Spectral line shape arising from collisional interference between electric-dipole-allowed and collision-induced transitions

B. Gao, G. C. Tabisz,* M. Trippenbach,† and J. Cooper
Joint Institute for Laboratory Astrophysics, University of Colorado and National Institute of Standards and Technology, Boulder, Colorado 80309-0440
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A theory is developed to describe the spectral line shape due to interference between electric-dipole-allowed and collision-induced transitions in pure rotational molecular spectra. Motivation was provided by experimental data available for HD-inert gas systems. This theory is based on a master-equation approach to induced spectra employed by Alber and Cooper [Phys. Rev. A **33**, 3084 (1986)]. The active molecule is considered to be immersed in a bath of perturbers. An expression for the absorption coefficient is obtained within the binary collision approximation that contains terms due to allowed, induced, and interference contributions. Effects due to m mixing, J mixing, and successive collisions are included. Low-order approximations of the theory eventually reduce to results of earlier efforts, namely, the pioneering description of collisional interference by Herman, Tipping, and Poll [Phys. Rev A **20**, 2006 (1979)] and refinements to it through consideration of rotational level mixing. The principal attribute of this approach is the treatment of allowed and collision-induced transitions in a consistent manner.

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I. INTRODUCTION

The theory of spectral line broadening is described in a voluminous amount of literature, the greatest part of which concerns electric-dipole-allowed transitions. The line shape accompanying transitions proceeding via collision-induced electric dipole moments has received less, but appreciable, attention. Usually allowed lines have an intensity that is sufficiently large to dominate collision-induced effects, and the two types of contributions need not be considered for the same transitions. In recent years, interest has been renewed in the infrared spectrum of the hydrogen molecular isotope HD [1]. The small permanent dipole moment of HD yields allowed transitions comparable in magnitude to the collision-induced transitions, and an observable interference effect occurs between these contributions [2].

Considerable experimental data have been gathered on the total intensity and spectral line shape for both the pure rotational and rotation-vibrational spectra [3,4]. A theory of the effect developed by Herman, Tipping, and Poll [5,6] predicts the correct order of magnitude of the interference but is not reliable for a detailed description of the behavior of the intensity with density or of the spectral line shape [4,7,8]. The present study was undertaken with the goal of providing a more general description of the phenomenon. The theory here described treats both allowed and induced contributions in a consistent manner and includes provisions for both m- and J-mixing collisions. Calculations based on application of the theory to HD-inert gas systems will be reported in a separate paper.

The outline of this paper is as follows. In Sec. II the density-matrix equations are written. An expression for the spectrum is obtained in Sec. III. This expression is simplified within the impact approximation in Sec. IV and its angular average is taken in Sec. V. The absorption coefficient is given in Sec. VI. The paper concludes with a discussion in Sec. VII that centers on comparison with previous work.

The system considered is a single neutral radiator contained within a gas of N neutral foreign perturbers and immersed in a radiation field consisting of modes described by wave vector $\mathbf{k}$ and polarization vector $\boldsymbol{\lambda}$. The radiator has a series of low-lying, closely spaced energy levels (which eventually will be taken as vibration-rotational levels); the perturbers on the other hand have widely spaced levels (which will be taken as electronic levels). Electric-dipole-allowed transitions are assumed possible between levels in both the radiator and perturbers. For convenience, the ground state of the perturber is taken as a $J=0$ state. In addition, interactions between radiator and perturber will induce cluster dipole moments that may also act in radiative transitions occurring at the same frequencies as the allowed transitions. It is the interference between these induced and allowed transitions that is our main interest. Absorption and stimulated emission events are considered. The lifetimes of excited states are long compared to both the duration of a collision τ_c and the time between collisions. Therefore, spontaneous emission may be ignored. The spacing of the radiator states, however, is not taken as large compared to $\hbar/\tau_c$ or to kT, where k is Boltzmann's constant and T is the temperature. As a result, the radiator-perturber interaction may cause inelastic transitions among the radiator states.

The general approach is that of Alber and Cooper [9], who studied the collisionally induced excitation and pho-

toemission of a similar system within the binary collision approximation. They derived an equation of motion for the reduced density matrix of the radiator and obtained an expression for the spectrum of the spontaneously emitted photons, including components due to collisionally induced radiation, which is valid in both the impact and quasistatic limits. Their analysis, in fact, incorporates the essential elements of the present problem, namely transitions due to allowed and induced moments, the possibility of interference between them, and the effects of single and successive collisions.

Here we construct the density matrix of the gas in which the collisions take place, then describe the evolution of the density matrix in the presence of the incident radiation and obtain the absorption and stimulated emission spectra. The equations are written in the Liouville space form, which is convenient for line-shape problems [10] and in which Liouville operators act in a manner corresponding to normal operators in Hilbert space.

II. DENSITY-MATRIX EQUATIONS

The density operator ρ of the full system obeys the equation of motion:

$$\frac{\partial}{\partial t}\rho = L\rho \ , \tag{1}$$

where the Liouville operator L is defined as

$$L\hat{O} \equiv \frac{1}{i\hbar}[H,\hat{O}] \tag{2}$$

and $\hat{O}$ is an arbitrary operator in Hilbert space (specified by the careted symbol). The Hamiltonian H results from several contributions:

$$H = H_R + \sum_{j=1}^{N} H_j + \sum_{j=1}^{N} \hat{V}(\mathbf{x}_j - \mathbf{x}_R) + H_F + H_{\mathrm{RF}} + \sum_j H_{\mathrm{PF}}^j + H_K \ . \tag{3}$$

H_R and H_j are, respectively, the Hamiltonians for the internal degrees of freedom of the radiator and the jth perturber; $\hat{V}$ describes the interaction between them. H_F is the Hamiltonian of a single-mode radiation field,

$$H_F = \hbar\omega_{k\lambda} a_{k\lambda}^{\dagger} a_{k\lambda} \ , \tag{4}$$

where $\omega_{k\lambda}$ is the frequency of the incident radiation with wave vector k and polarization λ; $a_{k\lambda}^{\dagger}$ and $a_{k\lambda}$ are, respectively, photon creation and destruction operators. H_{RF} and H_{PF}^j give the interaction between the radiation field and, respectively, the radiator and the jth perturber:

$$H_{\mathrm{RF}} + H_{\mathrm{PF}}^j = -(\boldsymbol{\mu}_R + \boldsymbol{\mu}_j)\cdot\mathbf{E} \ , \tag{5}$$

where $\boldsymbol{\mu}_R$ and $\boldsymbol{\mu}_j$ are the dipole moments of the radiator and jth perturber, $\mathbf{E}$ is the incident field, and H_K is the Hamiltonian associated with the kinetic energies of the radiator and the perturbers. As a simplification, the center-of-mass motion of the radiator is neglected (heavy radiator limit) and $\mathbf{x}_R$ can thus be set at zero. For convenience we will adopt a classical path approach, although the change to the quantum-mechanical treatment of the relative motion is straightforward.

Alber and Cooper [9] solve Eq. (1) with Eq. (3). They describe in detail how the collisional interaction in association with the allowed dipole transitions results in the binary collision approximation in the induction of pair dipole moments that also participate in the radiative transitions. Rather than follow that procedure, we adopt here an alternative but equivalent route that leads to the desired final result more directly. To this end, we write an effective Hamiltonian as

$$\begin{aligned} H_e &= H_R + \sum_{j=1}^{N}\left[\frac{1}{2m}\mathbf{p}_j^2 + \sum_{j=1}^{N}\hat{V}_e^{(0)}(\mathbf{R}_j)\right] \\ &\quad + H_F + \sum_{j=1}^{N}\hat{V}_e^{a}(\mathbf{R}_j) - \boldsymbol{\mu}_R\cdot\mathbf{E} - \sum_{j=1}^{N}\boldsymbol{\mu}_e(\mathbf{R}_j)\cdot\mathbf{E} \\ &= H_0 + \sum_{j=1}^{N}\hat{V}_e^{a}(\mathbf{R}_j) - \boldsymbol{\mu}_R\cdot\mathbf{E} - \sum_{j=1}^{N}\boldsymbol{\mu}_e(\mathbf{R}_j)\cdot\mathbf{E} \ . \end{aligned} \tag{6}$$

Here $\mathbf{p}_j$ is the momentum of the jth perturber and $\mathbf{R}_j = \mathbf{x}_j - \mathbf{x}_R$ is intermolecular distance between the radiator and jth perturber. $\hat{V}_e$ is the effective interaction potential between the radiator and a perturber and acts only on the states of the radiator, which are actually accessible in the interaction, that is, to which real transitions may occur. High-energy radiator states and the perturber states have been adiabatically eliminated as described, for example, by Callaway and Bauer [11]. $V_e^{(0)}$ is that part of the interaction which is spherically symmetric with respect of radiator orientation and which consequently does not couple different radiator states but does determine the classical trajectories. V_e^a is the anisotropic part of the effective interaction and can couple different radiator states. In the same manner, $\boldsymbol{\mu}_e(R_j)$ is the effective dipole moment arising through the radiator-perturber interaction and couples unperturbed states of the radiator. That Eq. (6) is indeed a valid and appropriate Hamiltonian is demonstrated by the fact that both Eqs. (3) and (6) lead to Eq. (51) below, from which further analysis proceeds. An outline of the treatment starting from first principles with the use of Eq. (3) is given in the Appendix.

