Master-equation approach to collisionally induced absorption and emission

G. Alber and J. Cooper
Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, Boulder, Colorado 80309
and Department of Physics, University of Colorado, Boulder, Colorado 80309
(Received 12 November 1985)

We study the collisionally induced excitation and photon emission of a neutral radiator atom surrounded by a gas of neutral foreign perturbers within the binary-collision approximation. We derive an equation of motion for the reduced density matrix of the radiator and obtain the spectrum of the spontaneously emitted photons including components due to collisionally induced radiation and to Rayleigh scattering, which is valid in both impact and quasistatic regimes. In our formulation single and subsequent collisional contributions are taken into account, and various coherent and incoherent corrections are examined.

I. INTRODUCTION

Collisionally induced transitions are intrinsically interesting for spectral line broadening studies and intermolecular interactions. They are also of interest for their possible applications in high-energy laser amplifier devices.[1] In these processes, which are of the type

$$R(i)+P(g)+\hbar\omega \rightarrow R(f)+P(g) \quad \text{(excitation)} ,$$

$$R(f)+P(g) \rightarrow R(i)+P(g)+\hbar\omega_k \quad \text{(emission)} ,$$

a neutral atom or molecule (radiator R), which undergoes collisions with neutral perturber atoms (P), is excited by a laser field of frequency ω from its ground state $|i\rangle$ to an excited state $|f\rangle$, or it decays from this excited state back to its ground state, emitting a photon of frequency ω_k. As the transition $|i\rangle \rightarrow |f\rangle$ is dipole forbidden, these processes can be due to (a) a higher-order multiple transition (e.g., electric quadrupole) or (b) a dipole moment, which is induced in the radiator by collisions with perturbers.

The transition rate due to mechanism (a) is centered around the frequency of the dipole-forbidden transition $(E_f-E_i)/\hbar$ with a width determined by a typical (impact) collision rate γ_c. In contrast, the collisionally induced transition band due to process (b) typically extends from $(E_f-E_i)/\hbar$ to a few times the inverse duration of a collision $(1/\tau_c)$ into the red or blue. These collisionally induced transitions, which are the main subject of this paper, have been studied in absorption and emission, both experimentally and theoretically, and are usually interpreted in terms of (free-free) dipole transitions between two molecular states of the radiator-perturber molecular collision complex.[2–6] The lifetime of this transient collision complex, which is of the order of the duration of a collision τ_c, determines the scale of the frequency dependence of the collisionally induced transition rate. Ueda and Fukuda[6] have pointed out that for a satisfactory explanation of the excitation profiles, the dipole moments of the radiator *and* the perturber are important. In their Ca-Xe $4s^2\,{}^1S_0$–$4s\,3d\,{}^1D_2$ excitation experiment, for example, they attributed the central peak around $(E_f-E_i)/\hbar$ (width $\sim 1/\tau_c$) to a molecular transition involving the perturber dipole, whereas the huge satellite peak in the blue wing was assigned to a transition due to the radiator dipole.

Collisionally induced excitation (or emission) experiments are usually performed in a gas cell with a radiator density that is small in comparison with the perturber density. If the perturber density is low enough so that (strong) collisions are well separated in time (binary-collision regime), we can distinguish between single (intra-) collisional and subsequent (inter-) collisional contributions to the observable of interest. The single collisional contribution to the excitation rate, for example, is given by the excitation rate of a single radiator-perturber collision complex multiplied by the number of perturbers and radiators.

This molecular point of view, however, is not adequate for treating the subsequent collisional contributions. Lewis and Van Kranendonk[7–10] have shown that intercollisional contributions can lead to a dip in the excitation rates of rotational or vibrational molecular transitions. This dip is centered at $(E_f-E_i)/\hbar$ and has a width that is small in comparison with $1/\tau_c$ and is proportional to the perturber density. This intercollisional effect is due to interferences associated with a correlation of the relative orientations of the dipole moments induced during subsequent collisions. These dipole moments are not randomly oriented but are most likely pointing in opposite directions. This effect is predicted to lead to a peak in the emission rate at $(E_f-E_i)/\hbar$. Herman's[11] calculations reveal that in HD-Kr this intercollisional contribution is competitive with the interference contribution between a (small) permanent dipole and the dipole induced during single collisions. Interpretation of the work of Lewis and Van Kranendonk[7] indicates that these intercollisional effects are expected to become negligible if collisions are not velocity changing as far as their effect on the mean induced dipole moment is concerned. This is usually the case in atomic or electronic molecular transitions, for which a small lower-state interaction leads to the dipole moving on a straight trajectory, whereas rotational or vibrational molecular transitions, for which the collisional interactions in upper and lower states are almost equal, tend to change the velocity associated with the mean induced dipole significantly (and at the same time give a relatively small phase change to the mean induced dipole moment).[12]

In this paper we study collisionally induced excitation of a dipole-forbidden atomic transition and the spectrum of the photon that is spontaneously emitted during this process. We start from the full density matrix equations, which describe the dynamics of the radiator surrounded by a dilute gas of foreign perturbers. The radiator and perturbers thereby interact with the exciting laser field and all other (unoccupied) modes of the radiation field. Within the binary-collision approximation[13,14] (BCA) we derive the reduced density matrix equation of the radiator and an expression for the spectrum of the spontaneously emitted photon. The exciting laser field is assumed to be weak so that it does not significantly modify the collision dynamics, but we allow for saturation of the dipole-forbidden radiator transition. Our treatment automatically takes into account single and subsequent collisional contributions and is uniformly valid for impact excitation (or emission) as well as in the quasistatic limit. Our expressions also include effects due to degeneracy of the excited radiator state. For simplicity, we assume the ground state of the radiator and the perturber to be nondegenerate. Our investigation focuses mainly on heavy radiators whose velocity is essentially unchanged by collisions with the perturbers. This simplifies the analysis considerably, as the collision environment of the radiator is spherically symmetric in this case. However, we also comment on modifications that are necessary if velocity changes of the radiator become significant. As effects due to the radiator velocity are usually small, if velocity-changing collisions can be neglected, we expect our analysis also to be valid for lighter radiators as long as only atomic or electronic molecular transitions are considered.[12,15]

In Sec. II we present the physical system under investigation and discuss the reduced density matrix equation of the radiator together with the approximations involved in its derivation. In Sec. III we derive the corresponding equation for the spectrum of the spontaneously emitted photon and discuss the physical significance of the various terms. Details of the derivations can be found in Appendixes A and C. In Appendix B we discuss the gauge invariance of the collisionally induced spontaneous decay rate.

II. DENSITY MATRIX EQUATIONS

We consider one neutral radiator atom, which collisionally interacts with N neutral (noninteracting) perturber atoms in a gas cell. (The generalization to $N_R \ll N$ radiator atoms is straightforward.) The radiator and the perturbers interact with an (assumed) classical monochromatic laser field

$$\mathbf{E}_c(\mathbf{x},t)=\mathscr{E}_0\mathbf{e}e^{-i(\omega t-\mathbf{k}_c\cdot\mathbf{x})}+\text{c.c.} \tag{1a}$$

and the (transverse) spontaneous modes of the radiation field represented by the electric field operator

$$\hat{\mathbf{E}}_s(\mathbf{x})=\sum_{k,\lambda}[\hat{\mathbf{E}}_{k,\lambda}(\mathbf{x})+\text{H.c.}] \tag{1b}$$

with

$$\hat{\mathbf{E}}_{k,\lambda}(\mathbf{x})=i\left[\frac{\hbar\omega_k}{2\epsilon_0\bar{V}}\right]^{1/2}\boldsymbol{\varepsilon}_{k,\lambda}e^{i\mathbf{k}\cdot\mathbf{x}}a_{k,\lambda}$$

and $|\mathbf{k}|=\omega_k/c$. $\boldsymbol{\varepsilon}_{k,\lambda}$ is the polarization of mode $(\mathbf{k},\lambda)$ and $a_{k,\lambda}$ is the associated photon destruction operator. $\bar{V}$ is the quantization volume. The Hamiltonian determining the time evolution of this system is, for the radiative interaction in the dipole approximation, given by

$$\begin{aligned}H=H_R+\sum_{j=1}^{N}\left[\frac{\mathbf{p}_j}{2M}+H(j)\right]+\sum_{j=1}^{N}V(|\mathbf{x}_R-\mathbf{x}_j|)\\ -\sum_{j=R,1,\ldots,N}\boldsymbol{\mu}_j\cdot\mathbf{E}_c(\mathbf{x}_j,t)\\ -\sum_{j=R,1,\ldots,N}\boldsymbol{\mu}_j\cdot\hat{\mathbf{E}}_s(\mathbf{x}_j)+H_F\end{aligned} \tag{2}$$

with the free-field Hamiltonian

$$H_F=\sum_{k,\lambda}\hbar\omega_k a_{k,\lambda}^{\dagger}a_{k,\lambda}\ .$$

H_R and $H(j)$ are the Hamiltonians of the internal degrees of freedom of the radiator and the perturbers, and $V(|\mathbf{x}_R-\mathbf{x}_j|)$ is the collisional interaction between them. $\boldsymbol{\mu}_j$ is the dipole moment of atom j. For simplicity, we have neglected the center-of-mass motion of the radiator in the Hamiltonian of Eq. (2), which corresponds to considering a heavy-radiator limit ($M_R \gg M$), although we will comment about its effect when we compare spherical and cylindrical symmetry of the collision environment. We can therefore set $\mathbf{x}_R=0$.

The density operator of the whole system obeys the equation of motion

$$\frac{d}{dt}\rho_s(t)=\frac{1}{i\hbar}[H,\rho_s(t)],\quad t\geq 0\ . \tag{3}$$

In the interaction picture defined by

$$\rho_s(t)=U_0(t,0)\rho_I(t)$$

with

$$U_0(t,0)=\exp\left[\left[L_R+L_F+\sum_{j=1}^{N}(L_{P_j}+L_j)\right]t\right]$$

this reduces to

$$\frac{d}{dt}\rho_I(t)=\left[L_c^{(R)}(t)+L_s^{(R)}(t)+\sum_{j=1}^{N}[V_j(t)+L_c^{(j)}(t)+L_s^{(j)}(t)]\right]\rho_I(t)\ . \tag{4a}$$

The Liouville operators are defined as follows (see, for example, Appendix A of Ref. 16, and also Ref. 17), where $\{\cdots\}$ refers to an arbitrary Hilbert-space operator:

$$L_{P_j}(\{\cdots\}) = \frac{1}{i\hbar}\left[\frac{\hat{\mathbf{p}}_j^2}{2M}, \{\cdots\}\right],$$

$$L_R(\{\cdots\}) = \frac{1}{i\hbar}[H_R, \{\cdots\}],$$

$$L_j(\{\cdots\}) = \frac{1}{i\hbar}[H(j), \{\cdots\}],$$

$$V_j(t)[\{\cdots\}] = \frac{1}{i\hbar}[V(|\mathbf{x}_R - \mathbf{x}_j|, t), \{\cdots\}], \quad \text{(4b)}$$

$$L_c^{(k)}(t)[\{\cdots\}] = \frac{1}{i\hbar}[-\boldsymbol{\mu}_k(t)\cdot\mathbf{E}_c(\mathbf{x}_k, t), \{\cdots\}],$$

$$L_s^{(k)}(t)[\{\cdots\}] = \frac{1}{i\hbar}[-\boldsymbol{\mu}_k(t)\cdot\hat{\mathbf{E}}_s(\mathbf{x}_k, t), \{\cdots\}],$$

$$L_F(\{\cdots\}) = \frac{1}{i\hbar}[H_F, \{\cdots\}],$$

with

$$\mathcal{O}(t) = \bar{U}_0^{\dagger}(t,0)\mathcal{O}\bar{U}_0(t,0) \quad \text{(4c)}$$

and

$$\bar{U}_0(t,0) = \exp\left\{\frac{1}{i\hbar}\left[H_R + H_F + \sum_{j=1}^{N}\left[H(j) + \frac{\hat{\mathbf{p}}_j^2}{2M}\right]\right]t\right\} \quad \text{(4d)}$$

for an arbitrary Schrödinger-picture operator $\mathcal{O}$.

Define a projection operator (see, e.g., Ref. 16) in tetradic notation (for a discussion of tetradics see, e.g., Appendix B of Ref. 17) by

$$\mathcal{P}(\cdots) = |\{0\},\{0\}\rangle\rangle \, \mathrm{Tr}_{\mathrm{RAD}}\left[\prod_{j=1}^{N} p_j\right], \quad \text{(5)}$$

where RAD denotes spontaneous radiative modes, with

$$p_j = |g,g\rangle\rangle \rho(\mathbf{p}_j)\,\mathrm{Tr}_j(\cdots).$$

The reduced density operator of the radiator $\sigma_I(t)$ in the interaction picture is given by

$$\sigma_I(t) = \mathrm{Tr}_{\mathrm{RAD},\{p\}}(\mathcal{P}\rho_I(t)). \quad \text{(6)}$$

Thus $|g\rangle$ is the ground state of the perturbers, which for simplicity is assumed to be nondegenerate. $\rho(\mathbf{p}_j)$ is the density operator for the center-of-mass motion of the jth perturber. We assume in the following that it describes an equilibrium situation, i.e., $L_{p_j}\rho(\mathbf{p}_j)=0$, and is normalized in the sense that $\int d^3p_j\rho(\mathbf{p}_j)=1$. $|\{0\}\rangle$ is the ground state of the spontaneous modes of the electromagnetic field so that $|\{0\},\{0\}\rangle\rangle$ denotes the initial density matrix for the spontaneous radiation field (compare Ref. 16). Tr_j ($\mathrm{Tr}_{\mathrm{RAD}}$) denotes the trace over the degrees of freedom of the jth perturber (spontaneous modes). $\mathrm{Tr}_{\{p\}}$ indicates the trace over all perturber variables. The projected equation of motion for the density operator, which fulfills the initial condition for decorrelation at $t=0$ (as discussed below), namely, $\mathcal{Q}\rho_I(t=0)=0$, with $\mathcal{Q}=\mathbb{1}-\mathcal{P}$, is easily obtained from Eq. (4a), namely,

$$\begin{aligned}\frac{d}{dt}\mathcal{P}\rho_I(t) = {} & \left[L_c^{(R)}(t) + \mathcal{P}\sum_{j=1}^{N} V_j(t)\mathcal{P}\right]\rho_I(t) \\ & + \mathcal{P}\left[L_s^{(R)}(t) + \sum_{j=1}^{N} V_j(t)\right] \\ & \times \int_0^t dt' G(t,t')\left[L_s^{(R)}(t') + \sum_{i=1}^{N}[\mathcal{Q}V_i(t') + L_c^{(i)}(t') + L_s^{(i)}(t')]\right]\mathcal{P}\rho_I(t'), \quad t \geq 0\end{aligned} \quad \text{(7a)}$$

with

$$\frac{d}{dt}G(t,t') = \left[L_c^{(R)}(t) + \mathcal{Q}L_s^{(R)}(t) + \sum_{j=1}^{N}[L_c^{(j)}(t) + L_s^{(j)}(t) + \mathcal{Q}V_j(t)]\right]G(t,t'), \quad t \geq t' \quad \text{(7b)}$$

and $G(t',t')=\mathbb{1}$. This projected equation therefore assumes complete decorrelation between all constituents of the system at $t=0$ with all perturbers and all spontaneous modes in their ground states. However, as correlations within our system decay roughly on a time scale of order $\max\{\tau_c, \tau_{\mathrm{RAD}}\}$, where $\tau_c \approx 10^{-12}$ s is the typical duration of a (strong) collision and $\tau_{\mathrm{RAD}} \approx 10^{-16}-10^{-18}$ s is the typical correlation time associated with the spontaneous modes of the radiation field,[16] Eq. (7a) is valid for times $t \gg \max\{\tau_c, \tau_{\mathrm{RAD}}\}$ even if the above initial condition, i.e., $\mathcal{Q}\rho_I(t=0)=0$, is slightly violated (because the effect of any initial correlation will have decayed away[16]). Equation (7a) is more general than the corresponding equation of Ref. 16 because we also allow the perturbers to interact with the laser field and we have not eliminated the spontaneous modes of the radiation field in a Born-Markov approximation.[16,18]

Starting from the general equation (7a) we want to derive a reduced equation of motion for the radiator, which describes collisionally induced laser excitation and collisionally induced spontaneous decay. To simplify matters as much as possible we restrict our further investigations to the following situation.

(1) For radiator-perturber collisions we assume a low perturber density so that different (strong) collisions are well separated in time, which is the usual BCA.[13,14,16] We therefore require that the duration of a (strong) collision τ_c be much less than the time between different collisions, i.e.,

$$\tau_c \ll 1/\gamma_c \,, \tag{8}$$

where γ_c is a typical (impact) collision rate. Further, we assume a spherically symmetric collision environment for the radiator, consistent with the neglect of the radiator motion in Eq. (2) (heavy-radiator limit). However, as mentioned earlier, we later comment on what occurs if the radiator is no longer heavy and spherical symmetry has to be replaced by cylindrical symmetry due to the motion of the radiator through the perturber ensemble.

(2) We focus our attention on a laser excitation process as schematically represented in Fig. 1. A monochromatic laser field of frequency ω is almost in resonance with the dipole-forbidden radiator transition $|i\rangle \to |f\alpha\rangle$. For simplicity we assume that $|i\rangle$ is the nondegenerate ground state, which is initially populated, and $|f\alpha\rangle$ is the first excited-state manifold with total angular momentum $j_f=2$ (α labels the various substrates). We allow only for collisionally induced transitions and neglect radiative higher-order multipole transitions. It is further assumed that within the radiator or perturber, there is no other transition that is in resonance with the exciting laser field. The radiator states $|k\rangle$ are considered to be sufficiently separated from $|f\alpha\rangle$ and $|i\rangle$ so that inelastic collisions can be neglected. Thus we have

$$|E_i+\hbar\omega-E_f|\,,\;\; 1/\tau_c \ll |E_f-E_k|\,,\;\; |E_i-E_k| \,. \tag{9}$$

This adiabaticity condition assures that there is no population transfer between $|f\alpha\rangle$ and any higher excited radiator manifold, which may couple to $|i\rangle$ via a dipole transition.

