Here $\varphi(t)$ is the envelope of the pulse amplitude, $G_2(t)$ is the line-broadening (or "coherence") Green's function related to the correlation function for the dipolar transition (T_2 -type correlation), whereas $G_1(t)$ is the level-damping Green's function (T_1 -type correlation) which describes the dynamics of the level population.

The extension of the two-photon problem, in the

$$P_e^{(2)}(t) = -2 \operatorname{Re} \langle s | \beta | g \rangle |^2 |E_1|^2 |E_2|^2 \int d\tau d\tau' \theta(t-\tau) \theta(t-\tau') \varphi_1(\tau) \varphi_2(\tau) \varphi_1^*(\tau') \varphi_2^*(\tau') \\ \times \langle \langle ss | G_1(t-\tau) | ss \rangle \rangle \langle \langle sg | G_2(\tau-\tau') | sg \rangle \rangle, \quad (49)$$

where the subscripts 1 and 2 denote the two-photon beams, and E_i ($i = 1, 2$) is the maximal field amplitude of the i th beam. It should be noted, however, that there will be nonresonant contributions in which $\langle \langle sg | G_2 | sg \rangle \rangle$ is replaced by other (off-resonance) terms. These will add a broad background which will follow adiabatically the pulse shape. Therefore the adiabatic component will not vanish completely even when the frequency sum is right in resonance, contrary to the one-

case where the two photons are absorbed simultaneously, is immediately obvious. All we have to do is to replace the dipolar correlation functions by the corresponding correlations involving the operator β (in order to obtain the resonant part of the decay pattern of level s), and the field amplitudes $\varphi(\tau)$, by appropriate binary forms. We thus get, for simultaneous two-photon absorption,

photon case. In the case where the mean frequencies of the two beams are equal (and the mean momenta opposite) the Doppler broadening will cease to play a role, and the transition to the adiabatic-type scattering will occur at a much smaller frequency mismatch, of the order of the linewidth. Moreover, interference effects which usually are smeared out by the Doppler broadening, may be exhibited in this case.

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