The Liouville operator associated with H_e is

$$L = L_0 + \sum_j V_e^a(t;j) + L_{\mathrm{RF}} + \sum_j L_{eF}(t;j) \ . \tag{7}$$

To solve Eq. (1) with Eq. (7), we first transform Eq. (1) to the interaction picture

$$\frac{\partial}{\partial t}\rho^I(t) = \left[\sum_j V_e^{aI}(t;j) + L_{\mathrm{RF}}^I(t) + \sum_j^N L_{eF}^I(t;j)\right]\rho^I(t) \ , \tag{8}$$

with

$$\rho^I(t) = e^{-L_0 t}\rho(t) \ , \tag{9}$$

$$V_e^{aI}(t;j) = e^{-L_0 t}V_e^a(t;j)e^{+L_0 t} = e^{-L_R t}V_e^a(t;j)e^{+L_R t} \ , \tag{10}$$

$$L^I_{\rm RF}(t)=e^{-L_0 t}L_{\rm RF}e^{+L_0 t}\ , \tag{11}$$

$$L^I_{eF}(t,j)=e^{-L_0 t}L_{eF}(t;j)e^{+L_0 t}\ . \tag{12}$$

The time dependence of V^I_e and L^I_{eF} arises not only from the exponential operators which transform them to the interaction picture but also, if we adopt a classical path approach, from their dependence on the radiator-perturber distance R, which, in turn, is a function of time as the collision proceeds.

The treatment of the interaction of the field with the molecule requires some elaboration. The field $\mathbf{E}$ is given by

$$\mathbf{E}=i\left[\frac{2\pi\hbar\omega_{k\lambda}}{V_q}\right]^{1/2}\boldsymbol{\lambda}e^{i\mathbf{k}\cdot\mathbf{x}}a_{k\lambda}+\text{H.c.}\ , \tag{13}$$

where V_q is the quantization volume. A photon-number state corresponds to an electromagnetic wave with the definite amplitude,

$$E_0=\left[\frac{8\pi\hbar\omega_{k\lambda}n}{V_q}\right]^{1/2}\quad(n\gg1) \tag{14}$$

where n is the number of photons. Also [12], the flux of photons is given by

$$\langle n|\text{flux}|n\rangle=\frac{n}{V_q}c\ , \tag{15}$$

where c is the speed of light. Thus, the operator L^I_{eF} becomes, from Eq. (12),

$$\begin{aligned}L^I_{eF}(t;j)&=e^{-L_R t}[\hat{D}_e(t;j)a_{k\lambda}e^{-i\omega_{k\lambda}t}\\&\quad-\hat{D}^\dagger_e(t;j)a^\dagger_{k\lambda}e^{+i\omega_{k\lambda}t},\dots]e^{+L_R t}\\&=[\hat{D}^I_e(t;j)a_{k\lambda}e^{-i\omega_{k\lambda}t}-\hat{D}^{I\dagger}_e(t;j)a^\dagger_{k\lambda}e^{+i\omega_{k\lambda}t},\dots]\ ,\end{aligned} \tag{16}$$

where in the dipole approximation,

$$\hat{D}_e(t;j)=-\left[\frac{2\pi\omega_{k\lambda}}{\hbar V_q}\right]^{1/2}\boldsymbol{\lambda}\cdot\boldsymbol{\mu}_e(\mathbf{R}_j(t)) \tag{17}$$

and

$$\hat{D}^I_e(t;j)=e^{iH_R t/\hbar}\hat{D}_e(t;j)e^{-iH_R t/\hbar}\ . \tag{18}$$

There are similar expressions for $\hat{D}_R(t;j)$.

Let us now consider solving Eq. (8), to which end we use the projection operator technique of Zwanzig [13]. The operator P is defined generally in tetradic notation [10], under the assumption of uncorrelated perturbers at some time in the remote past, which we take here as $t=0$, as

$$P=\prod_{j=1}^{N}p_j \tag{19}$$

with

$$p_j(\cdots)=|g,g\rangle\rangle\frac{\rho(\mathbf{p}_j)}{V}\text{Tr}_j(\cdots)\ . \tag{20}$$

$|g\rangle$ is the ground state of the perturber, $|g,g\rangle\rangle$ is a tetradic vector, for which the general form is $|a,b\rangle\rangle\equiv|a\rangle\langle b|$, and $\rho(\mathbf{p}_j)$ is the noninteracting density operator (at $t=0$) for the center-of-mass motion of the jth perturber, normalized so that

$$\int d^3p_j\rho(\mathbf{p}_j)=1\ . \tag{21}$$

Tr_j is the trace over the translational degrees of freedom of the jth perturber and, in principle, also a trace over the internal states of the perturber. However, after obtaining effective interactions and dipole moments, only the perturber ground state occurs and, for convenience, in what follows, we omit the internal $|g,g\rangle\rangle$ projector from our equations. The operator Q is also defined as

$$Q=1-P\ . \tag{22}$$

In the classical path approximation, p_j becomes

$$p_j=\frac{w(v_j(0))}{V}\text{Tr}_j \tag{23}$$

where w is the Maxwell distribution of velocities v_j, V is the volume, and

$$\begin{aligned}\text{Tr}_j(\cdots)&=\int d\mathbf{v}_j(0)\int d\mathbf{R}_j(0)(\cdots)\\&=\int_0^\infty dv_j 4\pi v_j^2\int_0^\infty db\,2\pi b\int_{-\infty}^{\infty}v_j dt_0\int\frac{d\Omega}{8\pi^2}\cdots.\end{aligned} \tag{24}$$

Here b is the impact parameter, t_0 is the time of closest approach, and the integral over Ω represents an angular average [14]. The time convention whereby $\rho(\mathbf{p}_j)$ is the density matrix at $t=0$ differs from that of Refs. [9] and [10] where $t=-\infty$ is used. We shall eventually take the long-time limit and $t=0$ can be considered to be in the distant past.

Eventually we will require the density matrix (and similar operators) averaged (traced) over perturber coordinates. The most convenient way to perform this average is to form $P\rho^I$ and then perform the trace at the end of the calculations [noting that $\text{Tr}(P\rho)=\text{Tr}(\rho)$].

With the application of Eqs. (19) and (22) to Eq. (8), the latter may be written as two separate equations,

$$\begin{aligned}\frac{\partial}{\partial t}P\rho^I(t)&=\left[L^I_{\rm RF}+P\sum_j[V^{aI}_e(t;j)+L^I_{eF}(t;j)]\right]P\rho^I(t)\\&\quad+P\sum_j[V^{aI}_e(t;j)+L^I_{eF}(t;j)]Q\rho^I(t)\ ,\end{aligned} \tag{25}$$

$$\begin{aligned}\frac{\partial}{\partial t}Q\rho^I(t)&=\left[L^I_{\rm RF}+Q\sum_j[V^{aI}_e(t;j)+L^I_{eF}(t;j)]\right]Q\rho^I(t)\\&\quad+Q\sum_j[V^{aI}_e(t;j)+L^I_{eF}(t;j)]P\rho^I(t)\ .\end{aligned} \tag{26}$$

$PL^I_{\rm RF}Q$ and $QL^I_{\rm RF}P$ both vanish since $L^I_{\rm RF}$ is independent of perturber variables and $QP=PQ=0$.