(3) The Rabi frequencies associated with the exciting laser field are assumed to be small in the sense that collisions between radiator and perturber are not affected by the laser field, i.e.,

$$\frac{1}{\hbar}|\boldsymbol{\mu}_R\cdot\mathbf{e}\mathscr{E}_0|\,,\;\; \frac{1}{\hbar}|\boldsymbol{\mu}_j\cdot\mathbf{e}\mathscr{E}_0| \ll 1/\tau_c \ll \omega \,. \tag{10a}$$

We also neglect effects due to spontaneous emission of

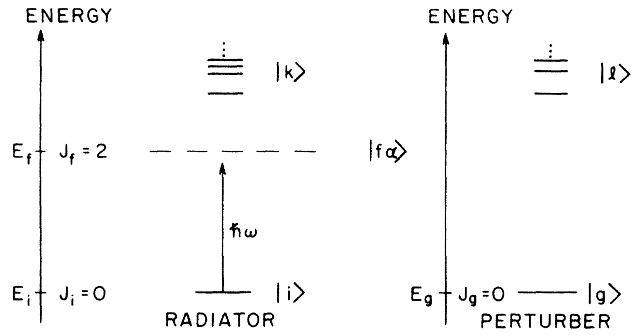

FIG. 1. Schematic representation of the excitation process.

photons on the collision dynamics, which assumes that

$$\gamma \ll 1/\tau_c \,. \tag{10b}$$

However, because the excited radiator manifold $|f\alpha\rangle$ can only emit a photon during a collision, γ is a collisionally induced spontaneous decay rate and relation (10b) is not a severe restriction.

(4) We assume that the excited radiator manifold is much more polarizable than the ground state, i.e., we assume no lower-state interaction [see Eq. (A23)]. This type of situation is usually found in studies of collisionally induced absorption of, e.g., an alkaline-earth atom perturbed by noble-gas atoms. If collisionally induced rotational or vibrational transitions in a molecule (as the radiator) are investigated, this assumption is unrealistic.[12] We comment later on the differences between such transitions and the collisionally induced atomic transitions, which are the main subject of this paper. For simplicity we also restrict ourselves to detunings $|E_f-E_i-\hbar\omega| \ll kT$, so that trajectory effects due to the perturber center-of-mass motion are negligible [see Eq. (A24)].[16]

Condition (3) allows us to perturbatively expand the propagator $G(t,t')$ of Eq. (7b), which describes collisions between the radiator and perturbers in the presence of spontaneous modes and an exciting laser field, in terms of $L_s^{(k)}, L_c^{(k)}$. Inserting this expansion into Eq. (7a) and taking into account the adiabaticity condition [Eq. (9)], we can write the reduced density matrix equation for the excited-state manifold of the radiator in the form

$$\begin{aligned}
\frac{d}{dt}\langle\langle ffKQ\,|\,\sigma_I(t)\rangle\rangle = {}& \int_0^t dt'\langle\langle ffKQ\,|\,M_0^{(0)}(t,t')\,|\,ffKQ\rangle\rangle\langle\langle ffKQ\,|\,\sigma_I(t')\rangle\rangle \\
&+\sum_{Q'}\int_0^t dt'\langle\langle ffKQ\,|\,M_1^{(0)}(t,t')\,|\,fi\,K'=2\,Q'\rangle\rangle\langle\langle fi\,K'=2\,Q'\,|\,\sigma_I(t')\rangle\rangle \\
&+\sum_{Q'}\int_0^t dt'\langle\langle ffKQ\,|\,M_1^{(0)}(t,t')\,|\,if\,K'=2\,Q'\rangle\rangle\langle\langle if\,K'=2\,Q'\,|\,\sigma_I(t')\rangle\rangle \\
&+\sum_{K',Q'}\int_0^t dt'\langle\langle ffKQ\,|\,M_2^{(0)}(t,t')\,|\,ffK'Q'\rangle\rangle\langle\langle ffK'Q'\,|\,\sigma_I(t')\rangle\rangle \\
&+\int_0^t dt'\langle\langle ffKQ\,|\,M_2^{(0)}(t,t')\,|\,ii\,K'=Q'=0\rangle\rangle\langle\langle ii\,K'=Q'=0\,|\,\sigma_I(t')\rangle\rangle \\
&+\sum_{K',Q'}\int_0^t dt'\langle\langle ffKQ\,|\,M_0^{(2)}(t,t')\,|\,ffK'Q'\rangle\rangle\langle\langle ffK'Q'\,|\,\sigma_I(t')\rangle\rangle
\end{aligned} \tag{11}$$

and a similar set of equations for the ground-state population, $\langle\langle ii\,K=Q=0\,|\,\sigma_I(t)\rangle\rangle$, and the optical coherences, $\langle\langle fi\,K=2Q\,|\,\sigma_I(t)\rangle\rangle$, $\langle\langle if\,K=2Q\,|\,\sigma_I(t)\rangle\rangle$. The tetradic operators $M_n^{(m)}$ characterize couplings of nth order in $L_c^{(k)}$ and mth order in $L_s^{(k)}$ and are defined in Appendix A.

In Eq. (11) we have also used the fact that due to the spherically symmetric collision environment of the radiator, the pure collisional coupling, represented by $M_0^{(0)}(t,t')$, is diagonal in the radiator tetradics $|ffKQ\rangle\rangle$ [see Eq. (A9)].[19] The physical significance of the various terms of Eq. (11) is straightforward, and similar expressions with similar interpretations are found in other problems related to the redistribution of radiation (see, e.g., Appendix C of Ref. 17). The first term proportional to $M_0^{(0)}(t,t')$ describes collisional mixing within the radiator manifold $|f\alpha\rangle$ (inelastic collisions are neglected). Because the transition $|i\rangle\rightarrow|f\alpha\rangle$ is dipole forbidden, the radiator can only be excited by the combined action of the laser field and a collision, and it can only decay by collisionally induced spontaneous decay. These processes are represented by the other five terms of Eq. (11). It is shown in Appendix A that all the $M_n^{(m)}$'s in these terms reduce to one-perturber averages within the BCA and are therefore proportional to the perturber density N/V. The fifth term in Eq. (11) describes collisionally induced laser excitation from the radiator ground state $|i\rangle$ during single collisions, while the second and third terms characterize the same process occurring during subsequent collisions. For subsequent collisions the creation of an optical radiator coherence, which corresponds to a mean induced dipole moment, is involved. The fourth and the last terms give rise to stimulated and spontaneous decay of the excited radiator manifold $|f\alpha\rangle$ during single collisions. As the radiator coherences $\langle\langle fi\,K=2Q\,|\,\sigma_I(t)\rangle\rangle$, $\langle\langle if\,K=2Q\,|\,\sigma_I(t)\rangle\rangle$ are also influenced by $\langle\langle ffKQ\,|\,\sigma_I(t)\rangle\rangle$, the second and third terms in Eq. (11) also contain subsequent collisional contributions to the stimulated decay rate of the excited-state manifold.

In Appendix A we outline the evaluation of the various matrix elements of Eq. (11) within the BCA and show that the reduced density matrix equation of the radiator is given by

$$\left[\frac{d}{dt}+\gamma+\frac{W}{2j_f+1}\right]\sigma_{ff}(t)=W\sigma_{ii}(t)\,,$$
$$\left[\frac{d}{dt}+W\right]\sigma_{ii}(t)=\left[\gamma+\frac{W}{2j_f+1}\right]\sigma_{ff}(t)\,, \tag{12}$$

which has to be solved with the initial condition

$$\sigma_{ii}(t=0)=1,\quad \sigma_{ff}(t=0)=0\,.$$

The total excited- [ground-] state population of the radiator is denoted $\sigma_{ff}(t)=\sqrt{2j_f+1}\langle\langle ff\,K=Q=0\,|\,\sigma_I(t)\rangle\rangle$ $[\sigma_{ii}(t)=\langle\langle ii\,K'=Q'=0\,|\,\sigma_I(t)\rangle\rangle]$ [see Eq. (A9)].

The collisionally induced laser excitation rate W is given by

$$W=N\int d^3p_1\int\cdots\int d^3p_4\rho(\mathbf{p}_4)$$
$$\times 2\,\mathrm{Re}\sum_{\alpha,\beta}\int_0^t dt' e^{i\omega t'}\frac{1}{\hbar^2}\langle f\alpha g\mathbf{p}_1\,|\,[D_c^{(R)}(t')+D_c^{(1)}(t')]\,|\,ig\mathbf{p}_2\rangle^*$$
$$\times\langle\langle f\alpha g\mathbf{p}_1,ig\mathbf{p}_2\,|\,U_1^e(t',0)\,|\,f\beta g\mathbf{p}_3,ig\mathbf{p}_4\rangle\rangle\langle f\beta g\mathbf{p}_3\,|\,[D_c^{(R)}(0)+D_c^{(1)}(0)]\,|\,ig\mathbf{p}_4\rangle \tag{13a}$$

with the collisionally induced dipole coupling

$$\langle f\alpha g\mathbf{p}\,|\,D_c^{(j)}(t)\,|\,ig\mathbf{p}'\rangle=\left\langle f\alpha g\mathbf{p}\,\middle|\,\left[\boldsymbol{\mu}_j(t)\cdot\mathbf{e}\mathscr{E}_0\frac{1}{H_R+H(1)-E_i-E_g}V(|\mathbf{x}_1|,t)\right.\right.$$
$$\left.\left.+V(|\mathbf{x}_1|,t)\frac{1}{H_R+H(1)-E_f-E_g}\boldsymbol{\mu}_j(t)\cdot\mathbf{e}\mathscr{E}_0\right]\,\middle|\,ig\mathbf{p}'\right\rangle,\quad j=R,1\,. \tag{13b}$$

Here $V(|\mathbf{x}_1|,t)$ is the "true" collisional interaction between the radiator and perturber 1, which is off diagonal in the electronic radiator-perturber states; $U_1^e(t',0)$ is the effective tetradic collisional propagator of Eq. (A7b). In Eq. (12) we have assumed that times $t\gg\tau_c$ are of interest so that the integration in Eq. (13a) can be extended to infinity, and the radiator density matrix elements are slowly varying on a time scale of order τ_c [see Eqs. (A29) and (A30)]. Because of the resonance condition (9) the energy denominators in Eq. (13a) are independent of the laser frequency ω. We further neglect the center-of-mass motion of the perturber in these denominators, because $kT\ll\hbar\omega$, and put $e^{i\mathbf{k}_c\mathbf{x}_1}\rightarrow 1$ since we always have to deal with the product $e^{i\mathbf{k}_c\mathbf{x}_1}V(|\mathbf{x}_1|)$ in Eq. (13a) and the collisional interaction is short range, i.e., $|\mathbf{k}_c|b_w\ll 1$ [b_w is the Weisskopf radius; see Eq. (C8)]. Note that Eq. (13b) contains terms that are usually considered "off resonant," as well as "resonant" terms.

In Appendix A 2 it is shown that in a spherically symmetric collision environment of the radiator, no optical radiator coherence $\langle\langle fi\,K=2Q\,|\,\sigma_i(t)\rangle\rangle$ or $\langle\langle if\,K=2Q\,|\,\sigma_I(t)\rangle\rangle$ can be excited. The average collisionally induced dipole moment of the radiator, which is dominated by these optical coherences, is therefore zero and the second and third terms of Eq. (11) do not contribute to Eq. (12). For the optical radiator coherence, the collision environment of the radiator can usually be considered as spherically symmetric whenever the associated trajectory of the induced dipole is essentially a straight line, which is unaffected by collisions with perturbers. This is the case when the radiator either is heavy or its ground-state interaction is negligible [see condition (4)]. However, a moving radiator sees a "wind" of perturbers moving by it with a velocity $-\mathbf{v}$ (Ref. 20) and the various m substates are differently affected by this wind. Effects due to this breaking of the spherical symmetry by the velocity of the radiator are expected to be small. This expectation is based on studies of radiator velocity effects in line broadening (see, e.g., Refs. 15 and 20). However, an analogous calculation for these collisionally induced transitions has not yet been performed. In general, the breaking of the spherical symmetry by the velocity of the radiator will create an optical coherence, which will give rise to a subsequent collisional contribution to the excitation rate. This contribution will have a maximum at $(E_f-E_i)/\hbar$ with a width determined by a typical (impact) collision rate γ_c. The value of the maximum will be proportional to N in contrast to the peak height associated, for example, with an $E2$ transition, which is inversely proportional to N. However, the maximum of this peak is expected to be down by a factor $\epsilon^2 \ll 1$ in comparison with the single collisional contribution to the excitation rate. Here ϵ is a measure for the breaking of the spherical symmetry of the collision environment of the radiator (e.g., $\epsilon \lesssim 0.1$ for velocities of importance around the mean velocity in the study of Cooper and Stacey[15] of radiator velocity effects in the line broadening by dipole-dipole interactions). If upper- and lower-state interactions of the radiator are comparable in magnitude (e.g., in rotational or vibrational molecular transitions), then collisions tend to change the radiator velocity significantly.[12] It has been shown by Lewis and Van Kranendonk[7–10] that in this case the dipole moments induced in subsequent collisions are correlated and each collision on the average tends to change the direction (by approximately 180°) of the collisionally induced dipole. This leads to a dip in the excitation rate at exact resonance, i.e., $E_i+\hbar\omega-E_f=0$, whose width is proportional to the perturber density. The value of this dip can even become zero indicating that single and subsequent collisional contributions are equally important.

W in Eq. (13a) is the collisionally induced excitation rate due to single collisions and is valid for both impact excitation, i.e., $\hbar^{-1}|E_i+\hbar\omega-E_f|\tau_c \ll 1$, and quasistatic excitation, where $\hbar^{-1}|E_i+\hbar\omega-E_f|\tau_c \gg 1$. It also determines the stimulated emission rate $W/(2j_f+1)$ from the excited radiator manifold. As discussed in Appendix A, W in Eq. (13a) describes both of these processes properly, if condition (A24), i.e., $|E_i+\hbar\omega-E_f| \ll kT$, is fulfilled. Otherwise, trajectory effects within the excited radiator manifold might become important and the stimulated emission rate as determined by Eq. (13a) must be modified. Collisional mixing before the excitation process $|i\rangle \rightarrow |f\alpha\rangle$ is unimportant if there is no lower-state interaction [see Eq. (A23)], and it is negligible after excitation or stimulated emission if one is only interested in total rates into a radiator manifold ($K=0$ multipole components) and inelastic collisions are neglected (see Appendix A 3).[16] Equation (13a) properly takes into account collisionally induced excitation (and stimulated emission) due to the radiator *and* the perturber dipoles $\boldsymbol{\mu}_R$ and $\boldsymbol{\mu}_1$ and allows for interferences between them. Strong collisions between the radiator and a perturber, where $\hbar^{-1}|V_1^e|\tau_c \gtrsim 1$ [V_1^e is the effective collisional interaction of Eq. (A7c)], have been taken into account within the BCA by the effective tetradic propagator $U_1^e(t',0)$.

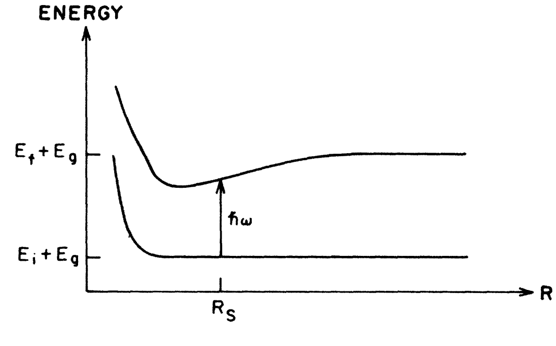

FIG. 2. Molecular potential curves as a function of the internuclear distance R.