Equation (26) is solved by the Green-function method and the solution substituted into Eq. (25) to yield

$$\frac{\partial}{\partial t}P\rho^I(t)=\left[L^I_{\mathrm{RF}}+P\left[\sum_j [V_e^{aI}(t;j)+L^I_{eF}(t;j)]\right]\right]P\rho^I(t)$$
$$+P\sum_j[V_e^{aI}(t;j)+L^I_{eF}(t;j)]\int_0^t dt' G_e^I(t,t')Q\sum_j[V_e^{aI}(t';j)+L^I_{eF}(t';j)]P\rho^I(t')\ , \tag{27}$$

where

$$G_e^I(t,t')=T\exp\int_{t'}^t\left[L^I_{\mathrm{RF}}(t'';j)+Q\sum_j[V_e^{aI}(t'';j)+L^I_{eF}(t'';j)]\right]dt''\ . \tag{28}$$

T is the time-ordering operator. Also $Q_\rho^I(0)$ has been taken as zero, equivalent to the assumption of no correlations in the system at $t=0$.

III. THE SPECTRUM

A. General considerations

Following the procedure developed by Mollow [15], we assume that the photon is absorbed from the field mode specified by $\mathbf{k}$ and λ and the rate of absorption from this mode is given by [15,16]

$$W^A_{k\lambda}(t)=\frac{\partial}{\partial t}\left\langle n-1\left|\mathrm{Tr}_R\prod_{j=1}^N\mathrm{Tr}_j\rho^I(t)\right|n-1\right\rangle$$
$$=\left\langle\!\left\langle n-1,n-1\left|\mathrm{Tr}_R\prod_{j=1}^N\mathrm{Tr}_j\frac{\partial}{\partial t}P\rho^I(t)\right|\right\rangle\!\right\rangle\ . \tag{29}$$

The mode $(\mathbf{k},\lambda)$ is assumed to originally have had n photons. Tr_R is the trace over all radiator variables. The collision average implied in the trace in Eq. (29) will be reduced to a binary collision average and the trace over perturber variables will yield in the classical path approximation an angle average and the average over v, b, and t_0, respectively, the relative velocity, impact parameter and time of closest approach [14] [see Eq. (24)].

The interest is in the long-time limit of $W^A_{k\lambda}$ and we shall use the property that

$$\lim_{t\to\infty}f(t)=\lim_{s\to 0}sF(s)\ , \tag{30}$$

where $F(s)$ is the Laplace transform of $f(t)$. The time derivative in Eq. (29) is given by Eq. (27). We determine $W^A_{k\lambda}$ in the lowest nonvanishing (second) order of the molecule-field coupling.

It is convenient to express $W^A_{k\lambda}(t)$ as

$$\lim_{t\to\infty}W^A_{k\lambda}(t)=W_{A1}(\omega_{k\lambda})+W_{A2}(\omega_{k\lambda})\ , \tag{31}$$

where $W_{A1}(\omega_{k\lambda})$ and $W_{A2}(\omega_{k\lambda})$ explicitly contain L^I_{Rf} and L^I_{eF} respectively. They are given from Eqs. (27) and (29) as

$$W_{A1}(\omega_{k\lambda})=\lim_{t\to\infty}\left\langle\!\left\langle n-1,n-1\left|\mathrm{Tr}_R\prod_{j=1}^N\mathrm{Tr}_jL^I_{\mathrm{RF}}(t)P\rho^I(t)\right|\right\rangle\!\right\rangle \tag{32}$$

and

$$W_{A2}(\omega_{k\lambda})=\lim_{t\to\infty}\left\langle\!\left\langle n-1,n-1\left|\mathrm{Tr}_R\prod_{j=1}^N\mathrm{Tr}_j\sum_{j=1}^N L^I_{eF}(t;j)\left[P\rho^I(t)+\int_0^t G_e^I(t,t')Q\sum_{j=1}^N[V_e^{aI}(t';j)+L^I_{eF}(t';j)]P\rho^I(t')dt'\right]\right|\right\rangle\!\right\rangle\ . \tag{33}$$

The terms preceded on the left by V_e^{aI} in Eq. (27) do not contribute to $W_{A2}(\omega)$. The mathematical reason is that any tetradic operator when traced over all its variables vanishes, i.e., $\mathrm{Tr}_R\mathrm{Tr}_jV_e^{aI}(\cdots)=0$. Physically, the vanishing of these terms occurs because the observable in the problem is associated with the square of the dipole moment operator and V_e^{aI} on the left describes an interaction occurring after the dipole operator has acted twice within the collision.

The total cross section for absorption is

$$\sigma_A(\omega_{k\lambda})=[W_{A1}(\omega_{k\lambda})+W_{A2}(\omega_{k\lambda})]/(n/V_q)c\ . \tag{34}$$

We shall consider W_{A1} and W_{A2} in turn.

B. $W_{A1}(\omega_{k\lambda})$

From the expression for L^L_{RF} analogous to Eq. (16), Eq. (32) becomes

$$W_{A1}(\omega_{k\lambda})=\lim_{t\to\infty}\left[\sqrt{n}\left\langle\!\left\langle n,n-1\left|\mathrm{Tr}_R\prod_{j=1}^{N}\mathrm{Tr}_j\hat{D}_R P\rho^I(t)\right|\right\rangle\!\right\rangle\right.$$
$$\left.+\sqrt{n}\left\langle\!\left\langle n-1,n\left|\mathrm{Tr}_R\prod_{j=1}^{N}\mathrm{Tr}_j[e^{L_R t+i\omega_{k\lambda}t}P\rho^I(t)]\hat{D}_R^*\right|\right\rangle\!\right\rangle\right]=\lim_{t\to\infty}2\,\mathrm{Re}[\mathrm{Tr}_R F^A(t)\hat{D}_R^*]\,, \tag{35}$$

where

$$F^A(t)=\sqrt{n}\left\langle\!\left\langle n-1,n\left|\prod_{j=1}^{N}\mathrm{Tr}_j e^{L_R t+i\omega_{k\lambda}t}P\rho^I(t)\right|\right\rangle\!\right\rangle\,. \tag{36}$$

The portion of the equation of motion (27) which is first order in E_0 either explicitly by the presence of L^I_{RF} or L^I_{eF} or implicitly through appropriate elements of $\rho^I(t)$ is as follows:

$$\frac{\partial}{\partial t}P\rho^I(t)=NPV_e^{aI}(t)P\rho^I(t)+NPV_e^{aI}(t)\int_0^t dt'U_e^I(t,t')V_e^{aI}(t')P\rho^I(t')+L^I_{\mathrm{RF}}(t)P\rho^I(t)$$
$$+NPL^I_{eF}(t)P\rho^I(t)+NPL^I_{eF}(t)\int_0^t dt'U_e^I(t,t')V_e^{aI}(t')P\rho^I(t')+NPV_e^{aI}(t)\int_0^t dt'U_e^I(t,t')L^I_{eF}(t')P\rho^I(t')$$
$$+NPV_e^{aI}(t)\int_0^t dt'\int_{t'}^t dt_1U_e^I(t,t_1)L^I_{\mathrm{RF}}(t_1)U_e^I(t_1,t')V_e^{aI}(t')P\rho^I(t')$$
$$+NPV_e^{aI}(t)\int_0^t dt'\int_{t'}^t dt_1U_e^I(t,t_1)L^I_{eF}(t_1)U_e^I(t_1,t')V_e^{aI}(t')P\rho^I(t')\,. \tag{37}$$

The double integral terms arise from the expansion of $G_e^I(t,t')$ to first order in L^I_{RF} and L^I_{eF}:

$$G_e^I(t,t')=G_{ec}^I(t,t')+\int_{t'}^t dt_1G_{ec}^I(t,t_1)\left[L^I_{\mathrm{RF}}(t_1)+Q\sum_{j=1}^{N}L^I_{eF}(t_1;j)\right]G_{ec}^I(t_1,t')\,, \tag{38}$$

with

$$G_{ec}^I(t,t')=T\exp\left[\int_{t'}^t Q\sum_{j=1}^{N}V_e^{aI}(t_1;j)dt_1\right]\,. \tag{39}$$

In writing Eq. (37), we have made the binary collision approximation (BCA) as detailed in Appendix A of Ref. [9]. $U_e^I(t,t')$ is the one perturber collisional propagator,

$$U_e^I(t,t')=T\exp\left[\int_{t'}^t dt_1V_e^{aI}(t_1)\right]\,. \tag{40}$$

The symbols $V_e^{aI}(t)$ and $L^I_{eF}(t)$ [as well as $\hat{D}_eI(t)$ in Eq. (43) below] indicate no dependence on j and are the one (i.e., representative) perturber operators. The thermodynamic limit has been taken by replacing $1-p_j$ by unity [9].

1. Simplification

In this section, the procedures of Smith, Vidal, and Cooper [17] and Trippenbach *et al.* [16] are followed to obtain a formal expression for the spectral intensity. First, the function $\Sigma^{(0)}(t)$, defined as

$$\Sigma^{(0)}(t)\equiv\left\langle\!\left\langle n,n\left|e^{L_R t}\prod_{j=1}^{N}\mathrm{Tr}_jP\rho^I(t)\right|\right\rangle\!\right\rangle\,, \tag{41}$$

is the element of the density matrix of the molecular system unperturbed by the external field, in the Schrödinger picture. Then by Eq. (30),

$$\lim_{t\to\infty}\Sigma^{(0)}(t)=\lim_{s\to0}s\Sigma^{(0)}(s)=\Sigma^B \tag{42}$$

where Σ^B is the Boltzmann distribution function for the molecular states.

Now returning to Eq. (36), differentiating $F^A(t)$ with respect to time, and using Eqs. (37) and (42), we get the equation of motion,

$$\frac{\partial}{\partial t}F^A(t)=(L_R+i\omega_{k\lambda})F^A(t)+N\langle V_e^{aI}(0)\rangle_{\mathrm{av}}F^A(t)$$
$$+N\int_0^t\langle V_e^{aI}(0)U_e^I(0,-(t-t'))V_e^{aI}(-(t-t'))\rangle_{\mathrm{av}}e^{(L_R+i\omega_{k\lambda})(t-t')}F^A(t')dt'+n\hat{D}_R\Sigma^{(0)}(t)+n\langle\hat{D}_e^I(0)\rangle_{\mathrm{av}}\Sigma^{(0)}(t)$$
$$+nN\int_0^t\langle\hat{D}_e^I(0)U_e^I(0,-(t-t'))V_e^{aI}(-(t-t'))\rangle_{\mathrm{av}}e^{L_R(t-t')}\Sigma^{(0)}(t')dt'$$
$$+nN\int_0^t e^{(L_R+i\omega_{k\lambda})(t-t')}\langle V_e^{aI}(t-t')U_e^I(t-t',0)\hat{D}_e^I(0)\rangle_{\mathrm{av}}\Sigma^{(0)}(t')dt'$$

$$+nN\int_0^t e^{(L_R+i\omega_{k\lambda})(t-t_1)}\Big\langle V_e^{aI}(t-t_1)U_e^I(t-t_1,0)\hat{D}_R^I(0)\times\int_0^{t_1}U_e^I(0,-(t-t'))V_e^{aI}(-(t_1-t'))\Big\rangle_{\rm av}e^{L_R(t_1-t')}\Sigma^{(0)}(t')dt'dt_1$$

$$+nN\int_0^t e^{(L_R+i\omega_{k\lambda})(t-t_1)}\Big\langle V_e^{aI}(t-t_1)U_e^I(t-t_1,0)\hat{D}_e^I(0)\times\int_0^{t_1}U_e^I(0,-(t_1-t'))V_e^{aI}(-(t_1-t'))\Big\rangle_{\rm av}e^{L_R(t_1-t')}\Sigma^{(0)}(t')dt'dt_1\ . \tag{43}$$

Here

$$\langle\cdots\rangle_{\rm av}=\int d\mathbf{v}(0)w(v(0))\int d\mathbf{R}(0)\frac{1}{V}\{\cdots\}\ , \tag{44}$$

which is a result of Eqs. (23) and (24). The time origin has been translated with the help of the identity

$$\langle O_1^I(t+t_1)\cdots O_n^I(t+t_n)\rangle_{\rm av}=e^{-L_Rt}\langle O_1^I(t_1)\cdots O_n^I(t_n)\rangle_{\rm av}e^{+L_Rt}\ , \tag{45}$$

where O^I is an operator in the interaction picture [17]. Then, taking the long-time limit through Eq. (30), we obtain

$$\lim_{t\to\infty}F^A(t)=\lim_{s\to0}\Bigg[\Big\{-(L_R+i\omega_{k\lambda})+N\int_0^\infty\langle V_e^{aI}(0)U_e^I(0,-\tau)\rangle_{\rm av}e^{(L_R+i\omega_{k\lambda})\tau-s\tau}d\tau(L_R+i\omega_{k\lambda})\Big\}^{-1}\times\Big[n\hat{D}_R\Sigma^B-nN(L_R+i\omega_{k\lambda})\int_0^\infty e^{(L_R+i\omega_{k,\lambda})\tau-s\tau}\langle U_e^I(\tau,0)\hat{D}_e^I(0)U_e^I(0,-\infty)\rangle_{\rm av}d\tau\Sigma^B$$

$$+nN\int_0^\infty e^{(L_R+i\omega_{k\lambda})\tau-s\tau}\langle V_e^{aI}(\tau)U_e^I(\tau,0)\hat{D}_R[U_e^I(0,-\infty)-1]\rangle_{\rm av}d\tau\Sigma^B\Big]\Bigg]\ . \tag{46}$$

The symbol τ represents $t-t'$.

In arriving at this simplified result, the methods described in Smith, Vidal, and Cooper [17] have been used. These involve applying the following relationships:

$$\frac{dU_e^I(t,t')}{dt'}=-U_e^I(t,t')V_e^{aI}(t') \tag{47}$$

and

$$\int_0^t U_e^I(t,t')V_e^{aI}(t')dt'=U_e^I(t,0)-1\ , \tag{48}$$

after taking the Laplace transform.

C. $W_{A2}(\omega_{k\lambda})$

We now return to $W_{A2}(\omega_{k\lambda})$ in Eqs. (31) and (33), which may be rewritten in a manner similar to $W_{A1}(\omega_{k\lambda})$ to give in the BCA

$$W_{A2}(\omega_{k\lambda})=\lim_{t\to\infty}2\,\mathrm{Re}\Bigg[\sqrt{n}N\Big\langle\Big\langle n-1,n\Big|\mathrm{Tr}_R\prod_{j=1}^N\mathrm{Tr}_j\hat{D}_e^{I\dagger}(t)\Big[e^{i\omega_{k\lambda}t}P\rho^I(t)+e^{i\omega_{k\lambda}t}\int_0^t U_e^I(t,t')V_e^{aI}(t')P\rho^I(t')dt'\Big]\Big\rangle\Big\rangle$$

$$+nN\,\mathrm{Tr}_R\int_0^t\langle\hat{D}_e^{I\dagger}(t)e^{i\omega_{k\lambda}t}U_e^I(t,t')\hat{D}_e^I(t')\rangle_{\rm av}e^{-(L_R+i\omega_{k\lambda})t'}\Sigma^{(0)}(t')dt'$$

$$+nN\,\mathrm{Tr}_R\int_0^t\int_{t'}^t\langle\hat{D}_e^{I\dagger}(t)e^{i\omega_{k\lambda}t}U_e^I(t,t_1)[\hat{D}_R^I(t_1)+\hat{D}_e^I(t_1)]\times U_e^I(t_1,t')e^{-i\omega_{k\lambda}t_1}V_e^{aI}(t')\rangle_{\rm av}e^{-L_Rt'}\Sigma^{(0)}(t')dt_1dt'\Bigg]\ . \tag{49}$$

Then, after application of the same simplifying relationships used in the previous section, W_{A2} becomes

$$W_{A2}(\omega_{k\lambda})=\lim_{s\to0}2\,\mathrm{Re}\Bigg[-N\,\mathrm{Tr}_R\int_0^\infty\langle\hat{D}_e^{I\dagger}(0)U_e^I(0,-\tau)\rangle_{\rm av}e^{(L_R+i\omega_{k\lambda})\tau-s\tau}d\tau(L_R+i\omega_{k\lambda})sF^A(s)$$

$$+nN\,\mathrm{Tr}_R\int_0^\infty\langle\hat{D}_e^{I\dagger}(\tau)U_e^I(\tau,0)\hat{D}_e^I(0)U_e^I(0,-\infty)\rangle_{\rm av}e^{i\omega_{k\lambda}\tau-s\tau}d\tau\Sigma^B$$

$$+nN\,\mathrm{Tr}_R\int_0^\infty\langle\hat{D}_e^{I\dagger}(\tau)U_e^I(\tau,0)\hat{D}_R[U_e^I(0,-\infty)-1]\rangle_{\rm av}e^{i\omega\tau-s\tau}d\tau\Sigma^B\Bigg]\ . \tag{50}$$