In the quasistatic limit of Eq. (13a) we can easily get some insight into the dependence of W on the laser frequency ω by assuming classical paths for the perturbers with straight-line trajectories. Assuming that there is only one point of stationary phase R_s, where the laser photon is absorbed instantaneously during a collision (see Fig. 2), one finds[4] (see also methods of Appendix E of Ref. 17)

$$W=\frac{2\pi}{\hbar}\frac{N}{V}\int d^3R_0\,|D(R_0)|^2\delta(E_i+\hbar\omega-E_f-\Delta V_{f,i}(R_0))$$

$$=\frac{2\pi}{\hbar}\frac{N}{V}|D(R_s)|^2\frac{4\pi R_s^2}{\left|\dfrac{d\Delta V_{f,i}(R)}{dR}\right|_{R=R_s}} . \quad (13c)$$

R_0 thereby indicates the initial positions of the perturber and

$$D(R)=\left\langle fg\left|\left[(\boldsymbol{\mu}_R+\boldsymbol{\mu}_1)\mathbf{e}\mathscr{E}_0\frac{1}{H_R+H(1)-E_i-E_g}V(R)+V(R)\frac{1}{H_R+H(1)-E_f-E_g}(\boldsymbol{\mu}_R+\boldsymbol{\mu}_1)\mathbf{e}\mathscr{E}_0\right]\right|ig\right\rangle \quad (13d)$$

characterizes the collisionally induced laser coupling. The position of the stationary-phase point is determined by

$$E_i+\hbar\omega-E_f-\Delta V_{f,i}(R_s)=0 . \quad (13e)$$

The interatomic difference potential is given by

$$\frac{1}{i\hbar}\Delta V_{f,i}(R_0)=\langle\langle fg,ig\,|\,V_1^e(R_0)\,|\,fg,ig\rangle\rangle$$

[see Eq. (A7c)]. (Note that Eq. (13c) can be obtained directly from Eq. (13a) with $t\rightarrow\infty$, since the stationary-phase evaluation is equivalent to $t'\rightarrow 0$ with $D(t)\rightarrow D(0)$ and $U_1^e(t',0)\rightarrow\exp[V_1^e(0)t']$. In obtaining Eq. (13c) we have, for convenience of expression, assumed $V_1^e(0)$ is diagonal, so that $\int_0^\infty \exp\{i[\Delta\omega - V_1^e(0)]t'\}dt'$ reduces to the δ function in Eq. (13c). However, in general $V_1^e(R)$ is not diagonal, so we should in principle be dealing with the "molecular states" that do diagonalize it, rather than $|ig\rangle$ and $|fg\rangle$. The structure of Eq. (13c) is of course unchanged by such a unitary transformation.) If we assume that

$$\Delta V_{f,i}(R)=\frac{C}{R^n} \tag{14a}$$

and

$$D(R)=\frac{\mathscr{D}}{R^m} \tag{14b}$$

in the region of the stationary-phase point R_s, we find that in the quasistatic wing the transition rate scales as

$$W\propto |E_i+\hbar\omega-E_f|^{(2m-n-3)/n} . \tag{14c}$$

For a radiator transition with $|i\rangle=|{}^1S_0\rangle$ and $|f\rangle=|{}^1D_2\rangle$, for example, this implies that for the excitation rate due to the perturber dipoles, i.e., $\mu_R=0$ in Eq. (13d), $m=4$ for large internuclear separations because a collisional quadrupole (radiator)—dipole (perturber) transition is involved. If we assume van der Waals–type behavior of the molecular potential curves, i.e., $n=6$, we find[4,6]

$$W_p\propto |E_i+\hbar\omega-E_f|^{-1/6} \tag{14d}$$

and the transition rate is therefore monotonically decreasing. For the excitation rate due to the radiator dipole, i.e., $\mu_1=0$ in Eq. (13d), we have $m=7$ for large internuclear separations, because there has to be a second-order effective collisional coupling involving a dipole-dipole and a quadrupole-dipole interaction. Assuming again $n=6$, we find

$$W_R\propto |E_i+\hbar\omega-E_f|^{5/6} , \tag{14e}$$

which is monotonically increasing.[6] As long as R_s is large so that radiator and perturber are well separated and a lowest-order multipole expansion for the collisional interaction is appropriate, $W_p \gg W_R$ due to the fact that W_R involves a second-order collisional coupling. However, because of the different dependence on the detuning of the laser from resonance, W_R is expected to become dominant for sufficiently large detunings. There has been some recent experimental evidence for this type of behavior in the study of the collisionally induced transition $4s^2\,{}^1S_0\rightarrow 4s\,3d\,{}^1D_2$ in a Ca-Xe system.[6] However, in the region where $W_R\approx W_p$, interference effects due to $D_c^{(R)}$ and $D_c^{(1)}$, which are properly described by Eq. (13a) or (13d), should be taken into account.

As we have neglected inelastic collisions, the excited radiator manifold $|f\alpha\rangle$ is metastable with respect to spontaneous emission of photons and collisional decay. Only the combined action of a collision and the coupling of the radiator and perturbers to the spontaneous modes of the radiation field can cause a depopulation of the excited-state manifold of the radiator. This collisionally induced spontaneous decay rate is given by (see Appendix A)

$$\gamma=\sum_\lambda \int d^3k\frac{2\pi}{\hbar}\delta(E_f-E_i-\hbar\omega_k)\frac{\hbar\omega_k}{2\epsilon_0(2\pi)^3}N\int d^3p_1d^3p_2\rho(\mathbf{p}_2)\frac{1}{2j_f+1}\sum_\alpha |\langle ig\mathbf{p}_1|[d_c^{(R)}(0)+d_c^{(1)}(0)]|f\alpha g\mathbf{p}_2\rangle|^2 \tag{15a}$$

and

$$\langle ig\mathbf{p}|d_c^{(j)}(t)|f\alpha g\mathbf{p}'\rangle=\left\langle ig\mathbf{p}\left|\left[V(|\mathbf{x}_1|,t)\frac{1}{H_R+H(1)-E_i-E_g}\boldsymbol{\mu}_j(t)\cdot\boldsymbol{\varepsilon}^*_{k,\lambda}+\boldsymbol{\mu}_j(t)\cdot\boldsymbol{\varepsilon}^*_{k,\lambda}\frac{1}{H_R+H(1)-E_f-E_g}V(|\mathbf{x}_1|,t)\right]\right|f\alpha g\mathbf{p}'\right\rangle,\quad j=R,1 . \tag{15b}$$

Therefore, we make the same assumptions as in the derivation of W in Eq. (13a). We have also used the fact that the time of interest associated with spontaneous decay is short, i.e., $\tau_{\mathrm{RAD}}\ll\tau_c$, so that strong collisions are unimportant during that time and $U_1^e(t,t')\rightarrow 1$ (see Appendix C). The frequency of the emitted photon corresponds to the energy difference of the radiator states $|f\alpha\rangle$ and $|i\rangle$ because the spontaneous decay rate of Eq. (15a) is due to the transition between two molecular radiator-perturber states $|I\alpha\rangle$ and $|F\rangle$, brought about by the coupling of the radiator and the perturber dipole moment to the spontaneous modes of the electromagnetic field (see Appendix B). If we correctly use the vector potential $\hat{\mathbf{A}}_s(\mathbf{x})$ instead of $\hat{\mathbf{E}}_s(\mathbf{x})$ for calculating the collisionally induced spontaneous decay rate, we obtain the same result, namely Eq. (15a). Incorrect use can give rise to large differences as explained in Appendix B. Furthermore, if spontaneous decay is treated in the usual Born approximation,[16,18] which neglects collisional effects during the time the atoms interact with the spontaneous modes [e.g., $G_c(t_1,t')\rightarrow 1$ in Eq. (A25a)], we fail to obtain Eq. (15a). This shows that the Born approximation is inadequate for treating collisionally induced spontaneous decay, though the Markov approximation applies, yielding a time-independent decay rate [see Eq. (A30)].

If we assume that the radiator is excited by a broadband isotropic electromagnetic field with a mean frequency ω and a large bandwidth $b \gg 1/\tau_c$, we obtain a simple relation between the collisionally induced spontaneous decay rate and the averaged collisionally induced excitation rate. For that purpose we have to make the replacement

$$2\epsilon_0 |\mathscr{E}_0|^2 \to \int_0^\infty d\omega\, \rho(\omega) \tag{16}$$

in Eq. (13a). $\rho(\omega)$ is thereby the energy density per unit frequency of the exciting electromagnetic field. Noting that due to the integration over the broad frequency distribution with $b \gg 1/\tau_c$ the time of interest $|t'|$ in Eq. (13a) becomes much less than the duration of a collision τ_c, we can replace $U_1^e(t',0) \to 1$. This implies

$$\frac{\gamma}{B} = \frac{\hbar\omega^3}{(2\pi)^3 c^3} \frac{1}{2j_f+1} \times 8\pi \Big|_{\hbar\omega = E_f - E_i} , \tag{17a}$$

with the Einstein B coefficient defined by

$$B\rho \left[\omega = \frac{E_f - E_i}{\hbar}\right] = \frac{1}{8\pi} \sum_\mu \int d\Omega_{\mathbf{k}_c} W , \tag{17b}$$

and the replacement (16) is thus taken into account. The term μ characterizes the possible polarizations of the exciting laser field. Thereby we have assumed that kT is large enough that the translational motion of the perturber is not affected by the collisionally induced dipole transitions involved in Eqs. (13b) and (15b), i.e., there are only diagonal couplings such as $\langle f\alpha g\mathbf{p} | D_c^{(j)}(t) | ig\mathbf{p}\rangle$ and $\langle ig\mathbf{p} | d_c^{(j)}(t) | f\alpha g\mathbf{p}\rangle$. Equation (17a) is just the standard relation between Einstein A and B coefficients.[21]

Because the rate equations (12) conserve the total population, i.e., $(d/dt)[\sigma_{ii}(t)+\sigma_{ff}(t)]=0$, the general solution is easily obtained for a square pulse of duration T and times $t \le T$, namely,

$$\sigma_{ff}(t) = \frac{W}{\gamma + W\left[\frac{1}{2j_f+1}+1\right]} \times \left[1 - \exp\left\{-\left[\gamma + W\left[\frac{1}{2j_f+1}+1\right]\right]t\right\}\right] . \tag{18a}$$

For short times t, i.e.,

$$\left[\gamma + W\left[\frac{1}{2j_f+1}+1\right]\right] t \ll 1 ,$$

we therefore have

$$\sigma_{ff}(t) \to Wt \tag{18b}$$

and the final-state population is proportional to the number of perturbers N. For long times t with

$$\left[\gamma + W\left[\frac{1}{2j_f+1}+1\right]\right] t \gg 1$$

the final-state population saturates in time, i.e.,

$$\sigma_{ff}(t) \to \frac{W}{\gamma + W\left[\frac{1}{2j_f+1}+1\right]} , \tag{18c}$$

and becomes independent of the perturber density since the collisionally induced spontaneous decay rate γ is proportional to N.

Equations (12) are only concerned with the total populations of the radiator manifolds $|i\rangle$ and $|f\alpha\rangle$ in a spherically symmetric collision environment. However, there are also higher multipoles $\langle\langle ffKQ | \sigma_I(t)\rangle\rangle$ with $K \neq 0$, which are excited from the radiator ground state by the combined action of the laser field and a collision. Since these multipoles always decay with a collisional rate $\gamma^{(K)}$ [see Eq. (A10a)] even if inelastic collisions are neglected (because this implies only that $\gamma^{(K=0)}=0$), their magnitude is approximately given by

$$\langle\langle ffKQ | \sigma_I(t)\rangle\rangle \approx W \min\{t, 1/\gamma^{(K)}\} \ll 1 , \tag{19a}$$

for times $t \le T$ [see Eq. (10a)]. In principle, these multipoles can couple to the rate equations (12), e.g., through matrix elements such as

$$\langle\langle ff K=Q=0 | M_2^{(0)}(t,t') | ffK'Q'\rangle\rangle ,$$

but because of relation (19a) this influence is at most of order $W/\gamma^{(K)}$ in comparison with unity and therefore negligible. Furthermore, if $1/\gamma^{(K)} \ll t$ these higher multipoles are negligible in comparison with $\langle\langle ff K=Q=0 | \sigma_I(t)\rangle\rangle$ [see Eqs. (18b) and (18c)], which implies that all radiator states $|f\alpha\rangle$ are equally populated (collisional equilibrium). Equation (19a) also shows that $\langle\langle ffKQ | \sigma_I(t)\rangle\rangle$ with $K \neq 0$ can only be comparable to $\langle\langle ff K=Q=0 | \sigma_I(t)\rangle\rangle$ if $1/\gamma^{(K)} \gtrsim t$. In this situation the ground state of the radiator is undepleted and $\langle\langle ffKQ | \sigma_I(t)\rangle\rangle$ can be determined from

$$\left[\frac{d}{dt}+\gamma^{(K)}\right]\langle\langle ffKQ\,|\,\sigma_I(t)\rangle\rangle$$

$$=N\int d^3p_1\int\cdots\int d^3p_6\rho(\mathbf{p}_6)\int_0^t dt'\sum_{\substack{\alpha,\beta,\gamma\\ \alpha',\beta'}}(-1)^{j_f-m_\beta-Q}(2K+1)^{1/2}\begin{bmatrix} j_f & j_f & K\\ m_\alpha & -m_\beta & -Q\end{bmatrix}$$

$$\times\langle\langle f\alpha g\mathbf{p}_1,f\beta g\mathbf{p}_1\,|\,U_1^e(t,t')\,|\,f\alpha' g\mathbf{p}_2,f\beta' g\mathbf{p}_3\rangle\rangle$$

$$\times\frac{1}{\hbar^2}\{\langle f\beta' g\mathbf{p}_3\,|\,[D_c^{(1)}(t')+D_c^{(R)}(t')]\,|\,ig\mathbf{p}_4\rangle^*\langle\langle f\alpha' g\mathbf{p}_2,ig\mathbf{p}_4\,|\,U_1^e(t',0)\,|\,f\gamma g\mathbf{p}_5,ig\mathbf{p}_6\rangle\rangle e^{i\omega t'}$$

$$\times\langle f\gamma g\mathbf{p}_5\,|\,[D_c^{(1)}(0)+D_c^{(R)}(0)]\,|\,ig\mathbf{p}_6\rangle$$

$$+\langle f\alpha' g\mathbf{p}_2\,|\,[D_c^{(1)}(t')+D_c^{(R)}(t')]\,|\,ig\mathbf{p}_4\rangle$$

$$\times\langle\langle ig\mathbf{p}_4,f\beta' g\mathbf{p}_3\,|\,U_1^e(t',0)\,|\,ig\mathbf{p}_6,f\gamma g\mathbf{p}_5\rangle\rangle e^{-i\omega t'}\langle f\gamma g\mathbf{p}_5\,|\,[D_c^{(1)}(0)+D_c^{(R)}(0)]\,|\,ig\mathbf{p}_6\rangle^*\}\ ,\quad K\neq 0\ . \tag{19b}$$

The right-hand side is the collisionally induced excitation rate of the excited-state multipole K. The major difference between this rate and W of Eq. (13a) is the appearance of the collisional time development operator $U_1^e(t,t')$, which describes the effects due to collisional mixing within the manifold $|f\alpha\rangle$ after the radiator has been excited at t'. This collisional mixing is unimportant for the $K=0$ component, i.e., $U_1^e(t,t')\to 1$, because it cannot affect the total excited-state population (if inelastic collisions are neglected), but it is important for the $K\neq 0$ components. This type of mixing has been studied recently in the context of polarization properties of dipole allowed transitions[19,22,23] (compare with the quantity $\Gamma^{(K)}$ of Burnett and Cooper[19]).

III. THE SPECTRUM

In this section we study the spectrum of the photon $(\mathbf{k},\lambda)$, which is spontaneously emitted during the excitation process discussed in Sec. II. In particular, we are interested in the frequency regime, which corresponds to the dipole-forbidden transition $|f\alpha\rangle\to|i\rangle$, i.e.,

$$|E_i+\hbar\omega_k-E_f|\ll\hbar\omega\ . \tag{20}$$

In general, the spectrum consists of two very different features (see Fig. 3). First, there is a narrow peak centered at the laser frequency ω, which is caused by Rayleigh scattering. It is scarcely influenced by the collisions between the radiator and the perturbers since for most of the time the Rayleigh scatterers are not subject to collisions. This peak is surrounded by a broad asymmetric structure, which is due to photons emitted during collisions. This second feature is very sensitive to details of the collision process and it vanishes in the absence of collisions. In addition, there is usually another narrow peak at $\omega_k\approx(E_f-E_i)/\hbar$ with a width determined by a typical (impact) collision rate γ_c. It is due to photons spontaneously emitted, e.g., in a higher-order multipole transition. In the following we neglect this type of decay mechanism. In general, this narrow peak also contains contributions from photon emission involving subsequent collisions. However, as long as lower-state interaction is negligible and the collision environment of the radiator is approximately spherically symmetric, we expect these contributions to be unimportant (see also the discussion of the corresponding contributions to the excitation rate in Sec. II).

To study the spontaneous emission process we consider the physical system of Sec. II with assumptions (1)—(4). In addition, we make the following simplifications.

(1) We assume that only the dipoles of the perturbers interact with the spontaneous modes of the radiation field and the laser field, i.e., $\boldsymbol{\mu}_R=0$. Because the number of perturbers is much larger than the number of radiators (in our model we have only one radiator in the interaction volume), this is certainly a good approximation as far as Rayleigh scattering is concerned. From detailed balance we expect the collisionally induced spontaneous emission to be characterized essentially by W of Eq. (13a) with ω replaced by ω_k. The arguments following Eq. (14e) then show that the dipole moment of the radiator is likely to become important for $|E_i+\hbar\omega_k-E_f|/\hbar\gg 1/\tau_c$. For moderate detunings $|E_f-E_i-\hbar\omega_k|/\hbar\gtrsim 1/\tau_c$ we there-

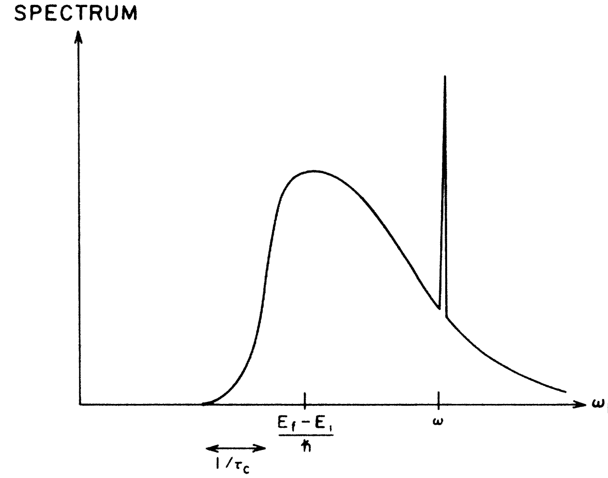

FIG. 3. Schematic representation of the spectrum.

fore expect $\boldsymbol{\mu}_R=0$ to be a good approximation for collisionally induced spontaneous emission involving a $j_f=2\rightarrow j_i=0$ transition. This approximation may obviously be removed if one is prepared for more tedious algebraic manipulations.