D. Full spectrum

Now after the combining of Eqs. (31), (35), (46), and (50) and dropping of the subscript $k\lambda$ on ω, the full absorption spectrum $W^A(\omega)$ is as follows:

$$
\begin{aligned}
W^A(\omega)=\lim_{s\to 0} 2\,\mathrm{Re}\Bigg[\mathrm{Tr}_R\Bigg\{\Bigg[& n[\mathcal{L}(\omega)]^{-1}\hat{D}_R\Sigma^B \\
& -nN[\mathcal{L}(\omega)]^{-1}(L_R+i\omega)\left[\int_0^\infty e^{(L_R+i\omega)\tau-s\tau}\langle U_e^I(\tau,0)\hat{D}_e^I(0)U_e^I(0,-\infty)\rangle_{\mathrm{av}}d\tau\right]\Sigma^B \\
& +nN[\mathcal{L}(\omega)]^{-1}\left[\int_0^\infty e^{(L_R+i\omega)\tau-s\tau}\langle V_e^{aI}(\tau)U_e^I(\tau,0)\hat{D}_R[U_e^I(0,-\infty)-1]\rangle_{\mathrm{av}}d\tau\right]\Sigma^B\Bigg]\hat{D}_R^* \\
& -nN\left[\int_0^\infty\langle\hat{D}_e^{I\dagger}(0)U_e^I(0,-\tau)\rangle_{\mathrm{av}}e^{(L_R+i\omega)\tau-s\tau}d\tau\right](L_R+i\omega)[\mathcal{L}(\omega)]^{-1}\hat{D}_R\Sigma^B \\
& +nN^2\left[\int_0^\infty\langle\hat{D}_e^{I\dagger}(0)U_e^I(0,-\tau)\rangle_{\mathrm{av}}e^{(L_R+i\omega)\tau-s\tau}d\tau\right](L_R+i\omega)[\mathcal{L}(\omega)]^{-1}(L_R+i\omega) \\
& \times\left[\int_0^\infty e^{(L_R+i\omega)\tau-s\tau}\langle U_e^I(\tau,0)\hat{D}_e^I(0)U_e^I(0,-\infty)\rangle_{\mathrm{av}}d\tau\right]\Sigma^B \\
& -nN^2\left[\int_0^\infty\langle\hat{D}_e^{I\dagger}(0)U_e^I(0,-\tau)\rangle_{\mathrm{av}}e^{(L_R+i\omega)\tau-s\tau}d\tau\right](L_R+i\omega)[\mathcal{L}(\omega)]^{-1} \\
& \times\left[\int_0^\infty e^{(L_R+i\omega)-s\tau}\langle V_e^{aI}(\tau,0)U_e^I(\tau,0)\hat{D}_R[U_e^I(0,-\infty)-1]\rangle_{\mathrm{av}}d\tau\right]\Sigma^B \\
& +nN\left[\int_0^\infty\langle\hat{D}_e^{I\dagger}(\tau)U_e^I(\tau,0)\hat{D}_e^I(0)U_e^I(0,-\infty)\rangle_{\mathrm{av}}e^{i\omega\tau-s\tau}\right]\Sigma^B \\
& +nN\left[\int_0^\infty\langle\hat{D}_e^{I\dagger}(\tau)U_e^I(\tau,0)\hat{D}_R[U_e^I(0,-\infty)-1]\rangle_{\mathrm{av}}e^{i\omega\tau-s\tau}\right]\Sigma^B\Bigg\}\Bigg],
\end{aligned}
\tag{51}
$$

where

$$
\mathcal{L}(\omega)=-(L_R+i\omega)+N\left[\int_0^\infty\langle V_e^{aI}(0)U_e^I(0,-\tau)\rangle_{\mathrm{av}}e^{(L_R+i\omega)\tau-s\tau}d\tau\right](L_R+i\omega)\ . \tag{52}
$$

Each term in (51) describes a contribution to the spectrum of a particular physical origin. The first term describes the purely allowed spectrum. The second is an interference term between allowed and collision-induced transitions. The third arises from purely allowed transitions and is designated as a correlated term, the nature of which will be discussed below. The fourth term is again an interference between allowed and collision-induced contributions. The fifth term describes purely collision-induced transitions, occurring in successive collisions. The sixth term is an interference term, involving successive collisions and a correlated-type term. The seventh term comes from collision-induced transitions occurring in a single collision and is the main contribution to the purely collision-induced spectrum. The eighth, (and last), term is an interference effect occurring in a single collision and is a correlated term.

Note that $[\mathcal{L}(\omega)]^{-1}$ appears in the first six terms. It is the usual line-shape operator [17] and will be shown to be responsible for narrow spectral features. Thus these terms will all have spectral features of similar widths and shifts to that of the first or allowed term. They may not be identical to those of the allowed term because of the presence of the evolution operator U_e^I in the integrands of terms two to six. The last two terms in Eq. (51) depend solely on propagation during a collision and therefore their widths will depend on the duration of a collision. Hence these terms give broad spectral features.

The correlated terms were so named by Burnett and Cooper [18], in analogy to similar terms appearing in statistical mechanics. They depend explicitly on the $Q\rho$ component of the density matrix. A simple argument can be given to assess their importance. The correlated terms contain the factor $V_e^{aI}U_e^I$. The integrals are of the form $\int V_e^{aI}U_e^I\hat{D}_R(U_e^I-1)d\tau$, where the integrands are nonzero essentially only for the duration of the collision τ_c. From Eq. (52) [or Eq. (55) below], it is seen that $V_e^{aI}U_e^I$ is of the order of a collisional width γ, to be defined explicitly in Sec. V, and thus the correlated term is of the order of $\hat{D}_R\gamma\tau_c$. In contrast, the purely allowed term contains only $\hat{D}_R$. For a typical allowed line, γ is of the order of 0.01 or 10^9 Hz. The duration of collision is about 10^{-12} s. (These values are consistent with those found for the HD pure rotational lines [4]). The correlated terms are then less than the terms involving just $\hat{D}_R$ by a factor of 10^3. Therefore, in comparison, the correlated terms in Eq. (51) may be neglected, as we shall do. This argument applies to intensities near the line center. In the spectral wings, the contribution of the correlated terms may be

very significant; in the consideration of the redistribution of radiation in the line wings these terms must be retained [18].

IV. IMPACT APPROXIMATION

Expression (51) for the spectrum is valid in general. We are interested in the effects of interference on the sharp spectral features close to line center controlled by $\mathcal{L}(\omega)$, since these may be separated readily from the broad background [1–8]. It is thus appropriate to work within the impact approximation. This approximation is valid when $\Delta\tau_c \ll 1$, where Δ is the detuning and

$$\Delta \equiv \omega - \omega_{eg} \tag{53}$$

for $g_R \rightarrow e_R$, g_R and e_R being the initial and final states of the radiator transition under consideration. (For the HD pure rotational spectrum, $\Delta\tau_c$ is about 10^{-5} and the approximation is quite suitable.)

For isolated lines, it is easy to show that Tr_R in Eq. (51) reduces to $\langle\langle g_R, g_R|$ for the first three terms and to $\langle\langle e_R, e_R|$ for the next three terms. Both $|g_R\rangle$ and $|e_R\rangle$ may be degenerate (see Sec. V). Terms involving other matrix elements are of the order of γ/ω_{eg} and are consequently small. The last two terms of Eq. (51) will be ignored since they contribute only to the broad feature. As a result, all the $(L_R + i\omega)$ in Eq. (51) may be replaced by $i\Delta$. Within the impact approximation, the formulas of Eq. (51) may be further simplified. For example, the line-shape term is

$$\mathcal{L}(\omega) = -i\Delta + \lim_{s\rightarrow 0} i\Delta N \int_0^\infty \langle V_e^{aI}(0) U_e^I(0,-\tau)\rangle_{\mathrm{av}} \times e^{i\Delta\tau - s\tau} d\tau \ . \tag{54}$$

After integration by parts and the setting of $e^{i\Delta\tau} \approx e^{i\Delta\tau_c} \approx 1$, where τ_c is the only interval in which $V_e^{aI} U_e^I V_e^{aI}$ is essentially nonzero, Eq. (54) becomes

$$\mathcal{L}(\omega) = -i\Delta - N\langle V_e^{aI}(0) U_e^I(0,-\infty)\rangle_{\mathrm{av}} \ . \tag{55}$$

The expression for the absorption spectrum (51) is then

$$\begin{aligned} W^A(\omega) = 2\,\mathrm{Re}\lim_{s\rightarrow 0} [\mathrm{Tr}_R(\{n[\mathcal{L}(\omega)]^{-1}\hat{D}_R\Sigma^B + nN[\mathcal{L}(\omega)]^{-1}\langle U_e^I(\infty,0)\hat{D}_e^I(0)U_e^I(0,-\infty)\rangle_{\mathrm{av}}\Sigma^B\}\hat{D}_R^* \\ + nN\langle \hat{D}_e^{I\dagger}(0)U_e^I(0,-\infty)\rangle_{\mathrm{av}}[\mathcal{L}(\omega)]^{-1}\hat{D}_R\Sigma^B \\ + nN^2\langle \hat{D}_e^{I\dagger}(0)U_e^I(0,-\infty)\rangle_{\mathrm{av}}[\mathcal{L}(\omega)]^{-1}\langle U_e^I(\infty,0)\hat{D}_e^I(0)U_e^I(0,-\infty)\rangle_{\mathrm{av}}\Sigma^B)] \ . \end{aligned} \tag{56}$$

V. ANGULAR AVERAGE

These expressions within the impact approximation are now isotropically averaged over all orientations of the radiator and of the intermolecular axis. The assumption is made that the incident field is weak. Consequently, there is no relationship between the polarization vector of the incident field and the orientation of the perturber. The distribution of perturbers about the radiator is assumed to have spherical symmetry and therefore it is convenient to write the tetradic states involved in an irreducible tetradic basis with respect to the rotation group. This is defined by [9]

$$|J_1 J_2 K Q\rangle\rangle = \sum_{m_1,m_2} |J_1 m_1, J_2 m_2\rangle\rangle (-1)^{J_1 - m_1} \times \begin{pmatrix} J_1 & J_2 & K \\ m_1 & -m_2 & -Q \end{pmatrix} (2K+1)^{1/2} \ . \tag{57}$$

The collisional angle average is then easily obtained through the properties of the irreducible tensor under rotation [19,20].

By taking a spherical collision environment, we ignore velocity-changing collisions, which are described by a perturber distribution of cylindrical symmetry due to the radiator moving through the perturber ensemble. We thereby do not consider the intercollisional interference effect elucidated by Lewis and Van Kranendonk [21,22]. This effect manifests itself as a narrow "dip" in the absorption spectrum and results from anticorrelated interference between the dipole moments induced in successive velocity-changing collisions, arising from the tendency of the radiator to hit the perturber "head-on."

After the angular averaging of Eqs. (55) and (56), the absorption cross section, defined by Eq. (34), becomes

$$\sigma_A(\omega) = \frac{4\pi\omega}{3\hbar c}\mathrm{Re}[(\Delta + i\gamma)^{-1} i X_1^A X_2^A] \ , \tag{58}$$

where

$$X_1^A=\langle J_e\|\hat{\mu}_R\|J_g\rangle^*+n_p\sum_{\substack{J_\alpha,q_c\\ m_e,m_g,m_\alpha}}(-1)^{J_e-m_e}\begin{pmatrix}J_e & 1 & J_g\\ -m_e & q_c & m_g\end{pmatrix}\langle\langle J_\alpha m_\alpha,J_\alpha m_\alpha|[\hat{\mu}_e^I(0)]_{q_c}^* U_e^I(0,-\infty)|J_e m_e,J_g m_g,\rangle\rangle_{\rm av}\ , \tag{59}$$

$$X_2^A=\langle J_e\|\hat{\mu}_R\|J_g\rangle\frac{1}{2J_g+1}\Sigma^B_{J_gJ_g}+n_p\sum_{\substack{J_i,q_c\\ m_e,m_g,m_i}}(-1)^{J_e-m_e}\begin{pmatrix}J_e & 1 & J_g\\ -m_e & q_c & m_g\end{pmatrix}\times\langle\langle J_e m_e,J_g m_g|U_e^I(\infty,0)[\hat{\mu}_e^I(0)]_{q_c}U_e^I(0,-\infty)|J_i m_i,J_i m_i\rangle\rangle_{\rm av}\frac{1}{(2J_i+1)}\Sigma^B_{J_iJ_i} \tag{60}$$

$$\gamma=n_p\left[1-\sum_{\substack{q_c\\ m_e',m_g'\\ m_e,m_g}}(-1)^{m_e+m_e'}\begin{pmatrix}J_e & 1 & J_g\\ -m_e' & q_c & m_g\end{pmatrix}\begin{pmatrix}J_e & 1 & J_g\\ -m_e & q_c & m_g\end{pmatrix}\langle J_e m_e'|\hat{S}|J_e m_e\rangle\langle J_g m_g'|\hat{S}|J_g m_g\rangle^*\right]_a\ , \tag{61}$$

where $n_p=N/V$ is the number density of perturbers. The states J_e and J_g are, respectively, the excited and initial states of the transition considered. The states J_i and J_α represent arbitrary states, respectively, before and after the dipole-inducing collision. The element $\langle J_e\|\hat{\mu}_R\|J_g\rangle$ is the reduced matrix element of $\hat{\mu}_R$ after application of the Wigner-Eckart theorem. $\begin{pmatrix}\cdots\\ \cdots\end{pmatrix}$ indicates the 3-j symbol [20]. The subscript q_c denotes a spherical component of the effective dipole moment. The average is now, after the angular average, a collisional average over velocity, impact parameter and time of closest approach [14]:

$$\langle\cdots\rangle_{\rm av}=\int_0^\infty dv\,4\pi v^2\omega(v)\int_0^\infty db\,2\pi b\int_{-\infty}^\infty v\,dt_0\cdots\ . \tag{62}$$

Equation (61) is the usual expression for the line-shape function [19,23]. In order to obtain Eq. (61), the average over the time of closest approach has been taken, so that

$$[\cdots]_a=\int_0^\infty dv\,4\pi v^3 w(v)\int_0^\infty db\,2\pi b\cdots\ . \tag{63}$$

The S matrix is defined as

$$\hat{S}=\hat{U}_e^I(\infty,-\infty)\ . \tag{64}$$

The real and imaginary parts of γ give, respectively, the width and shift of the spectral line. By restricting the J elements of γ to J_e and J_g in Sec. IV, we have assumed that the lines are isolated. The tetradic matrix $\mathcal{L}(\omega)$ [Eq. (52)], which should in principle be inverted, is now diagonal and $1/\mathcal{L}(\omega)$, is simply the inverse of the diagonal elements.

VI. ABSORPTION COEFFICIENT

There is, or course, the possibility of stimulated emission, as well as of absorption. In principle, the analysis of Secs. III–V can be repeated for the stimulated emission process. However, because of the inclusion of J-changing collisions and classical trajectories in the present treatment, the relationship between the cross sections for the two radiative processes described by detailed balance cannot be strictly obtained. When inelastic collisions occur, there is not a unique trajectory. For the absorption spectrum, in general, the change in trajectory due to inelastic effects will be small in the region where the interactions are important and we expect the classical trajectory to be a reasonable approximation. Quantum calculations are straightforward but obviously more tedious. For a critique of the problems of incorporating detailed balance in classical calculations of induced line shapes, the reader is referred to the work of Frommhold and his collaborators [24]. We shall take the detailed balance result to pertain, and write the cross section for stimulated emission as

$$\sigma_E(\omega)=\sigma_A(\omega)e^{-\hbar\omega/kT}\ . \tag{65}$$

The absorption coefficient $\alpha(\omega)$ is

$$\alpha(\omega)=n_R[\sigma_A(\omega)-\sigma_E(\omega)]\ , \tag{66}$$

where the number density of radiators is now taken as n_R.