(2) During the generation of the spontaneously emitted photon $(\mathbf{k},\lambda)$ the influence of all other spontaneous modes on the dynamics is neglected. Except for the Rayleigh scattering contribution, this is valid as long as condition (10b) is fulfilled, because a photon $(\mathbf{k},\lambda)$ can only be generated during a collision. As long as the Doppler width is much larger than any spontaneous decay rate this is also expected to be a good approximation for the calculation of Rayleigh scattering.

Using assumption (1) in Eq. (4a), i.e., $L_c^{(R)}=L_s^{(R)}=0$, we find

$$\frac{d}{dt}\mathscr{B}\rho_I(t)=\mathscr{B}\sum_{j=1}^{N}V_j(t)\mathscr{B}\rho_I(t)+\mathscr{B}\sum_{j=1}^{N}[V_j(t)+L_s^{(j)}(t)]\int_0^t dt' G(t,t')\sum_{i=1}^{N}[(1-\mathscr{B})V_i(t')+L_c^{(i)}(t')+L_s^{(i)}(t')]\mathscr{B}\rho_I(t') \tag{21a}$$

with $\mathscr{B}$ given in Eq. (A2),

$$\frac{d}{dt}G(t,t')=\sum_{j=1}^{N}[(1-\mathscr{B})V_j(t)+L_c^{(j)}(t)+(1-\mathscr{B})L_s^{(j)}(t)]G(t,t'),\quad t\ge t' \tag{21b}$$

and $G(t,t')=1$. This projected equation assumes $(1-\mathscr{B})\rho_I(t=0)=0$. Following the procedure of Mollow[24] we assume that only one photon is emitted into a particular mode $(\mathbf{k},\lambda)$, so that the rate of emitting photons into that mode (which was initially unoccupied) is given by

$$\Gamma_{k,\lambda}=\frac{d}{dt}\langle\langle 1,1\,|\,\mathrm{Tr}_R\,\mathrm{Tr}_{\{p\}}\,\mathrm{Tr}_{\mathrm{RAD}'}[\mathscr{B}\rho_I(t)]\ . \tag{22}$$

Tr_R ($\mathrm{Tr}_{\mathrm{RAD}'}$) thereby indicates the trace over the internal states of the radiator [all spontaneous modes except $(\mathbf{k},\lambda)$]. The tetradic vector $|1,1\rangle\rangle=|1\rangle\langle 1|$ characterizes one photon in mode $(\mathbf{k},\lambda)$, i.e., $a^{\dagger}_{k,\lambda}a_{k,\lambda}|1\rangle=|1\rangle$. We use Eq. (22) for the spectrum rather than the standard dipole autocorrelation function approach because we have found that it is simpler with this form to invoke the BCA. Now we use assumption (2) and neglect all spontaneous modes except $(\mathbf{k},\lambda)$ in $G(t,t')$ of Eq. (21b) and replace

$$L_s^{(i)}(t')[\{\cdots\}]\rightarrow L_{k\lambda}^{(i)}(t')[\{\cdots\}]=\frac{1}{i\hbar}[-\boldsymbol{\mu}_i(t')[\hat{\mathbf{E}}_{k,\lambda}(\mathbf{x}_i,t')+\mathrm{H.c.}],\{\cdots\}]\ . \tag{23}$$

This implies

$$\Gamma_{k,\lambda}=\mathrm{Tr}_R\left\langle\!\!\left\langle 1,1\,\middle|\int_0^t dt'\mathscr{N}(t,t')\middle|\Sigma(t')\right\rangle\!\!\right\rangle \tag{24a}$$

with

$$\mathscr{N}(t,t')=\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[L_{k\lambda}^{(j)}(t)G'(t,t')\sum_{i=1}^{N}[(1-\mathscr{B})V_i(t')+L_c^{(i)}(t')+L_{k\lambda}^{(i)}(t')]\prod_{m=1}^{N}|g,g\rangle\rangle\rho(\mathbf{p}_m)\right], \tag{24b}$$

and

$$\frac{d}{dt}G'(t,t')=\sum_{j=1}^{N}[(1-\mathscr{B})V_j(t)+L_c^{(j)}(t)+(1-\mathscr{B})L_{k\lambda}^{(j)}(t)]G'(t,t'),\quad t\ge t'\ . \tag{24c}$$

As long as the probability of creating a photon in mode $(\mathbf{k},\lambda)$ remains much less than one, we can determine $\Gamma_{k,\lambda}$ perturbatively by keeping only the coupling to

$$\langle\langle 0,0\,|\,\Sigma(t')\rangle\rangle=\sigma_I(t') \tag{24d}$$

in second order in $L_{k\lambda}^{(j)}$. Equation (24d) thereby assumes that omission of mode $(\mathbf{k},\lambda)$ does not influence the dynamics of the radiator, and mode $(\mathbf{k},\lambda)$ is initially unoccupied. By expanding $G'(t,t')$ perturbatively in terms of $L_{k\lambda}^{(j)}$, we obtain $\mathscr{N}(t,t')=\mathscr{N}^{(1)}(t,t')+\mathscr{N}^{(2)}(t,t')$ (the upper index indicates the order in $L_{k\lambda}^{(j)}$) up to second order in $L_{k\lambda}^{(j)}$. Since none of the dipole-allowed transitions within the radiator or perturber is in resonance with the laser field, $G'(t,t')$ can also be expanded perturbatively in terms of $L_c^{(j)}$, which is valid as long as condition (10a) is fulfilled. Up to second order in $L_c^{(j)}$ we therefore find

$$\mathscr{N}(t,t')=\sum_{n=1,2}[\mathscr{N}_0^{(n)}(t,t')+\mathscr{N}_1^{(n)}(t,t')+\mathscr{N}_2^{(n)}(t,t')]\ , \tag{25}$$

where the lower index indicates the order in $L_c^{(j)}$.

According to our resonance conditions (9) and (20), Eq. (24a) therefore reduces to

$$\Gamma_{k,\lambda}=\sum_{\alpha}\mathrm{Tr}_R\left\langle\!\!\left\langle 1,1\left|\int_0^t dt'\mathcal{N}_0^{(1)}(t,t')\right|1,0\right\rangle\!\!\right\rangle|i,f\alpha\rangle\!\rangle\langle\!\langle i,f\alpha|\langle\!\langle 1,0|\Sigma(t')\rangle\!\rangle$$
$$+\sum_{\alpha}\mathrm{Tr}_R\left\langle\!\!\left\langle 1,1\left|\int_0^t dt'\mathcal{N}_0^{(1)}(t,t')\right|0,1\right\rangle\!\!\right\rangle|f\alpha,i\rangle\!\rangle\langle\!\langle f\alpha,i|\langle\!\langle 0,1|\Sigma(t')\rangle\!\rangle$$
$$+\sum_{n_1,n_1'}\mathrm{Tr}_R\left\langle\!\!\left\langle 1,1\left|\int_0^t dt'\mathcal{N}_1^{(1)}(t,t')\right|1,0\right\rangle\!\!\right\rangle|n_1,n_1'\rangle\!\rangle\langle\!\langle n_1,n_1'|\langle\!\langle 1,0|\Sigma(t')\rangle\!\rangle$$
$$+\sum_{n_1,n_1'}\mathrm{Tr}_R\left\langle\!\!\left\langle 1,1\left|\int_0^t dt'\mathcal{N}_1^{(1)}(t,t')\right|0,1\right\rangle\!\!\right\rangle|n_1,n_1'\rangle\!\rangle\langle\!\langle n_1,n_1'|\langle\!\langle 0,1|\Sigma(t')\rangle\!\rangle$$
$$+\mathrm{Tr}_R\left\langle\!\!\left\langle 1,1\left|\int_0^t dt'\mathcal{N}_0^{(2)}(t,t')\right|0,0\right\rangle\!\!\right\rangle\langle\!\langle 0,0|\Sigma(t')\rangle\!\rangle$$
$$+\mathrm{Tr}_R\left\langle\!\!\left\langle 1,1\left|\int_0^t dt'\mathcal{N}_2^{(2)}(t,t')\right|0,0\right\rangle\!\!\right\rangle\langle\!\langle 0,0|\Sigma(t')\rangle\!\rangle\ , \tag{26}$$

where the various radiator matrix elements involving $\langle\!\langle 1,0|\Sigma(t')\rangle\!\rangle$ or $\langle\!\langle 0,1|\Sigma(t')\rangle\!\rangle$ can be obtained from Eq. (21a) by making substitution (23) again. Note that this substitution implies that we neglect all spontaneous modes except $(\mathbf{k},\lambda)$ only in the process of generating the spontaneously emitted photon. Their influence on $\langle\!\langle 0,0|\Sigma(t')\rangle\!\rangle$ is properly taken into account by relation (24d) and the fact that the (reduced) radiator dynamics is determined in the presence of these modes, i.e., by Eq. (12). n_1 and n_1' in Eq. (26) are two degenerate radiator states.

In Appendix C we outline the calculation of the various matrix elements of Eq. (26) and show that they reduce to one-perturber averages within the BCA. Let us now consider the physical significance of the various terms in Eq. (26). All terms of zeroth order in the perturber-laser interaction describe collisionally induced emission of a photon $(\mathbf{k},\lambda)$ with the radiator initially in the excited-state manifold $|f\alpha\rangle$. In particular, the term proportional to $\mathcal{N}_0^{(2)}(t,t')$ describes this process occurring during single collisions and the terms proportional to $\mathcal{N}_0^{(1)}(t,t')$ represent the subsequent collisional contributions. All other contributions to Eq. (26) involve the participation of the laser field in the process of emitting the photon $(\mathbf{k},\lambda)$. $\mathcal{N}_2^{(2)}(t,t')$ specifically describes Rayleigh scattering by the perturbers and laser excitation and photon emission occurring during single collisions. The terms proportional to $\mathcal{N}_1^{(1)}(t,t')$ represent the same processes involving different perturbers (see Appendix C 3).

In Appendix C it is shown that the spectrum of the spontaneously emitted photon $(\mathbf{k},\lambda)$ consists of three contributions, i.e.,

$$\Gamma(\omega_k,\boldsymbol{\varepsilon},t)=\Gamma_R(\omega_k,\boldsymbol{\varepsilon},t)+\Gamma_S(\omega_k,\boldsymbol{\varepsilon},t)\ +\Gamma_{SS}(\omega_k,\boldsymbol{\varepsilon},t)\ . \tag{27a}$$

$\Gamma(\omega_k,\boldsymbol{\varepsilon},t)$ is thereby the rate of emitting a photon $(\omega_k,\boldsymbol{\varepsilon}_{k,\lambda})$ per unit solid angle and per unit frequency. The total rate of emitting a photon at time t is then given by

$$\Gamma(t)=\sum_{\lambda}\int d\Omega_k\int_0^\infty d\omega_k\Gamma(\omega_k,\boldsymbol{\varepsilon},t)\ . \tag{27b}$$

The rate due to Rayleigh scattering is

$$\Gamma_R(\omega_k,\boldsymbol{\varepsilon},t)=\frac{\omega_k^3}{4\pi\hbar\epsilon_0 c}\frac{1}{2\pi c^2}|D_R|^2\times N\int d^3v\,f(\mathbf{v})\times\frac{1}{\pi}\mathrm{Re}\int_0^t dt' e^{i[\omega-\omega_k+(\mathbf{k}-\mathbf{k}_c)\mathbf{v}](t-t')}\ , \tag{28}$$

with

$$D_R=\left\langle g\left|\left[\boldsymbol{\mu}_1\cdot\mathbf{e}\mathscr{E}_0\frac{1}{H(1)-E_g+\hbar\omega}\boldsymbol{\mu}_1\cdot\boldsymbol{\varepsilon}_{k,\lambda}^*+\boldsymbol{\mu}_1\cdot\boldsymbol{\varepsilon}_{k,\lambda}^*\frac{1}{H(1)-E_g-\hbar\omega}\boldsymbol{\mu}_1\cdot\mathbf{e}\mathscr{E}_0\right]\right|g\right\rangle \tag{28'}$$

and the perturber velocity distribution $f(\mathbf{v})$ with $\int d^3v\,f(\mathbf{v})=1$. For convenience we have assumed that the perturber is moving on a classical path with a straight-line trajectory, and when we can allow $t\to\infty$, it is proportional to $\delta(\omega-\omega_k-(\mathbf{k}-\mathbf{k}_c)\cdot\mathbf{v})$. A more general expression for $\Gamma_R(\omega_k,\boldsymbol{\varepsilon},t)$ can be found in Appendix C 3 [Eq. (C12)]. The Rayleigh scattering rate of Eq. (28) is due to the perturbers and does not depend on the state of the radiator. This is only valid as long as the particular part of $\mathcal{N}_2^{(2)}(t,t')$ in Eq. (26), which describes Rayleigh scattering, i.e., $\mathcal{N}_R(t,t')$ [see Eq. (C12)], is independent of radiator coordinates so that

$$\mathrm{Tr}_R \langle\langle 1,1 | \mathcal{N}_R(t,t') | 0,0 \rangle\rangle \sigma_I(t') = \langle\langle 1,1 | \mathcal{N}_R(t,t') | 0,0 \rangle\rangle \, \mathrm{Tr}_R \sigma_I(t') = \langle\langle 1,1 | \mathcal{N}_R(t,t') | 0,0 \rangle\rangle \quad (29)$$

due to conservation of the radiator population. It is shown in Appendix C 3 b that this is the case if inelastic collisions are neglected. According to Eq. (28) the width of the Rayleigh scattered peak, which is centered around the laser frequency ω, is determined either by the Doppler width Δ_{Dop} or by $1/t$, whichever is larger. The total rate due to Rayleigh scattering is given by

$$\Gamma_R(t) = \sum_\lambda \int d\Omega_k \int_{\omega-\Delta}^{\omega+\Delta} d\omega_k \Gamma_R(\omega_k, \boldsymbol{\varepsilon}, t) = \frac{\omega^3}{4\pi\epsilon_0 \hbar c} \frac{1}{2\pi c^2} N \sum_\lambda \int d\Omega_{\mathbf{k}} |D_R|^2 , \quad (28'')$$

where $\Delta \gg 1/t$, Δ_{Dop}.

The remaining two contributions to the spectrum in Eq. (27a), namely $\Gamma_S(\omega_k, \boldsymbol{\varepsilon}, t)$ and $\Gamma_{SS}(\omega_k, \boldsymbol{\varepsilon}, t)$, describe the spontaneous emission of the observed photon during collisions and they give rise to the broad asymmetric feature in Fig. 3.

Let us first consider the rate

$$\begin{aligned}
\Gamma_{SS}(\omega_k, \boldsymbol{\varepsilon}, t) = {} & \frac{\omega_k^3}{4\pi\epsilon_0 \hbar c} \frac{1}{2\pi c^2} \\
& \times \frac{1}{2\pi} N \int d^3p_1 \int \cdots \int d^3p_6 \rho(\mathbf{p}_6) \int_0^t dt' \sum_{\alpha_1,\alpha_2,\alpha_3} [\langle ig\mathbf{p}_1 | d_c^{(1)}(t) | f\alpha_1 g\mathbf{p}_2 \rangle \\
& \times \langle\langle f\alpha_1 g\mathbf{p}_2, ig\mathbf{p}_1 | U_1^e(t,t') | f\alpha_2 g\mathbf{p}_4, ig\mathbf{p}_3 \rangle\rangle e^{i\omega_k(t-t')} \\
& \times \langle ig\mathbf{p}_3 | d_c^{(1)}(t') | f\alpha_3 g\mathbf{p}_5 \rangle^* \\
& + \langle ig\mathbf{p}_1 | d_c^{(1)}(t) | f\alpha_1 g\mathbf{p}_2 \rangle^* \\
& \times \langle\langle ig\mathbf{p}_1, f\alpha_1 g\mathbf{p}_2 | U_1^e(t,t') | ig\mathbf{p}_3, f\alpha_3 g\mathbf{p}_5 \rangle\rangle e^{-i\omega_k(t-t')} \\
& \times \langle ig\mathbf{p}_3 | d_c^{(1)}(t') | f\alpha_2 g\mathbf{p}_4 \rangle] \\
& \times \sum_{K,Q} \sum_{\beta,\gamma} \langle\langle f\alpha_2 g\mathbf{p}_4, f\alpha_3 g\mathbf{p}_5 | U_1^e(t',0) | f\beta g\mathbf{p}_6, f\gamma g\mathbf{p}_6 \rangle\rangle \\
& \times (-1)^{j_f - m_\gamma - Q} (2K+1)^{1/2} \begin{pmatrix} j_f & j_f & K \\ m_\beta & -m_\gamma & -Q \end{pmatrix} \\
& \times \langle\langle ff\, KQ \mid \sigma_I(t) \rangle\rangle \ .
\end{aligned} \quad (30)$$