Finally,

$$\alpha(\omega)=\frac{4\pi\omega}{3\hbar c}n_R(1-e^{-\hbar\omega/kT})\mathrm{Re}\Bigg[(\Delta+i\gamma)^{-1}\Bigg\{i|\langle J_e\|\hat{\mu}R\|J_g\rangle|^2\frac{1}{2J_g+1}\Sigma^B_{J_gJ_g}$$
$$+in_p\langle J_e\|\hat{\mu}_R\|J_g\rangle^*\Bigg[\sum_{\substack{J_i,q_c\\ m_e,m_g,m_i}}(-1)^{J_e-m_e}\begin{pmatrix}J_e & 1 & J_g\\ -m_e & q_c & m_g\end{pmatrix}\langle\langle J_em_e,J_gm_g|U^I_e(\infty,0)[\hat{\mu}^I_e(0)]_{q_c}$$
$$\times U^I_e(0,-\infty)|J_im_i,J_im_i\rangle\rangle_{\mathrm{av}}\frac{1}{2J_i+1}\Sigma^B_{J_iJ_i}\Bigg]$$
$$+in_p\Bigg[\sum_{\substack{J_\alpha,q_c\\ m_e,m_g,m_{a_\alpha}}}(-1)^{J_e-m_e}\begin{pmatrix}J_e & 1 & J_g\\ -m_e & q_c & m_g\end{pmatrix}\langle\langle J_\alpha m_\alpha,J_\alpha m_\alpha|[\hat{\mu}^I_e(0)]^*_{q_c}U^I_e(0,-\infty)|J_em_e,J_gm_g\rangle\rangle_{\mathrm{av}}\Bigg]$$
$$\times\langle J_e\|\hat{\mu}_R\|J_g\rangle\frac{1}{2J_g+1}\Sigma^B_{J_gJ_g}$$
$$+in_p^2\Bigg[\sum_{\substack{J_\alpha,q_c\\ m_e,m_g,m_\alpha}}(-1)^{J_e-m_e}\begin{pmatrix}J_e & 1 & J_g\\ -m_e & q_c & m_g\end{pmatrix}\langle\langle J_\alpha m_\alpha,J_\alpha m_\alpha|[\hat{\mu}^I_e(0)]^*_{q_c}U^I_e(0,-\infty)|J_em_e,J_gm_g\rangle\rangle_{\mathrm{av}}\Bigg]$$
$$\times\Bigg[\sum_{\substack{J_i,q_c\\ m_e,m_gm_i}}(-1)^{J_e-m_e}\begin{pmatrix}J_e & 1 & J_g\\ -m_e & q_c & m_g\end{pmatrix}\langle\langle J_em_e,J_gm_g|U^I_e(\infty,0)[\hat{\mu}^I_e(0)]_{q_c}$$
$$\times U^I_e(0,-\infty)|J_im_i,J_im_i\rangle\rangle_{\mathrm{av}}\frac{1}{2J_i+1}\Sigma^B_{J_iJ_i}\Bigg]\Bigg\}\Bigg]. \tag{67}$$

VII. DISCUSSION

A. Inelastic collisions, J and m mixing

The expression (67) is rather general, including possible effects due to J and m mixing. The first term describes purely allowed transitions between states J_g and J_e. The second and third terms involve interference between allowed and induced transitions. In the second term, the radiator starts in an arbitrary state J_i at $t=-\infty$ and the system propagates to $t=0$, while the radiator possibly undergoes J or m mixing. At $t=0$, there is a dipole interaction, in general, between two intermediate Jm states of the radiator. The system then propagates to the end of the collision, with the radiator again possibly experiencing J and m mixing. At $t=+\infty$ (end of the collision), there remains a coherence between J_em_e and J_gm_g. The radiator dipole interacts with the light field at some later time to leave the radiator in the J_e state. This history of the system is perhaps more clearly seen if the tetradic element appearing in the second term is written, after a translation of the time origin from 0 to t_0 and with the specific inclusion of the complete sets of intermediate states, as

$$\langle\langle J_em_e,J_gm_g|U^I_e(\infty,0)[\hat{\mu}^I_e(0)]_{q_c}U^I_e(0,-\infty)|J_im_i,J_im_i\rangle\rangle$$
$$=\sum_{\substack{J_1,J_2,J_3\\ m_1,m_2,m_3}}e^{-i(\omega_{eg}-\omega_{32})t_0}\langle\langle J_em_e,J_gm_g|U^I_e(\infty,t_0)|J_3m_3,J_1m_1\rangle\rangle\langle J_3m_3|[\hat{\mu}_e(t_0)]_{q_c}|J_2m_2\rangle$$
$$\times\langle\langle J_2m_2,J_1m_1|U^I_e(t_0,-\infty)|J_im_i,J_im_i\rangle\rangle\ . \tag{68}$$

Similarly, in the third term, the radiator dipole initially creates an eg coherence and the system propagates to $t=0$, with the radiator possibly suffering J and m mixing. At $t=0$, the effective dipole operator acts, leaving the radiator in the arbitrary state J_α. The tetradic element in this term may be written as

$$\langle\langle J_\alpha m_\alpha,J_\alpha m_\alpha|[\hat{\mu}^I_e(0)]^*_{q_c}U^I_e(0,-\infty)|J_em_e,J_gm_g\rangle\rangle$$
$$=\sum_{\substack{J_1\\ m_1}}e^{+i(\omega_{eg}-\omega_{1\alpha})t_0}\langle J_1m_1|[\hat{\mu}_e(t_0)]_{q_c}|J_\alpha m_\alpha\rangle^*\langle\langle J_1m_1,J_\alpha m_\alpha|U^I_e(t_0-\infty)|J_em_e,J_gm_g\rangle\rangle\ . \tag{69}$$

In Eqs. (68) and (69), the time t_0 represents the time between the radiative event and the time of closest approach. This time is of the order of the duration of a collision for intracollisional absorption to occur. Thus, if the difference between the frequency ω_{eg} and ω_{32} or $\omega_{1\alpha}$ is great compared to τ_c^{-1}, the exponential oscillates rapidly and the contribution to the absorption coefficient of the transition J_2 to J_3 or J_1 to J_α is not large. J mixing, however, becomes important if $(\omega_{eg}-\omega_{32})\tau_c \leq 1$ or if $(\omega_{eg}-\omega_{1\alpha})\tau_c \leq 1$, as can be the case for the rotational spectrum of HD at 295 K.

The fourth term in Eq. (67) describes induced transitions occurring in successive collisions. The effective or induced dipole operator acts once in each collision. This term is not zero since in each collision the dipole moment induced has a component in the direction of the allowed dipole and hence successive collisions are correlated. Thus the line shape is controlled by the time between collisions, rather than the duration of a collision. As a result, the spectral feature is modulated by $\mathcal{L}(\omega)$ and is of similar width to the allowed line. Herman and coworkers [6,22,25] have emphasized the importance of this term in accounting for the total intensity of the narrow spectral features in the infrared spectrum of HD.

B. Elastic collisions; m mixing only

If we take $U_e^I(t,t')$ to be diagonal in J, then only elastic collisions can occur and the following simplifications in the formalism result. From Eqs. (59) and (60),

$$X_1^A=(\mu_R^*+n_p\mu_I) \tag{70}$$

and

$$X_2^A=(\mu_R+n_p\mu_I)\frac{1}{2J_g+1}\Sigma^B_{J_gJ_g}\ , \tag{71}$$

where

$$\mu_R=\langle J_e\|\hat{\mu}_R\|J_g\rangle \tag{72}$$

and

$$\mu_I=\sum_{\substack{q_c\\ m_e,m_g}}(-1)^{J_e-m_e}\begin{bmatrix} J_e & 1 & J_g\\ -m_e & q_c & m_g\end{bmatrix} \times\int_{-\infty}^{\infty}dt_0\,e^{-i\omega_{eg}t_0}\langle J_em_e|\hat{U}_e^I(\infty,t_0) \times[\mu_e(t_0)]_{q_c}\hat{U}_e^{I\dagger}(\infty,t_0)|J_gm_g\rangle_a\ , \tag{73}$$

with $\hat{U}_e^I$ being the Hilbert space evolution operator.

Taking μ_R to be real, writing μ_I as

$$\mu_I=|\mu_I|e^{i\delta}=|\mu_I|(\Delta'+i\Delta'')\ , \tag{74}$$

and γ as

$$\gamma=\gamma'+i\gamma''\ , \tag{75}$$

we get from Eqs. (58) and (66),

$$\alpha(\omega)=\frac{4\pi\omega}{3\hbar c}n_R(1-e^{-\hbar\omega/kT})\left[\frac{\gamma'}{(\gamma')^2+(\Delta-\gamma'')^2}[\mu_R^2+2\Delta'n_p\mu_R|\mu_I|+(\Delta'^2-\Delta''^2)n_p^2\mu_I^2] -\frac{2(\Delta-\gamma'')}{(\gamma')^2+(\Delta-\gamma'')^2}(\Delta''n_p\mu_R|\mu_I|+\Delta'\Delta''n_p^2|\mu_I|^2)\right]\frac{1}{2J_g+1}\Sigma^B_{J_gJ_g}\ . \tag{76}$$

This equation is the sum of a Lorentzian and a dispersion profile and as such is of the same form as that obtained by Herman, Tipping, and Poll [6] in their pioneering theory of the interference effect. They assumed that the evolution operator $U(t,t')$ is diagonal in both J and m and therefore only elastic non-m-changing collisions are included in their treatment. Their expression for the absorption coefficient can then be written in terms of the mean induced dipole moment. In our Eq. (76), m-changing collisions are permitted and the phase factor in Eq. (74) associated with the induced dipole moment includes the effects of propagation. Moreover, we see no simple relationship between the mean induced dipole moment and Eq. (74). The phase factor $\Delta'+i\Delta''$ in Eq. (74) is not identical to that of Herman, Tippings and Poll [6], although in both treatments Δ' and Δ'' are constrained to remain between $+1$ and -1.

C. Rotational level mixing

There have been attempts to include inelastic collisions in the analysis by rotational level mixing effects through the anisotropic part of the intermolecular potential [26,27]. In their approach to the problem, Tabisz and Nelson [26] assume there is no propagation and that U is diagonal. The leading anisotropic term in the interaction between a HD molecule and an inert gas atom is of the form $P_1(\cos\theta)$. Only contributions from the anisotropic overlap that are part of the pair-induced dipole moment are found to contribute to the rotational level mixing, and the effect of this mixing on the magnitude of the calculated interference is small [4,26,27].

The present formalism includes propagation. If ΔE is the energy difference between the states coupled by V_e^a and the evolution operator is expanded in time, under the

assumption that $\Delta E\tau_c \gg 1$ (which in general is not true), then

$$U_e^I(t,0)=1+\int_0^t dt' e^{i\Delta Et/h}V_e^a(t') \sim 1-\frac{V_e^a(0)}{(\Delta E/\hbar)}+\cdots . \quad (77)$$

The leading term in the expansion of U_e^I beyond the diagonal term is of the same form as the first-order time-independent perturbation theory result used by Tabisz and Nelson [26] to describe rotational level mixing. Therefore, the present analysis contains earlier attempts at including inelastic collisions. It goes further, however. Because the full propagator U_e^I is used and inelastic transitions may occur at times during the collision other than when the dipole operator acts, several components of the induced dipole moment may participate in the optical transition. In particular, the strong isotropic overlap induced dipole component, which alone cannot connect the initial and final states involved in the $\Delta J=1$ transitions [R (J) lines], may play a role and the magnitude of the interference effect calculated by the present theory may differ markedly from earlier efforts.

VIII. SUMMARY

A theory has been described which gives an expression for the spectral line shape due to the interference between allowed and collision-induced transitions in pure molecular spectra. It includes effects due to J and m mixing, as well as a contribution from successive collisions. The only fundamental approximation is the binary collision approximation. The formalism remains the same without the classical trajectory approximation. Calculations are now underway in which the theory is applied to HD-He and HD-Ar systems. The results and their physical implications will be reported in a future paper.

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APPENDIX

To approach the problem from first principles, the full Hamiltonian given by Eq. (3) is used in the equation of motion (1). The operators $L_{\rm RF}$ and $L_{\rm PF}$, associated with $H_{\rm RF}$ and $H_{\rm PF}$, are expressed in a manner analogous to Eq. (16). Equation (1) is transformed to the interaction picture and the projection operators Eqs. (19)–(22) are applied to give an equation of motion for $P\rho(t)$ of the same form as Eq. (27). The spectrum is found by the methods of Sec. III, starting from Eq. (29). The required portion of the equation of motion for $P\rho(t)$, which is in first order in E_0 is

$$\frac{\partial}{\partial t}P\rho^I(t)=NPV^I(t)\int_0^t U^I(t,t')V^I(t')P\rho^I(t')dt'+PL_{\rm RF}^I(t)P\rho^I(t) +NPL_{\rm PF}^I(t)\int_0^t U^I(t,t')V^I(t')P\rho^I(t')dt'+NPV^I(t)\int_0^t U^I(t,t')L_{\rm PF}^I(t')P\rho^I(t')dt' +NPV^I(t)\int_0^t dt'\int_{t'}^t dt_1 U^I(t,t_1)[L_{\rm RF}^I(t_1)+L_{\rm PF}^I(t_1)]U^I(t_1,t')V^I(t')P\rho^I(t') . \quad (A1)$$

The binary collision approximation has been made in writing Eq. (A1). V^I is the full interaction potential between the radiator and a single perturber. $U^I(t,t')$ is the single-particle collisional propagator. The term $PL_{\rm PF}^I P\rho^I$ vanishes as $P\rho^I$ is diagonal in perturber states and $L_{\rm PF}^I$ is off-diagonal in those states.

The derivation of the effective interaction V_e and the effective dipole $\hat{D}_e$ proceeds in the same way as in Alber and Cooper [9]. Basically, it is a procedure that [by formally integrating by parts the equation for $U^I(t,t')$] eliminates the fast time variations due to the virtual transitions in the perturber. The contribution of these rapidly varying terms to the spectrum is smaller than the retained terms by a factor $\Delta/(E_{e_1}-E_{g_1})$ where e_1 and g_1 are the ground and excited states of the perturber and E is their energy.

In this manner we have shown that one obtains from Eq. (A1) the same spectrum as in Eq. (51) with $\hat{D}_e$ and V_e defined in terms of the perturber dipole $\hat{D}_p$ and $\hat{V}$ by the following expressions:

$$\langle\langle \alpha_R g_1,\gamma_R\alpha_1|\hat{D}_e|\beta_R g_1,\gamma_R\alpha_1\rangle\rangle=\sum_{e_1}\left[\frac{\langle g_1|\hat{D}_P|e_1\rangle\langle\alpha_R e_1|\hat{V}|\beta_R g_1\rangle}{E_{\beta_R}+E_{g_1}-E_{\alpha_R}-E_{e_1}}+\frac{\langle\alpha_R g_1|\hat{V}|\beta_R e_1\rangle\langle e_1|\hat{D}_P|g_1\rangle}{E_{\alpha_R}+E_{g_1}-E_{\beta_R}-E_{e_1}}\right] \quad (A2)$$

and

$$\langle\langle \alpha_R g_1,\beta_R g_1|V_e|\gamma_R g_1,\delta_R g_1\rangle\rangle =\frac{1}{i\hbar}\left[\sum_{\alpha_R',e_1}\frac{\langle\alpha_R g_1|\hat{V}|\alpha_R' e_1\rangle\langle\alpha_R' e_1|\hat{V}|\gamma_R g_1\rangle}{E_{\gamma_R}+E_{g_1}-E_{\alpha_R'}-E_{e_1}}\delta_{\beta_R\delta_R}-\sum_{\alpha_R' e_1}\frac{\langle\delta_R g_1|\hat{V}|\alpha_R' e_1\rangle\langle\alpha_R' e_1|\hat{V}|\beta_R g_1\rangle}{E_{\delta_R}+E_{g_1}-E_{\alpha_R'}-E_{e_1}}\delta_{\alpha_R\gamma_R}\right] . \quad (A3)$$

The difference here from the treatment of Alber and Cooper [9] is that we allow $\hat{V}_e$ to couple a whole manifold of radiator states instead of just the degenerate ones. Also it is interesting to note that only the second term of Eq. (A2) is obtained if the RWA is made on the perturber-light field interactions. This would be an incorrect procedure for this case, which is far from resonance with the perturber states.

It is seen in Eq. (A2) that $\hat{D}_e$ results from an allowed transition occurring in the perturber during an interaction between the perturber and the radiator. Thus $\hat{D}_e$ may be considered as involving the dipole moment induced in the pair. In subsequent computations with the formalism developed in this paper, $\hat{D}_e$ and $\hat{V}_e$ will be identified with empirical, semiempirical, or calculated expressions, which apply in the adiabatic or quasistatic limit.

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*Permanent address: Department of Physics, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2.

†Present address: Department of Chemistry, University of Rochester, Rochester, NY 14627.

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