Details of the derivation can be found in Appendix C 1. As in Eq. (12) we assume that $\langle\langle ff\,KQ \mid \sigma_I(t)\rangle\rangle$ is slowly varying on a time scale of order τ_c [Markov approximation; see also Eqs. (A29) and (A30)]. Equation (30) describes a process where initially an excited-state multipole (K,Q) of the radiator is prepared and then a photon $(\omega_k, \boldsymbol{\varepsilon})$ is emitted during a subsequent collision. However, before this photon is emitted there is collisional mixing within the excited radiator manifold, which is described by the collisional propagator $U_1^e(t',0)$. This mixing is unimportant for fluorescence from $\langle\langle ff\,K=Q=0 \mid \sigma_I(t)\rangle\rangle$, if

$$|E_i + \hbar\omega_k - E_f| \ll kT , \quad (31)$$

which essentially implies that the motion of the perturber is not significantly influenced by the effective collisional interaction V_1^e.[16] However, it is important for fluorescence from all other excited-state radiator multipoles (K,Q) with $K \neq 0$. Because $|\langle\langle ff\,K\neq 0\,Q \mid \sigma_I(t)\rangle\rangle| \ll \langle\langle ff\,K=Q=0 \mid \sigma_I(t)\rangle\rangle$ for $t \gg 1/\gamma^{(K)}$ [see Eqs. (19a) and (18b)] only fluorescence from $\langle\langle ff\,K=Q=0 \mid \sigma_I(t)\rangle\rangle$ is significant for these long times and Eq. (30) can in this case be greatly simplified. Taking (31) into account we find

$$\Gamma_{SS}(\omega_k, \boldsymbol{\varepsilon}, t) = C(\omega_k, \boldsymbol{\varepsilon}) \sigma_{ff}(t) \quad (32a)$$

with the emission rate

$$\begin{aligned}
C(\omega_k, \boldsymbol{\varepsilon}) = {} & \frac{\omega_k^3}{4\pi\epsilon_0 \hbar c} \frac{1}{2\pi c^2} \\
& \times \frac{1}{\pi} N \int d^3p_1 \int \cdots \int d^3p_4 \rho(\mathbf{p}_4) \, \mathrm{Re} \int_0^t dt' \frac{1}{2j_f + 1} \\
& \times \sum_{\alpha,\beta} \langle ig\mathbf{p}_1 | d_c^{(1)}(t) | f\alpha g\mathbf{p}_2 \rangle \langle\langle f\alpha g\mathbf{p}_2, ig\mathbf{p}_1 | U_1^e(t,t') | f\beta g\mathbf{p}_4, ig\mathbf{p}_3 \rangle\rangle e^{i\omega_k(t-t')} \\
& \times \langle ig\mathbf{p}_3 | d_c^{(1)}(t') | f\beta g\mathbf{p}_4 \rangle^* ,
\end{aligned} \quad (32b)$$

which is time independent, because $t \gg \tau_c$ (i.e., $t \to \infty$ can be used). This expression involves only the perturber dipole $\boldsymbol{\mu}_1$, because the radiator—spontaneous-modes interaction has been neglected in the process of generating the photon $(\omega_k, \boldsymbol{\varepsilon})$. If we also neglect the radiator dipole in the excitation process $|i\rangle \to |f\alpha\rangle$, i.e., we put $\boldsymbol{\mu}_R = 0$ in Eq. (13a), we obtain a simple relation between absorption and emission rates, namely

$$\frac{C(\omega_k=\omega, \boldsymbol{\varepsilon}=\mathbf{e})}{B^{(1)}(\omega,\mathbf{e})} = \frac{\hbar\omega^3}{(2\pi)^3 c^3}\frac{1}{2j_f+1} \tag{33a}$$

[provided kT is large enough; compare with Eq. (17a)]. The Einstein B coefficient, $B^{(1)}(\omega,\mathbf{e})$, is thus defined by

$$W = B^{(1)}(\omega,\mathbf{e}) 2\epsilon_0 |\mathscr{E}_0|^2 \tag{33b}$$

with $\boldsymbol{\mu}_R = 0$. If we had not neglected the radiator dipole during the process of generating the photon $(\omega_k, \boldsymbol{\varepsilon})$, we would have obtained Eq. (32b) with the replacement

$$d_c^{(1)} \to d_c^{(1)} + d_c^{(R)} \,. \tag{34}$$

Equation (33a) would still be valid, if $B^{(1)}(\omega,\mathbf{e})$ were determined by Eq. (33b) and the full excitation rate W of Eq. (13a). The total rate corresponding to Eq. (32a) is given by

$$\Gamma_{SS}(t) = \sum_\lambda \int d\Omega_k \int_{(E_f - E_i/\hbar)-\Delta}^{(E_f-E_i/\hbar)+\Delta} d\omega_k \Gamma_{SS}(\omega_k, \boldsymbol{\varepsilon}, t) = \gamma \sigma_{ff}(t) \tag{35}$$

with $\Delta \gg 1/\tau_c$ and the collisionally induced spontaneous decay rate γ of Eq. (15a). The detailed balance relation of Eq. (33a) implies that the considerations concerning the excitation rate W also apply for the emission rate. Therefore, we expect the radiator dipole to become important in the emission process involving a $j_f = 2 \to j_i = 0$ transition only in the far wing, where $\hbar^{-1} |E_i + \hbar\omega_k - E_f| \tau_c \gg 1$.

Equation (30) does not contain contributions to collisionally induced fluorescence, where the observed photon is emitted in subsequent collisions. As is shown in Appendix C 1, such contributions do not exist in the case of a spherically symmetric collision environment of the radiator, since the mean induced dipole moment vanishes. As argued in Sec. II, we expect this to be a good approximation not only in the heavy-radiator limit but also for arbitrary radiators as long as the interaction between radiator and perturber is very different for the upper and lower states $|f\alpha\rangle$ and $|i\rangle$, and consequently the velocity associated with the mean induced dipole moment is not significantly changed by collision. In the opposite case, when upper- and lower-state interactions are comparable and velocity-changing collisions are extremely important, it has been shown by Lewis and Van Kranendonk[9,10] that subsequent collisional contributions may become important and generally lead to an enhancement of the emission rate at $\omega_k = (E_f - E_i)/\hbar$.

The single collisional contribution to the collisionally induced photon emission rate is determined by

$$\begin{aligned}
\Gamma_S(\omega_k,\boldsymbol{\varepsilon},t) = {} & \frac{\omega_k^3}{4\pi\epsilon_0 \hbar c}\frac{1}{2\pi c^2}\frac{1}{\hbar^2} \\
& \times \frac{1}{\pi}\,\mathrm{Re} \sum_{\substack{\alpha,\alpha',0\\ \beta,\beta'}} \int_0^t dt' \int_{t'}^t dt_1 \int_{t'}^{t_1} dt_2\, N \int d^3p_1 \int \cdots \int d^3p_8\, \rho(\mathbf{p}_8) \\
& \quad \times [\langle ig\mathbf{p}_1 | d_c^{(1)}(t) | f\alpha g\mathbf{p}_2\rangle e^{i\omega_k(t-t_1)} \langle\langle f\alpha g\mathbf{p}_2, ig\mathbf{p}_1 | U_1^e(t,t_1) | f\beta g\mathbf{p}_4, ig\mathbf{p}_3\rangle\rangle \\
& \quad \times \langle f\beta g\mathbf{p}_4 | D_c^{(1)}(t_1) | ig\mathbf{p}_5\rangle]^* e^{i(\omega-\omega_k)(t_1-t_2)} \\
& \quad \times [\langle ig\mathbf{p}_3 | d_c^{(1)}(t_2) | f\alpha' g\mathbf{p}_6\rangle e^{i\omega(t_2-t')} \langle\langle f\alpha' g\mathbf{p}_6, ig\mathbf{p}_5 | U_1^e(t_2,t') | f\beta' g\mathbf{p}_7, ig\mathbf{p}_8\rangle\rangle \\
& \quad \times \langle f\beta' g\mathbf{p}_7 | D_c^{(1)}(t') | ig\mathbf{p}_8\rangle] \sigma_{ii}(t) \\
& + \frac{\omega_k^3}{4\pi\epsilon_0\hbar c}\frac{1}{2\pi c^2}\frac{1}{\hbar^2}\frac{1}{\pi}\,\mathrm{Re}\sum_{\substack{\alpha,\beta,\gamma,\\ \alpha',\beta',\gamma'}} \int_0^t dt' \int_{t'}^t dt_1 \int_{t'}^{t_1} dt_2\, N \int d^3p_1 \int \cdots \int d^3p_{10}\, \rho(\mathbf{p}_{10}) \\
& \quad \times \langle ig\mathbf{p}_1 | d_c^{(1)}(t) | f\alpha g\mathbf{p}_2\rangle \langle\langle f\alpha g\mathbf{p}_2, ig\mathbf{p}_1 | U_1^e(t,t_1) | f\beta g\mathbf{p}_4, ig\mathbf{p}_3\rangle\rangle e^{i\omega_k(t-t_1)} \\
& \quad \times \langle ig\mathbf{p}_3 | d_c^{(1)}(t_1) | f\gamma g\mathbf{p}_5\rangle^* \langle\langle f\beta g\mathbf{p}_4, f\gamma g\mathbf{p}_5 | U_1^e(t_1,t_2) | f\beta' g\mathbf{p}_6, f\gamma' g\mathbf{p}_7\rangle\rangle \\
& \quad \times [\langle f\gamma' g\mathbf{p}_7 | D_c^{(1)}(t_2) | ig\mathbf{p}_8\rangle^* \langle\langle f\beta' g\mathbf{p}_6, ig\mathbf{p}_8 | U_1^e(t_2,t') | f\alpha' g\mathbf{p}_9, ig\mathbf{p}_{10}\rangle\rangle \\
& \quad \times f\alpha' g\mathbf{p}_9 | D_c^{(1)}(t') | ig\mathbf{p}_{10}\rangle e^{i\omega(t_2-t')} \\
& \quad + \langle f\beta' g\mathbf{p}_6 | D_c^{(1)}(t_2) | ig\mathbf{p}_8\rangle \langle\langle ig\mathbf{p}_8, f\gamma' g\mathbf{p}_7 | U_1^e(t_2,t') | ig\mathbf{p}_{10}, f\alpha' g\mathbf{p}_9\rangle\rangle \\
& \quad \times \langle f\alpha' g\mathbf{p}_9 | D_c^{(1)}(t') | ig\mathbf{p}_{10}\rangle^* e^{-i\omega(t_2-t')}] \sigma_{ii}(t) \,.
\end{aligned} \tag{36}$$

Details can be found in Appendix C 3. We have kept only the coupling to $\sigma_{ii}(t)$, which is assumed to vary slowly on a time scale of order τ_c. The contribution, which involves a coupling to $\langle\langle ffKQ | \sigma_I(t)\rangle\rangle$, is always negligible in comparison with $\Gamma_{SS}(\omega_k,\varepsilon,t)$. Physically, Eq. (36) describes collisionally induced resonant scattering of the laser photon $(\omega,\mathbf{e})$ during single collisions with the radiator initially in its ground state. It properly takes into account the degeneracy of excited-state manifold $|f\alpha\rangle$ and therefore allows for reorientation effects during the propagation in $|f\alpha\rangle$. This scattering process is only possible during collisions because the radiator transition $|i\rangle \to |f\alpha\rangle$ is dipole forbidden. The three terms of Eq. (36) are the generalizations of the terms $F_{(i)},F_{(iii)},F_{(ii)}$ of Omont *et al.*,[25] which these authors discuss in connection with light scattering involving dipole-allowed transitions. These terms should also be compared with the $D_1^{(i)},D_1^{(ii)},D_1^{(iii)}$ terms of Burnett and Cooper.[26] The term $\Gamma_S(\omega_k,\varepsilon,t)$ contributes to the broad asymmetric structure of the spectrum in Fig. 3, in a way similar to $\Gamma_{SS}(\omega_k,\varepsilon,t)$ in Eq. (30) because absorption of the laser photon $(\omega,\mathbf{e})$ and emission of the spontaneous photon $(\omega_k,\varepsilon_{k,\lambda})$ are confined to a time interval of order τ_c. The total rate associated with $\Gamma_S(\omega_k,\varepsilon,t)$ is given by

$$\Gamma_S(t)=\frac{\omega_k^3}{4\pi\epsilon_0\hbar c}\frac{1}{2\pi c^2}$$
$$\times\frac{1}{\hbar^2}\mathrm{Re}\sum_\lambda\int d\Omega_k\sum_{\substack{\alpha,\alpha',\\ \beta,\beta',\gamma}}\int_0^t dt'\int_{t'}^t dt_1 N\int d^3p_1\int\cdots\int d^3p_8\rho(\mathbf{p}_8)$$
$$\times\langle ig\mathbf{p}_1|d_c^{(1)}(t)|f\alpha g\mathbf{p}_2\rangle\langle ig\mathbf{p}_1|d_c^{(1)}(t)|f\beta g\mathbf{p}_3\rangle^*$$
$$\times\langle\langle f\alpha g\mathbf{p}_2,f\beta g\mathbf{p}_3|U_1^e(t,t_1)|f\alpha' g\mathbf{p}_4,f\beta' g\mathbf{p}_5\rangle\rangle$$
$$\times[\langle f\beta' g\mathbf{p}_5|D_c^{(1)}(t_1)|ig\mathbf{p}_6\rangle^*\langle\langle f\alpha' g\mathbf{p}_4,ig\mathbf{p}_6|U_1^e(t_1,t')|f\gamma g\mathbf{p}_7,ig\mathbf{p}_8\rangle\rangle$$
$$\times e^{i\omega(t_1-t')}\langle f\gamma g\mathbf{p}_7|D_c^{(1)}(t')|ig\mathbf{p}_8\rangle$$
$$+\langle f\alpha' g\mathbf{p}_4|D_c^{(1)}(t_1)|ig\mathbf{p}_6\rangle\langle\langle ig\mathbf{p}_6,f\beta' g\mathbf{p}_5|U_1^e(t_1,t')|ig\mathbf{p}_8,f\gamma g\mathbf{p}_7\rangle\rangle$$
$$\times e^{-i\omega(t_1-t')}\langle f\gamma g\mathbf{p}_7|D_c^{(1)}(t')|ig\mathbf{p}_8\rangle^*]\sigma_{ii}(t)\;. \tag{37}$$

Note that the first term in Eq. (36), which corresponds to a $F_{(i)}$ term, does not contribute to Eq. (37).

Because $\Gamma_S(\omega_k,\varepsilon,t)$ is of second order in the laser field, it can only be important in comparison with $\Gamma_{SS}(\omega_k,\varepsilon,t)$ as long as $\sigma_{ff}\ll 1$. To estimate their relative importance we assume that the radiator is excited by a laser pulse of duration T. Furthermore, all matrix elements of $d_c^{(1)}$ and $D_c^{(1)}$ of Eqs. (30) and (36) are considered to be roughly equal. Estimating the number of perturbers that contribute to the collisionally induced quantities in Eqs. (30) and (36) by $(N/V)\pi b_w^3$ [b_w is the Weisskopf radius; see Eq. (C8)], we obtain

$$\frac{\Gamma_S(\omega_k,\varepsilon,t)}{\Gamma_{SS}(\omega_k,\varepsilon,t)}\approx\frac{\left[\dfrac{N}{V}\pi b_w^3\right]\tau_c}{\left[\dfrac{N}{V}\pi b_w^3\right]^2 t}\approx\frac{1}{\gamma_c t}\;, \tag{38}$$

for $t<T,1/\gamma,1/W$. $\sigma_{ff}(t)$ has thereby been estimated by Eq. (18b) with $\mu_R=0$ in W of Eq. (13a). Note that $\Gamma_S=0$ for $t>T$. The major differences between these quantities are therefore the density dependences and the time during which the radiator can be excited. The former arises from the fact that $\Gamma_S(\omega_k,\varepsilon,t)$ is brought about by single collisions, whereas $\Gamma_{SS}(\omega_k,\varepsilon,t)$ is generated in subsequent collisions. The excitation time τ_c in the numerator of Eq. (38) comes from the confinement of the whole absorption and emission process of Eq. (36) to the time of a single collision. As excitation and emission in $\Gamma_{SS}(\omega_k,\varepsilon,t)$ occur in subsequent collisions, there is no such confinement and the excitation time of the radiator is given by t. Equation (38) shows that $\Gamma_S(\omega_k,\varepsilon,t)$ is likely to be as important as $\Gamma_{SS}(\omega_k,\varepsilon,t)$ for observation times $t<1/\gamma_c$. In this case, we have to evaluate $\Gamma_{SS}(\omega_k,\varepsilon,t)$ by using Eqs. (30), (12), and (19b). For $t\gg 1/\gamma^{(K)}$, $\Gamma_{SS}(\omega_k,\varepsilon,t)$ gives the dominant contribution to the collisionally induced part of the spectrum, which is then completely determined by Eqs. (32a) and (12) because the excited radiator manifold is equally populated.

In Eq. (27a) we have neglected interference effects between Rayleigh scattering and $\Gamma_S(\omega_k,\varepsilon,t)$ (see Appendix C3c). As shown in Appendix C these effects are restricted to the frequency domain of the Rayleigh peak and are negligible within the BCA. Equation (27a) also neglects contributions to Rayleigh scattering which involve two different perturbers. It is shown in Appendix C2 that such contributions vanish in the thermodynamic limit [see Eq. (C7″)]. In principle, there exist collisional corrections to coherent Rayleigh scattering that are due to different perturbers (and scale as the square of the perturber density). However, these contributions are also negligible within the BCA.

IV. CONCLUSION

Within the BCA we have studied collisionally induced absorption and emission involving a dipole-forbidden atomic transition of the radiator. We have restricted ourselves to the situation in which the motion of the mean induced dipole moment is not significantly influenced by the perturbers, i.e., heavy-radiator limit or negligible lower-state interaction, and have shown that absorption from the radiator ground state and emission from the radiator excited state occur during single collisions and the corresponding rates obey detailed balance. It is noted that a contribution from subsequent collisions exists in principle, since the motion of the radiator through the perturber ensemble breaks the spherical symmetry. Although this contribution has not been, as yet, evaluated in detail, from consideration of similar problems in the theory of spectral line broadening it is expected to be quite small. Experimentally, such a term, with width the order of γ_c around the forbidden line, could be distinguished from radiation due to higher multipoles by its different density dependence. However, if multipole radiation exists, interference effects will also have to be considered, as pointed out by Herman.[11] Certainly, subsequent collisional contributions to these processes are likely to become important if the velocity of the mean induced dipole moment is changed significantly during collisions, as has been pointed out by Lewis and Van Kanendonk.[7-10]

We have also investigated the spectrum of the spontaneously emitted photon in the frequency range of the dipole-forbidden transition. It consists mainly of two different contributions, namely, Rayleigh scattering of the perturbers and spontaneous emission of the observed photon *during* collisions. This latter contribution gives rise to a broad asymmetric structure in the spectrum (typical width $\sim 1/\tau_c$) and vanishes in the absence of collisions. Collisional corrections to Rayleigh scattering and various interferences are shown to be negligible, and subsequent collisional contributions due to breakdown of spherical symmetry are also assumed to be negligible. In particular, we have distinguished between two mechanisms by which a photon can be emitted during collisions.

(1) Subsequent collisional contribution. The radiator is excited by the laser field during a collision and emits a photon during a subsequent collision. The excitation process is thereby limited by the duration of the laser pulse, whereas the emission process occurs during the time of a single collision.

(2) Single collisional contribution. The radiator is excited by the laser field and emits a photon during one single collision. Excitation and emission processes are therefore confined to the duration of a single collision.

Whereas process (1) is proportional to the square of the density of the perturbers as long as $\sigma_{ff}(t) \ll 1$ (because both excitation rate and emission rate are proportional to N), process (2) is proportional only to the perturber density. We have shown that for long observation times, $t \gg 1/\gamma_c$, process (1) dominates, whereas in the opposite limit, i.e., $t \lesssim 1/\gamma_c$, process (1) is at least as important as process (2). We stress that our analysis covers both the quasistatic and impact regimes.

ACKNOWLEDGMENTS

The work of G.A. was supported by National Science Foundation Grant No. PHY-82-00805, and that of J.C. by the U.S. Air Force Office of Scientific Research (AFOSR-840027).

APPENDIX A

In this appendix we outline the derivation of the density matrix Eqs. (12) for the radiator. Our major approximation is the BCA.

Starting from Eq. (7a) we expand the propagator $G(t,t')$ perturbatively in terms of $L_s^{(k)}$ and $L_c^{(k)}$, i.e.,

$$G(t,t') = G_c(t,t') + \int_{t'}^{t} dt_1 G_c(t,t_1) I(t_1) G_c(t_1,t') + \int_{t'}^{t} dt_1 \int_{t'}^{t_1} dt_2 G_c(t,t_1) I(t_1) \times G_c(t_1,t_2) I(t_2) G_c(t_2,t') + \cdots \tag{A1a}$$

with

$$I(t) = L_c^{(R)}(t) + (1-\mathscr{P}) L_s^{(R)}(t) + \sum_{j=1}^{N} [L_c^{(j)}(t) + L_s^{(j)}(t)] \tag{A1b}$$

and the collisional propagator

$$G_c(t,t') = \mathscr{T} \exp\left[\int_{t'}^{t} dt_1 \sum_{j=1}^{N} (1-\mathscr{P}) V_j(t_1)\right]. \tag{A1c}$$

$\mathscr{T}$ is thus the time ordering operator. Inserting this expression into Eq. (7a) we obtain the quantities $M_n^{(m)}(t,t')$ of Eq. (11). In the following, we discuss these terms and simplify them within the BCA.

1. Zeroth-order quantities

In zeroth order of $L_c^{(k)}$ and $L_s^{(k)}$ the coupling between the radiator density matrix elements is characterized by

$$M_0^{(0)}(t,t') = \mathrm{Tr}_{\{p\}}\left[\sum_{j=1}^{N} V_j(t) \bar{G}_c(t,t') \times \sum_{i=1}^{N} (1-\mathscr{B}) V_i(t') \times \prod_{m=1}^{N} |g,g\rangle\rangle \rho(\mathbf{p}_m)\right] \tag{A2a}$$

with

$$\bar{G}_c(t,t') = \mathscr{T} \exp\left[\int_{t'}^{t} dt_1 \sum_{j=1}^{N} (1-\mathscr{B}) V_j(t_1)\right] \tag{A2b}$$

and $\mathscr{B} = \prod_{j=1}^{N} p_j$. If inelastic collisions are neglected, $\mathscr{P} \sum_{j=1}^{N} V_j(t) \mathscr{P}$ does not contribute to the couplings, because $V_j(t)$ is assumed to be off diagonal in electronic radiator-perturber states. In the BCA the collisional propagator is approximated by

$$\bar{G}_c(t,t') = \theta_0 \prod_{j=1}^{N} G_j(t,t') \tag{A3a}$$

with

$$G_j(t,t') = \mathscr{T} \exp\left[\int_{t'}^{t} dt_1 (1-\mathscr{B}) V_j(t_1)\right] \tag{A3b}$$

and θ_0 a time-ordering operator. This time-ordering operator θ_0 orders different collisions,[13] whereas $\mathscr{T}$ orders the times within one collision. $\mathscr{T}$ is important because $V_j(t)$ usually does not commute with itself at different times. Equation (A3a) essentially assumes that strong collisions, which cannot be treated in lowest-order perturbation theory, do not overlap in time. Inserting Eq. (A3a) into (A2a) we find that terms with $i \neq j$ vanish, i.e.,

$$\begin{aligned}\mathscr{B}\, V_j(t)G_j(t,t')\prod_{l<j} G_l(t,t')(1-\mathscr{B})V_i(t')\mathscr{B} &= \mathscr{B}\, V_j(t)G_j(t,t')\mathscr{B}\prod_{l<j} G_l(t,t')(1-\mathscr{B})V_i(t')\mathscr{B}\\ &= \mathscr{B}\, V_j(t)G_j(t,t')\mathscr{B}(1-\mathscr{B})V_i(t')\mathscr{B}=0 \ . \qquad \text{(A4a)}\end{aligned}$$

Here, $l<j$ indicates that all the time-ordered collisions l occur before collision j starts. Thus we have used the identity $\mathscr{B}^2=\mathscr{B}$ and moved projection operators from the left and right between $G_j(t,t')$ and $\prod_{l<j} G_l(t,t')$ noting that $[p_k,G_l(t,t')]=[p_k,V_l]=0$ for $k\neq l$, and finally we have used

$$\prod_{\mu\neq j} p_\mu \prod_{\nu\neq\{l\}} p_\nu = \mathscr{B}$$

(Refs. 13 and 16). We also apply the identity

$$\mathscr{B}\, G_k(t,t')=\mathscr{B} \ , \qquad \text{(A4b)}$$

which can immediately be proved from Eq. (A3b). So Eq. (A2a) reduces to

$$M_0^{(0)}(t,t')=N\,\mathrm{Tr}_1[V_1(t)U_1(t,t')V_1(t')\,|\,g,g\rangle\rangle\rho(\mathbf{p}_1)] \qquad \text{(A5a)}$$

with the one perturber collisional propagator

$$U_1(t,t')=\mathscr{T}\exp\left[\int_{t'}^{t}dt_1\,V_1(t_1)\right] . \qquad \text{(A5b)}$$

Thereby we have performed the thermodynamic limit by replacing $1-p_1\rightarrow 1$.[13] As $V_1(t)$ is off diagonal in the electronic radiator-perturber states, which are typically separated by energies of the order of $\hbar\omega \gg \hbar/\tau_c$, we can further simplify Eq. (A5a) by adiabatically eliminating these off-resonant states. For this purpose we insert

$$\begin{aligned}U_1(t,t')&=1+\int_{t'}^{t}dt_1\,V_1(t_1)U_1(t_1,t')\\ &=1+\int_{t'}^{t}dt_1\,U_1(t,t_1)V_1(t_1) \qquad \text{(A6)}\end{aligned}$$

repeatedly into Eq. (A5a). Whenever $V_1(t)$ acts on an electronic radiator-perturber state $|\,k_1 l_1\rangle$ twice, we keep only the coupling to the degenerate state $|\,k_1' l_1'\rangle$. So we find[16,19]

$$\int_0^t dt' M_0^{(0)}(t,t')\sigma_I(t') \rightarrow N\,\mathrm{Tr}_1[V_1^e(t)\,|\,g,g\rangle\rangle\rho(\mathbf{p}_1)]\sigma_I(t)+N\,\mathrm{Tr}_1\left[V_1^e(t)\int_0^t dt' U_1^e(t,t')V_1^e(t')\,\Big|g,g\Big\rangle\!\Big\rangle\rho(\mathbf{p}_1)\right]\sigma_I(t') \qquad \text{(A7a)}$$

with the effective collisional propagator

$$U_1^e(t,t')=\mathscr{T}\exp\left[\int_{t'}^{t}dt_1\,V_1^e(t_1)\right] . \qquad \text{(A7b)}$$

The tetradic matrix elements of the effective collisional interaction are given by

$$\begin{aligned}&\langle\langle k_1 l_1 \mathbf{p}_1, k_2 l_2 \mathbf{p}_2\,|\,V_1^e(t)\,|\,k_1' l_1' \mathbf{p}_3, k_2' l_2' \mathbf{p}_4\rangle\rangle\\ &\quad=\frac{1}{i\hbar}\left[\langle k_1 l_1 \mathbf{p}_1\,|\,V(|\mathbf{x}_1|,t)\frac{1}{E_{k_1}+E_{l_1}-H_R-H(1)}V(|\mathbf{x}_1|,t)\,|\,k_1' l_1' \mathbf{p}_3\rangle\delta_{k_2 k_2'}\delta_{l_2 l_2'}\delta_{\mathbf{p}_2,\mathbf{p}_4}\right.\\ &\qquad\left.-\langle k_2' l_2' \mathbf{p}_4\,|\,V(|\mathbf{x}_1|,t)\frac{1}{E_{k_2}+E_{l_2}-H_R-H(1)}V(|\mathbf{x}_1|,t)\,|\,k_2 l_2 \mathbf{p}_2\rangle\delta_{k_1 k_1'}\delta_{l_1 l_1'}\delta_{\mathbf{p}_1,\mathbf{p}_3}\right] , \qquad \text{(A7c)}\end{aligned}$$

where $|\,k_1 l_1\rangle$ $(|\,k_2 l_2\rangle)$ and $|\,k_1' l_1'\rangle$ $(|\,k_2' l_2'\rangle)$ are two degenerate electronic radiator-perturber states. The motion of the perturber within a time interval of order $1/\omega$ has thereby been neglected, because $kT \ll \hbar\omega$.

If $\sigma_I(t')$ is slowly varying on a time scale of order τ_c, we can make the Markov approximation,[16] and relation (A7a) reduces to

$$\int_0^t dt' M_0^{(0)}(t,t')\sigma_I(t') \rightarrow M_0^{(0)}\sigma_I(t) \qquad \text{(A8a)}$$

with the time-independent tetradic collision operator

$$M_0^{(0)}=\lim_{t\rightarrow\infty} N\,\mathrm{Tr}_1\left[\left[V_1^e(t)+V_1^e(t)\int_0^t dt' U_1^e(t,t')V_1^e(t')\right]\Big|g,g\Big\rangle\!\Big\rangle\rho(\mathbf{p}_1)\right] . \qquad \text{(A8b)}$$

In a spherically symmetric collision environment of the radiator, $M_0^{(0)}$ is diagonal in the tetradic radiator states[19]

$$|\,k_1 k_2 KQ\rangle\rangle=\sum_{m_1,m_2}|\,k_1 m_1\rangle\langle k_2 m_2\,|\,(-1)^{j_1-m_2-Q}(2K+1)^{1/2}\begin{bmatrix} j_1 & j_2 & K\\ m_1 & -m_2 & -Q\end{bmatrix} . \qquad \text{(A9)}$$

The collisional decay rate of the Kth multipole of the excited radiator manifold is given by[19]

$$\gamma^{(K)} = -\mathrm{Re}\{\langle\langle ffKQ \mid M_0^{(0)} \mid ffKQ \rangle\rangle\} \ . \tag{A10a}$$

Neglecting inelastic collisions in particular implies that[16]

$$\gamma^{(K=0)} = 0 \tag{A10b}$$

due to unitarity.

2. First-order quantities

In first order in the atom-laser interactions, there are collisionally induced couplings between the slowly varying radiator density matrix elements $\langle\langle ffKQ \mid \sigma_I(t)\rangle\rangle$, $\langle\langle iiKQ \mid \sigma_I(t)\rangle\rangle$ and $\langle\langle fiK'Q' \mid \sigma_I(t)\rangle\rangle$, $\langle\langle ifK'Q' \mid \sigma_I(t)\rangle\rangle$. In particular, the collisionally induced coupling due to the perturber-laser interaction is determined by

$$\begin{aligned} M_1^{(0)p}(t,t') = {} & \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[V_j(t)\bar{G}_c(t,t') \sum_{i=1}^{N} L_c^{(i)}(t') \prod_{m=1}^{N} \left| g,g \right\rangle\!\!\right\rangle \rho(\mathbf{p}_m) \right] \\ & + \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[V_j(t) \int_{t'}^{t} dt_1 \bar{G}_c(t,t_1) \sum_{i=1}^{N} L_c^{(i)}(t_1)\bar{G}_c(t_1,t') \sum_{k=1}^{N} (1-\mathscr{B})V_k(t') \prod_{m=1}^{N} \left| g,g \right\rangle\!\!\right\rangle \rho(\mathbf{p}_m) \right] . \end{aligned} \tag{A11}$$

In the BCA we insert Eq. (A3a) into Eq. (A11). For the first term we obtain an expression such as

$$V_j G_j \prod_{l<j} G_l L_c^{(i)} , \tag{A12a}$$

where we have suppressed all summations and time arguments for simplicity of notation. If $i \neq j$ this term vanishes because of Eq. (A4b) and $p_i L_c^{(i)} = 0$. If $i = j$, we have

$$\mathscr{B} V_j G_j \prod_{\mu \neq j} p_\mu \prod_{l<j} G_l L_c^{(j)} \mathscr{B} = \mathscr{B} V_j G_j \prod_{l<j} U_l L_c^{(j)} \mathscr{B} \tag{A12b}$$

because

$$\begin{aligned} \prod_{\mu\neq j} p_\mu \prod_{l\neq j} G_l(t,t') L_c^{(j)}(t') &= \prod_{\mu\neq j} p_\mu \left[1 + \int_{t'}^{t} dt_1 (1-p_j) \sum_{l\neq j} V_l(t_1) \prod_{l'\neq j} G_{l'}(t_1,t') \right] L_c^{(j)}(t') \\ &= \prod_{\mu\neq j} p_\mu \left[1 + \int_{t'}^{t} dt_1 \sum_{l\neq j} V_l(t_1) \prod_{l'\neq j} G_{l'}(t_1,t') \right] L_c^{(j)}(t') \ . \end{aligned} \tag{A12c}$$

In the first step of Eq. (A12c) we use

$$\prod_{\mu\neq j} p_\mu (1-\mathscr{B}) = \prod_{\mu\neq j} p_\mu (1-p_j)$$

and in the second step we use $p_j L_c^{(j)} = 0$. Because $L_c^{(j)}(t')$ is off diagonal in the internal perturber states, the time of interest between the rightmost $V_j(t_1)$ $(t \geq t_1 \geq t')$ and $L_c^{(j)}(t')$ is much less than the duration of a collision, i.e., $|t_1 - t'| \approx \hbar/(|E_g + \hbar\omega - E_l|) \approx 1/\omega \ll \tau_c$. This implies that within the BCA we have $\prod_{l<j} U_l \to 1$ in Eq. (A12b), so that the first term in expression (A11) reduces to a one-perturber average. Note that $\prod_{l<j} U_l \to 1$ really means that we approximate $\prod_{l<j} U_l^e \to 1$ [U_l^e is the effective propagator of Eq. (A7b)] during a time of order $1/\omega \ll \tau_c$. This is due to the projection operators at the very left and very right of Eq. (A12b) and the fact that V_l is off diagonal in electronic radiator-perturber states. This approximation therefore neglects terms of order γ_c/ω $(\ll 1)$.

Inserting Eq. (A3a) into the second term of expression (A11), we notice that it is only nonzero if $i = j$ [because of Eq. (A4b) and $p_i L_c^{(1)} = 0$]. There cannot be any other collision between V_j and $L_c^{(j)}$ because of the short time of interest associated with a perturber-dipole excitation. Using Eq. (A4b) then implies that $k = j$ so that the second term of Eq. (A11) reduces to a one-perturber average.

We therefore find in the thermodynamic limit, i.e., $1 - p_j \to 1$,

$$\begin{aligned} M_1^{(0)p}(t,t') = {} & N\,\mathrm{Tr}_1[V_1(t)U_1(t,t')L_c^{(1)}(t') \mid g,g\rangle\rangle \rho(\mathbf{p}_1)] \\ & + N\,\mathrm{Tr}_1 \left[V_1(t) \int_{t'}^{t} dt_1 U_1(t,t_1) L_c^{(1)}(t_1) U_1(t_1,t') V_1(t') \left| g,g \right\rangle\!\!\right\rangle \rho(\mathbf{p}_1) \right] . \end{aligned} \tag{A13}$$

For the collisionally induced coupling due to the radiator-laser interaction we find

$$M_1^{(0)R}(t,t')=L_c^{(R)}(t)\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[\left[V_j(t')+\int_{t'}^{t}dt_1 V_j(t_1)\bar{G}_c(t_1,t')\sum_{i=1}^{N}(1-\mathscr{B})V_i(t')\right]\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_m)\right]$$
$$+\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[\left[V_j(t)+\int_{t'}^{t}dt_1 V_j(t)\bar{G}_c(t,t_1)\sum_{i=1}^{N}(1-\mathscr{B})V_i(t_1)\right]\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_m)\right]L_c^{(R)}(t')$$
$$+\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[V_j(t)\int_{t'}^{t}dt_1\bar{G}_c(t,t_1)L_c^{(R)}(t_1)\bar{G}_c(t_1,t')\sum_{i=1}^{N}(1-\mathscr{B})V_i(t')\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_m)\right]. \quad \text{(A14a)}$$

Because of Eq. (A4b) this expression is only nonzero if $i=j$. Therefore, we obtain in the thermodynamic limit

$$M_1^{(0)R}(t,t')=L_c^{(R)}(t)N\,\mathrm{Tr}_1\left[\left[V_1(t')+\int_{t'}^{t}dt_1 V_1(t_1)U_1(t_1,t')V_1(t')\right]\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_1)\right]$$
$$+N\,\mathrm{Tr}_1\left[\left[V_1(t)+\int_{t'}^{t}dt_1 V_1(t)U_1(t,t_1)V_1(t_1)\right]\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_1)\right]L_c^{(R)}(t')$$
$$+N\,\mathrm{Tr}_1\left[V_1(t)\int_{t'}^{t}dt_1 U_1(t,t_1)L_c^{(R)}(t_1)U_1(t_1,t')V_1(t')\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_1)\right]. \quad \text{(A14b)}$$

The total first-order coupling is given by

$$M_1^{(0)}(t,t')=M_1^{(0)P}(t,t')+M_1^{(0)R}(t,t'). \quad \text{(A15)}$$

In the spherically symmetric collision environment of the radiator, neither $M_1^{(0)P}(t,t')$ nor $M_1^{(0)R}(t,t')$ can give rise to a coupling between $\langle\langle fi\,K=2\,Q\mid\sigma_I(t)\rangle\rangle$, $\langle\langle if\,K=2\,Q\mid\sigma_I(t)\rangle\rangle$ and $\langle\langle ii\,K=Q=0\mid\sigma_I(t)\rangle\rangle$, $\langle\langle ff\,K=Q=0\mid\sigma_I(t)\rangle\rangle$. This can be seen by considering, e.g., the matrix element

$$\langle\langle fi\,K=2\,Q\mid M_1^{(0)P}(t,t')\mid ii\,K'=Q'=0\rangle\rangle$$
$$=\sum_{\substack{A,q,\\K_1,Q_1,q_1}} N\,\mathrm{Tr}_1[\langle\langle fi\,K=2q\mid V_1(t)U_1(t,t')\mid AK_1q_1\rangle\rangle$$
$$\times\langle\langle AK_1Q_1\mid L_c^{(1)}(t')\mid g,g\rangle\rangle\rho(\mathbf{p}_1)\mid ii\,K'=Q'=0\rangle\rangle\mathscr{D}_{Qq}^{K=2}(\mathscr{D}_{Q_1q_1}^{K_1})^*]$$
$$+\sum_{\substack{A,q,\\K_1,q_1,\\K_2,B,q_2}} N\,\mathrm{Tr}_1\left[\left\langle\!\!\left\langle fi\,K=2q\left|V_1(t)\int_{t'}^{t}dt_1 U_1(t,t_1)\right|AK_1q_1\right\rangle\!\!\right\rangle\right.$$
$$\times\sum_{Q_1,Q_2}\langle\langle AK_1Q_1\mid L_c^{(1)}(t_1)\mid BK_2Q_2\rangle\rangle$$
$$\times\langle\langle BK_2q_2\mid U_1(t_1,t')V_1(t')\mid g,g\rangle\rangle\rho(\mathbf{p}_1)\mid ii\,K'=Q'=0\rangle\rangle$$
$$\left.\times(\mathscr{D}_{Q_1q_1}^{K_1})^*\mathscr{D}_{Q_2q_2}^{K_2}\mathscr{D}_{Qq}^{K=2}\right]. \quad \text{(A16a)}$$

Hence A and B characterize everything except the multipole indices, which uniquely determine a tetradic radiator-perturber state. $Q,Q_1,Q_2,Q'(q,q_1,q_2)$ refer to a space-fixed (perturber-fixed) coordinate system and the various $\mathscr{D}_{Qq}^{K}$'s are the rotation matrices, which transform between these two coordinate systems (for details, see, e.g., Appendix C of Ref. 17). Because the collisional interaction is short range, the matrix elements of $L_c^{(1)}$ do not depend on the perturber center-of-mass motion. A spherically symmetric collision environment of the radiator then implies that none of the tetradic matrix elements in Eq. (A16a) depends on the orientation of the perturber-fixed coordinate system. Because of $\rho(\mathbf{p}_1)=\rho(|\mathbf{p}_1|)$ we can perform the integration over the directions of $\mathbf{p}_1$ in Eq. (A16a) by using $\int d\Omega_{\mathbf{p}_1}=(1/2\pi)\int d\Omega$, where Ω denotes all Euler angles, which uniquely determine the relation between the space-fixed and laboratory-fixed coordinate system. Using the relations[27]

$$\int d\Omega\,\mathscr{D}_{Qq}^{K=2}(\mathscr{D}_{Q_1q_1}^{K_1})^*=\frac{1}{2K+1}8\pi^2\delta_{KK_1}\delta_{QQ_1}\delta_{qq_1}, \quad \text{(A16b)}$$

$$\int d\Omega\,(\mathscr{D}_{Q_1q_1}^{K_1})^*\mathscr{D}_{Q_2q_2}^{K_2}\mathscr{D}_{Qq}^{K=2}$$
$$=(-1)^{Q_1-q_1}8\pi^2\begin{pmatrix}K_2 & K & K_1\\ Q_2 & Q & -Q_1\end{pmatrix}\begin{pmatrix}K_2 & K & K_1\\ q_2 & q & -q_1\end{pmatrix}, \quad \text{(A16c)}$$

we immediately see that the first term of Eq. (A16a) vanishes because the laser dipole interaction can only give rise to a multipole $K_1=1$ so that $\delta_{KK_1}=0$. For the second term of Eq. (A16a) we use formula (B5) of Ref. 17 together with relation (A16c), yielding a term such as

$$\sum_{Q_1,Q_2}\begin{pmatrix} K_2 & K & K_1 \\ Q_2 & Q & -Q_1\end{pmatrix}\begin{pmatrix} K_2 & 1 & K_1 \\ Q_2 & k & -Q_1\end{pmatrix}, \tag{A16d}$$

which is only nonzero if $K=1$. Thus k is an index characterizing the polarization of the laser field. This implies that the matrix element of Eq. (A16a) vanishes.

3. Second-order quantities

The couplings of second order in $L_c^{(k)},L_s^{(k)}$ $(k=R,j)$ can be written as

$$\begin{aligned} M_2^{(0)}(t,t') &= M_2^{(0)p}(t,t')+M_2^{(0)R}(t,t')+M_2^{(0)pR}(t,t') ,\\ M_0^{(2)}(t,t') &= M_0^{(2)p}(t,t')+M_0^{(2)R}(t,t')+M_0^{(2)pR}(t,t') .\end{aligned} \tag{A17}$$

$M_2^{(0)p}(t,t')$ and $M_0^{(2)p}(t,t')$ contain the perturber-dipole interactions $L_c^{(j)}$ and $L_s^{(j)}$ only, $M_2^{(0)R}(t,t')$ and $M_0^{(2)R}(t,t')$ are due to the radiator-dipole interactions $L_c^{(R)}$ and $L_s^{(R)}$ only, and $M_2^{(0)pR}(t,t')$ and $M_0^{(2)pR}(t,t')$ contain a perturber and a radiator-dipole interaction. In the following we discuss these three types of contributions and reduce them to one-perturber averages within the BCA.

a. Perturber-dipole—induced couplings

From Eq. (7a) we find

$$\begin{aligned} M_2^{(0)p}(t,t') = {}& \mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[V_j(t)\int_{t'}^{t}dt_1\bar{G}_c(t,t_1)\sum_{i=1}^{N}L_c^{(i)}(t_1)\bar{G}_c(t_1,t')\sum_{k=1}^{N}L_c^{(k)}(t')\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_m)\right] \\ &+\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[V_j(t)\int_{t'}^{t}dt_1\int_{t'}^{t_1}dt_2\bar{G}_c(t,t_1)\sum_{i=1}^{N}L_c^{(i)}(t_1)\bar{G}_c(t_1,t_2)\sum_{k=1}^{N}L_c^{(k)}(t_2)\bar{G}_c(t_2,t')(1-\mathscr{B})\right. \\ &\left.\times\sum_{l=1}^{N}V_l(t')\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_m)\right] . \end{aligned} \tag{A18}$$

Inserting Eq. (A3a) into the first term we have to distinguish between different cases depending on whether the perturber-laser interaction $L_c^{(i)}(t_1)$ occurs during the collision $V_j(t)$, i.e., $|t-t_1|<\tau_c$, or before. In the first case, i.e., $|t-t_1|<\tau_c$, we get terms such as

$$\mathscr{B}\,V_jG_jL_c^{(j)}G_j\prod_{l<j}G_lL_c^{(j)}\mathscr{B}=\mathscr{B}\,V_jG_jL_c^{(j)}G_j\prod_{l<j}U_jL_c^{(j)}\mathscr{B} . \tag{A19a}$$

Terms with $k\neq j$ or $i\neq j$ vanish because of $p_iL_c^{(i)}=0$ and Eq. (A4b). In the second case we find quantities such as

$$\mathscr{B}\,V_jG_j\prod_{l<j}G_lL_c^{(i)}\prod_{m\leq l}G_mL_c^{(k)}\mathscr{B} , \tag{A19b}$$

which are zero if i and k are not both equal to j, because of $p_kL_c^{(k)}=0$ and Eq. (A4b). $m\leq l$ indicates that the leftmost of the indices $\{m\}$ can be equal to l. If $k=j$ and $i\neq j$, the time of interest between the rightmost collision $V_j(t_1)$ and $L_c^{(j)}(t')$ is much less than the duration of a collision, so that, as before, $\prod_{l<j}G_l\to 1$ and the term also vanishes due to $p_iL_c^{(j)}=0$. If $i=j$ and $k\neq j$, we have $\prod_{l<j}G_l\to 1$ by the same argument, and because of $\mathscr{B}\prod_m G_mL_c^{(k)}\mathscr{B}=\mathscr{B}L_c^{(k)}\mathscr{B}=0$ this term vanishes, too. Expression (A19b) is therefore only nonzero for $i=k=j$, which implies that $|t_1-t'|\approx 1/\omega\ll\tau_c$ and $\prod_{m\leq l}G_m\to 1$. It can contribute further only if the time between the rightmost collision V_j and the interaction $L_c^{(i=j)}$ is larger than τ_c, because otherwise we have to deal with expression (A19a). Therefore, it is necessary to have a perturber tetradic $|l_1,l_1'\rangle\rangle$ ($|l_1\rangle,|l_1'\rangle$ are degenerate internal perturber states) left of $L_c^{(i=j)}$, which guarantees a long propagation time. However, because of

$$\left\langle\!\!\left\langle l_1,l_1'\right|\int_{t'}^{t}dt_1L_c^{(j)}(t_1)L_c^{(j)}(t')\left|g,g\right\rangle\!\!\right\rangle\to 0 \quad \text{as } \omega\,|t-t'|\to\infty , \tag{A20}$$

expression (A19b) does not contribute to $M_2^{(0)p}(t,t')$. Relation (A20) can be seen by evaluating the matrix elements. We are therefore left with expression (A19a). The dominant contribution to this quantity comes from situations that involve a long intermediate propagation somewhere within the time interval $|t-t'|$. In our case such a long propagation can either come from an electronic radiator-perturber tetradic of the form $|fl_1,il_1'\rangle\rangle$ or $|il_2',fl_1'\rangle\rangle$ between $L_c^{(i=j)}$ and $L_c^{(k=j)}$ or from a perturber tetradic $|l_1,l_1'\rangle\rangle$ between G_j and $L_c^{(i=j)}$ in (A19a). In the latter case we have $|t_1-t'|\approx 1/\omega\ll\tau_c$ and we can use relation (A20) so that such terms vanish. We are therefore left with contributions to (A19a) involving the intermediate excitation of the tetradic $|fl_1,il_1'\rangle\rangle$ or $|il_1,fl_1'\rangle\rangle$ which is only possible by the combined action of V_j and $L_c^{(j)}$. Due to the fact that $L_c^{(j)}$ is off diagonal in the internal perturber states, the time between the rightmost V_j (which has to be right of $L_c^{(i=j)}$) and $L_c^{(k=j)}$ is much less than the duration of a collision, so that we may, as before, set $\prod_{l<j}U_l\to 1$ and the first term of expression (A18) reduces to a one-perturber average.

Inserting Eq. (A3a) into the second term of expression (A18) we notice that this term is only nonzero if $i=k=j$ because of $p_k L_c^{(k)}=0$ and Eq. (A4b). With the above arguments it is straightforward to reduce also the second term of Eq. (A18) to a one-perturber average.

So we finally find for the collisionally induced coupling due to the perturber-laser interaction in the thermodynamic limit $(1-p_j \to 1)$

$$M_2^{(0)p}(t,t')=N\,\mathrm{Tr}_1\left[V_1(t)\int_{t'}^{t}dt_1\,U_1(t,t_1)L_c^{(1)}(t_1)\left[1+\int_{t'}^{t_1}dt_2\,U_1(t_1,t_2)V_1(t_2)\right]L_c^{(1)}(t')\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_1)\right]$$
$$+N\,\mathrm{Tr}_1\left[V_1(t)\int_{t'}^{t}dt_1\int_{t'}^{t_1}dt_2\,U_1(t,t_1)L_c^{(1)}(t_1)U_1(t_1,t_2)L_c^{(1)}(t_2)U_1(t_2,t')V_1(t')\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_2)\right], \qquad \text{(A21)}$$

where we have used Eq. (A6) in the first term of expression (A18). We can further simplify $M_2^{(0)p}(t,t')$ by using Eq. (A6) and adiabatically eliminating the off-resonant radiator-perturber electronic states, as we did in Appendix A 1. Noting that the dominant contribution to $M_2^{(0)p}(t,t')$ in our case involves the intermediate excitation of the electronic radiator-perturber tetradic state $|fl_1,il'_1\rangle\rangle$ or $|il_1,fl'_1\rangle\rangle$, we see that the first term in large parentheses in Eq. (A21) does not contribute as indicated earlier. In the no-lower-state-interaction approximation, neglecting inelastic collisions, we find, e.g.,

$$\langle\langle ff\,K=Q=0\,|\,M_2^{(0)p}(t,t')\,|\,ii\,K'=Q'=0\rangle\rangle$$
$$=N\int d^3p_1\int\cdots\int d^3p_4\,\rho(\mathbf{p}_4)$$
$$\times\sum_{\alpha,\beta}2\,\mathrm{Re}\left[\left\langle\!\!\left\langle ff\,K=Q=0\right|\left\langle\!\!\left\langle g\mathbf{p}_1,g\mathbf{p}_1\right|V_1(t)\frac{i}{-i(L_R+L_1)}L_c^{(1)+}(t)\left|f\alpha g\mathbf{p}_1,ig\mathbf{p}_2\right\rangle\!\!\right\rangle\right.\right.$$
$$\times\langle\langle f\alpha g\mathbf{p}_1,ig\mathbf{p}_2\,|\,U_1^e(t,t')\,|\,f\beta g\mathbf{p}_3,ig\mathbf{p}_4\rangle\rangle$$
$$\times\left\langle\!\!\left\langle f\beta g\mathbf{p}_3,ig\mathbf{p}_4\right|\left[V_1(t')\frac{i}{\omega-i(L_R+L_1)}L_c^{(1)-}(t')+L_c^{(1)-}(t')\right.\right.$$
$$\left.\left.\left.\times\frac{i}{-i(L_R+L_1)}V_1(t')\right]\left|g\mathbf{p}_4,g\mathbf{p}_4\right\rangle\!\!\right\rangle\right]\left|ii\,K'=Q'=0\right\rangle\!\!\right\rangle, \qquad \text{(A22a)}$$

where $L_c^{(1)}(t)=L_c^{(1)+}(t)+L_c^{(1)-}(t)$ has been decomposed into its positive and negative frequency parts, i.e., $L_c^{(1)\pm}(t)\propto e^{\pm i\omega t}$ and $V_1(t)$ is the "true" tetradic collisional interaction, which is off diagonal in the electronic radiator-perturber states. We have neglected the perturber motion on a time scale of order $1/\omega$. In general, there are also terms such as

$$\int_{t'}^{t}dt_1 N\,\mathrm{Tr}_1\left[V_1^e(t)U_1^e(t,t_1)V_1(t_1)\frac{i}{-i(L_R+L_1)}L_c^{(1)+}(t_1)U_1^e(t_1,t')\right.$$
$$\left.\times\left[V_1(t')\frac{i}{\omega-i(L_R+L_1)}L_c^{(1)-}(t')+L_c^{(1)-}(t')\frac{i}{-i(L_R+L_1)}V_1(t')\right]\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_1)\right], \qquad \text{(A22b)}$$

$$\int_{t'}^{t}dt_1 N\,\mathrm{Tr}_1\left[V_1(t)\frac{i}{-i(L_R+L_1)}L_c^{(1)+}(t)U_1^e(t,t_1)L_c^{(1)-}\frac{i}{-i(L_R+L_1)}V_1(t_1)U_1^e(t_1,t')V_1^e(t')\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_1)\right], \qquad \text{(A22c)}$$

and

$$\int_{t'}^{t}dt_1\int_{t'}^{t_1}dt_2 N\,\mathrm{Tr}_1\left[V_1^e(t)U_1^e(t,t_1)V_1(t_1)\frac{i}{-i(L_R+L_1)}L_c^{(1)+}(t_1)U_1^e(t_1,t_2)\right.$$
$$\left.\times L_c^{(1)}(t_2)\frac{i}{-i(L_R+L_1)}V_1(t_2)U_1^e(t_2,t')V_1^e(t')\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_1)\right], \qquad \text{(A22d)}$$

which contribute to $M_2^{(0)p}(t,t')$ after the adiabatic elimination of the off-resonant electronic radiator-perturber states. It is thereby implicitly understood that the intermediate propagation occurs in the tetradic state $|fl_1,il_1'\rangle\rangle$. A similar set of terms is obtained from expressions (A22b)–(A22d) by the replacements $L_c^{(1)\pm}\to L_c^{(1)\mp}$, $[\omega-i(L_R+L_1)]\to[-\omega-i(L_R+L_1)]$ with an intermediate propagation in the tetradic state $|il_1,fl_1'\rangle\rangle$. Physically, these terms describe collisional mixing of the radiator manifolds $|i\rangle$ or $|f\alpha\rangle$ before or (and) after the collisionally induced dipole transition within the same collision. Similar terms have been studied by Burnett and Cooper[19] in connection with dipole-allowed transitions. However, if we neglect inelastic collisions, terms (A22b) and (A22d) do not contribute to the couplings between $\langle\langle ffK=Q=0|\sigma_I(t)\rangle\rangle$ and $\langle\langle iiK=Q=0|\sigma_I(t)\rangle\rangle$, because they cannot affect the total population of a radiator manifold due to unitarity.[16] In expression (A22c) the collisional mixing of the radiator manifold occurs before the collisionally induced dipole transition and the situation is therefore somewhat different. If there is no ground-state interaction, i.e.,

$$V_1^e\,|ig\mathbf{p},ig\mathbf{p}\rangle\rangle=0\ , \tag{A23}$$

then matrix elements with $|i,i\rangle\rangle$ to the right vanish. The matrix elements with $|ffK=Q=0\rangle\rangle$ to the right are negligible, if

$$|E_i+\hbar\omega-E_f|\ll kT\ , \tag{A24}$$

as has been shown by Burnett *et al.*[16] This condition essentially implies that the center-of-mass motion of the perturber is not influenced by the effective interaction $V_1^e(t)$. However, this does not apply generally for matrix elements with $|ffKQ\rangle\rangle$ and $K\neq 0$ to the right since mixing within the excited-state manifold occurs even if Eq. (A24) is satisfied.[19] So expression (A22c) is also unimportant for the couplings between the radiator populations $\langle\langle ffK=Q=0|\sigma_I(t)\rangle\rangle$ and $\langle\langle iiK=Q=0|\sigma_I(t)\rangle\rangle$.

The coupling due to the perturber–spontaneous-modes interaction is determined by

$$\begin{aligned}M_0^{(2)p}(t,t')=&\,\mathrm{Tr}_{\mathrm{RAD}}\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[V_j(t)\int_{t'}^{t}dt_1G_c(t,t_1)\sum_{i=1}^{N}L_s^{(i)}(t_1)G_c(t_1,t')\sum_{k=1}^{N}L_s^{(i)}(t')\Big|\{0\},\{0\}\Big\rangle\Big\rangle\prod_{m=1}^{N}\Big|g,g\Big\rangle\Big\rangle\rho(\mathbf{p}_m)\right]\\&+\mathrm{Tr}_{\mathrm{RAD}}\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\Bigg[V_j(t)\int_{t'}^{t}dt_1\int_{t'}^{t_1}dt_2G_2(t,t_1)\sum_{i=1}^{N}L_s^{(i)}(t_1)G_c(t_1,t_2)\\&\qquad\times\sum_{k=1}^{N}L_s^{(k)}(t_2)G_c(t_2,t')\\&\qquad\times\sum_{l=1}^{N}(1-\mathscr{P})V_l(t')\Big|\{0\},\{0\}\Big\rangle\Big\rangle\prod_{m=1}^{N}\Big|g,g\Big\rangle\Big\rangle\rho(\mathbf{p}_m)\Bigg]\ .\end{aligned} \tag{A25a}$$

The reduction of this quantity to a one-perturber average is analogous to the steps that lead from Eq. (A18) to Eq. (A21). So we find within the BCA

$$\begin{aligned}M_0^{(2)p}(t,t')=&\,\mathrm{Tr}_{\mathrm{RAD}}N\,\mathrm{Tr}_1\left[V_1(t)\int_{t'}^{t}dt_1U_1(t,t_1)L_s^{(1)}(t_1)\left[1+\int_{t'}^{t_1}dt_2U_1(t_1,t_2)V_1(t_2)\right]L_s^{(1)}(t')\Big|\{0\},\{0\}\Big\rangle\Big\rangle\Big|g,g\Big\rangle\Big\rangle\rho(\mathbf{p}_1)\right]\\&+\mathrm{Tr}_{\mathrm{RAD}}N\,\mathrm{Tr}_1\left[V_1(t)\int_{t'}^{t}dt_1\int_{t'}^{t_1}dt_2U_1(t,t_1)L_s^{(1)}(t_1)U_1(t_1,t_2)L_s^{(1)}(t_2)U_1(t_2,t')V_1(t')\Big|\{0\},\{0\}\Big\rangle\Big\rangle\Big|g,g\Big\rangle\Big\rangle\rho(\mathbf{p}_1)\right]\ .\end{aligned} \tag{A25b}$$

Analogously, for $M_2^{(0)p}(t,t')$ we can adiabatically eliminate the off-resonant electronic radiator-perturber states, thereby noting that the matrix element $\langle\langle ffK=Q=0|M_0^{(2)p}(t,t')|ffK=Q=0\rangle\rangle$ is only nonzero if there is a propagation in the tetradic state $|fg,ig\rangle\rangle$ or $|ig,fg\rangle\rangle$ during the time between the two interactions $L_s^{(1)}$.

b. Radiator-dipole–induced couplings

From Eq. (7a) we find

$$\begin{aligned}M_2^{(0)R}(t,t')=&\,L_c^{(R)}(t)\int_{t'}^{t}dt_1\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[V_j(t_1)\prod_{m=1}^{N}\Big|g,g\Big\rangle\Big\rangle\rho(\mathbf{p}_m)\right]L_c^{(R)}(t')\\&+L_c^{(R)}(t)\int_{t'}^{t}dt_1\int_{t'}^{t_1}dt_2\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[V_j(t_1)\overline{G}_c(t_1,t_2)\sum_{i=1}^{N}(1-\mathscr{B})V_i(t_2)\prod_{m=1}^{N}\Big|g,g\Big\rangle\Big\rangle\rho(\mathbf{p}_m)\right]L_c^{(R)}(t')\end{aligned}$$

$$+L_c^{(R)}(t)\int_{t'}^{t}dt_1\int_{t'}^{t_1}dt_2\,\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[V_j(t_1)\overline{G}_c(t_1,t_2)L_c^{(R)}(t_2)\overline{G}_c(t_2,t')\sum_{i=1}^{N}(1-\mathscr{B})V_i(t')\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_m)\right]$$

$$+\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[V_j(t)\int_{t'}^{t}dt_1\int_{t'}^{t_1}dt_2\overline{G}_c(t,t_1)L_c^{(R)}(t_1)\overline{G}_c(t_1,t_2)L_c^{(R)}(t_2)\overline{G}_c(t_2,t')\right.$$
$$\left.\times\sum_{i=1}^{N}(1-\mathscr{B})V_i(t')\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_m)\right]$$

$$+\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[V_j(t)\int_{t'}^{t}dt_1\int_{t'}^{t_1}dt_2\overline{G}_c(t,t_1)L_c^{(R)}(t_1)\overline{G}_c(t_1,t_2)\sum_{i=1}^{N}(1-\mathscr{B})V_i(t_2)\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_m)\right]L_c^{(R)}(t')\,, \tag{A26a}$$

because [as in Eq. (A20)]

$$\int_0^t dt'\langle\langle k_2,k_2'\,|\,L_c^{(R)}(t)L_c^{(R)}(t')\,|\,k_1,k_1'\rangle\rangle\to 0\quad\text{as }\omega\,|\,t-t'\,|\to\infty\,. \tag{A26b}$$

With the arguments of Appendix A 1 it is straightforward to reduce Eq. (A26a) to a one-perturber average. The dominant contribution to $M_2^{(0)R}(t,t')$ comes from terms with an intermediate "long-time" propagation in the electronic radiator-perturber tetradic $|\,fl_1,il_1'\rangle\rangle$ or $|\,il_1,fl_1'\rangle\rangle$. Taking this into account and adiabatically eliminating off-resonant electronic radiator-perturber states by using Eq. (A6) repeatedly we find, e.g.,

$$\langle\langle ff\,K=Q=0\,|\,M_2^{(0)R}(t,t')\,|\,ii\,K=Q=0\rangle\rangle$$
$$=N\int d^3p_1\int\cdots\int d^3p_4\rho(\mathbf{p}_4)\sum_{\alpha,\beta}2\,\mathrm{Re}\left[\left\langle\!\!\left\langle ff\,K=Q=0\left|\left\langle\!\!\left\langle g\mathbf{p}_1,g\mathbf{p}_1\right|\left[V_1(t)\frac{i}{-i(L_R+L_1)}L_c^{(R)+}(t)+L_c^{(R)+}(t)\frac{i}{\omega-iL_R}V_1(t)\right]\right|f\alpha g\mathbf{p}_1,ig\mathbf{p}_2\right\rangle\!\!\right\rangle\right.\right.$$
$$\times\langle\langle f\alpha g\mathbf{p}_1,ig\mathbf{p}_2\,|\,U_1^e(t,t')\,|\,f\beta g\mathbf{p}_3,ig\mathbf{p}_4\rangle\rangle$$
$$\left.\times\left\langle\!\!\left\langle f\beta g\mathbf{p}_3,ig\mathbf{p}_4\right|\left[V_1(t')\frac{i}{\omega-iL_R}L_c^{(R)-}(t')+L_c^{(R)-}(t')\frac{i}{-i(L_R+L_1)}\times V_1(t')\right]\left|g\mathbf{p}_4,g\mathbf{p}_4\right\rangle\!\!\right\rangle\left|ii\,K=Q=0\right\rangle\!\!\right\rangle\right]\,, \tag{A26c}$$

which is valid under the same conditions as Eq. (A22a).

The coupling due to the radiator—spontaneous-modes interaction is given by

$$M_0^{(2)R}(t,t')$$
$$=\mathrm{Tr}_{\mathrm{RAD}}\mathrm{Tr}_{\{p\}}\left[L_s^{(R)}(t)G_c(t,t')L_s^{(R)}(t')\left|\{0\},\{0\}\right\rangle\!\!\right\rangle\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_m)\right]$$
$$+\mathrm{Tr}_{\mathrm{RAD}}\mathrm{Tr}_{\{p\}}\left[L_s^{(R)}(t)\int_{t'}^{t}dt_1G_c(t,t_1)(1-\mathscr{P})L_s^{(R)}(t_1)G_c(t_1,t')\sum_{i=1}^{N}(1-\mathscr{P})V_i(t')\left|\{0\},\{0\}\right\rangle\!\!\right\rangle\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_m)\right]$$
$$+\mathrm{Tr}_{\mathrm{RAD}}\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[V_j(t)\int_{t'}^{t}dt_1G_c(t,t_1)(1-\mathscr{P})L_s^{(R)}(t_1)G_c(t_1,t')L_s^{(R)}(t')\left|\{0\},\{0\}\right\rangle\!\!\right\rangle\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_m)\right]$$
$$+\mathrm{Tr}_{\mathrm{RAD}}\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[V_j(t)\int_{t'}^{t}dt_1\int_{t'}^{t_1}dt_2G_c(t,t_1)(1-\mathscr{P})L_s^{(R)}(t_1)G_c(t_1,t_2)(1-\mathscr{P})L_s^{(R)}(t_2)G_c(t_2,t')\right.$$
$$\left.\times\sum_{i=1}^{N}(1-\mathscr{P})V_i(t')\left|\{0\},\{0\}\right\rangle\!\!\right\rangle\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_m)\right]\,. \tag{A27}$$

The reduction to a one-perturber average is analogous to expression (A26a). We can eliminate off-resonant electronic radiator-perturber states adiabatically, noting that there is only a contribution to $\langle\langle ff\,K=Q=0\,|\,M_0^{(2)R}(t,t')\,|\,ff\,K=Q=0\rangle\rangle$ if there is an intermediate propagation in the tetradic $|\,fg,ig\,\rangle\rangle$ or $|\,ig,fg\,\rangle\rangle$ during the time between the two interactions $L_s^{(R)}$.

c. Mixed couplings

From Eq. (7a) we find

$$
\begin{aligned}
M_2^{(0)pR}(t,t')
&= L_c^{(R)}(t)\int_{t'}^{t} dt_1 \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[V_j(t_1)\bar{G}_c(t_1,t') \sum_{i=1}^{N} L_c^{(i)}(t') \prod_{m=1}^{N} \left| g,g \right\rangle\!\!\right\rangle \rho(p_m) \right] \\
&+ L_c^{(R)}(t)\int_{t'}^{t} dt_1 \int_{t'}^{t_1} dt_2 \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[V_j(t_1)\bar{G}_c(t_1,t_2) \sum_{i=1}^{N} L_c^{(i)}(t_2)\bar{G}_c(t_2,t') \sum_{k=1}^{M} (1-\mathscr{B})V_k(t') \prod_{m=1}^{N} \left| g,g \right\rangle\!\!\right\rangle \rho(\mathbf{p}_m) \right] \\
&+ \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[V_j(t) \int_{t'}^{t} dt_1 \bar{G}_c(t,t_1) \sum_{i=1}^{N} L_c^{(i)}(t_1) \prod_{m=1}^{N} \left| g,g \right\rangle\!\!\right\rangle \rho(\mathbf{p}_m) \right] L_c^{(R)}(t') \\
&+ \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[V_j(t) \int_{t'}^{t} dt_1 \int_{t'}^{t_1} dt_2 \bar{G}_c(t,t_1) \sum_{i=1}^{N} L_c^{(i)}(t_1)\bar{G}_c(t_1,t_2) \sum_{k=1}^{N} (1-\mathscr{B})V_k(t_2) \prod_{m=1}^{N} \left| g,g \right\rangle\!\!\right\rangle \rho(\mathbf{p}_m) \right] L_c^{(R)}(t') \\
&+ \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[V_j(t) \int_{t'}^{t} dt_1 \bar{G}_c(t,t_1) L_c^{(R)}(t_1)\bar{G}_c(t_1,t') \sum_{i=1}^{N} L_c^{(i)}(t') \prod_{m=1}^{N} \left| g,g \right\rangle\!\!\right\rangle \rho(\mathbf{p}_m) \right] \\
&+ \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[V_j(t) \int_{t'}^{t} dt_1 \int_{t'}^{t_1} dt_2 \bar{G}_c(t,t_1) L_c^{(R)}(t_1)\bar{G}_c(t_1,t_2) \right. \\
&\qquad\qquad \left. \times \sum_{i=1}^{N} L_c^{(i)}(t_2)\bar{G}_c(t_2,t') \sum_{k=1}^{N} (1-\mathscr{B})V_k(t') \prod_{m=1}^{N} \left| g,g \right\rangle\!\!\right\rangle \rho(\mathbf{p}_m) \right] \\
&+ \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[V_j(t) \int_{t'}^{t} dt_1 \int_{t'}^{t_1} dt_2 \bar{G}_c(t,t_1) \sum_{i=1}^{N} L_c^{(i)}(t_1)\bar{G}_c(t_1,t_2) L_c^{(R)}(t_2)\bar{G}_c(t_2,t') \right. \\
&\qquad\qquad \left. \times \sum_{k=1}^{N} (1-\mathscr{B})V_k(t') \prod_{m=1}^{N} \left| g,g \right\rangle\!\!\right\rangle \rho(\mathbf{p}_m) \right] .
\end{aligned}
\tag{A28}
$$

The reduction of $M_2^{(0)pR}(t,t')$ to a one-perturber average is analogous to the reduction of the terms in Appendix A 2. Again we can adiabatically eliminate off-resonant electronic radiator-perturber states, thereby noting that the dominant contribution to $M_2^{(0)pR}(t,t')$ comes from terms with a long-time intermediate propagation in the tetradic state $|\,fl_1,il_1'\,\rangle\rangle$ or $|\,il_1,fl_1'\,\rangle\rangle$ during the time between the two laser-atom interactions.

It is straightforward to derive an expression for $M_0^{(2)pR}(t,t')$ from Eq. (7a). The reduction to one-perturber averages is again analogous to Appendix A 2. Noting that there is only a contribution to $\langle\langle ff\,K=Q=0\,|\,M_0^{(2)pR}(t,t')\,|\,ff\,K=Q=0\rangle\rangle$ if there is an intermediate propagation in the tetradic $|\,fg,ig\,\rangle\rangle$ or $|\,ig,fg\,\rangle\rangle$, we can adiabatically eliminate off-resonant electronic radiator-perturber states.

The collisionally induced excitation rate W and the collisionally induced spontaneous decay rate γ are now determined by

$$
\int_0^t dt' \sqrt{2j_f+1}\,\langle\langle ff\,K=Q=0\,|\,[M_2^{(0)p}(t,t')+M_2^{(0)R}(t,t')+M_2^{(0)pR}(t,t')]\,|\,ii\,K=Q=0\rangle\rangle\langle\langle ii\,K=Q=0\,|\,\sigma_I(t')\rangle\rangle \rightarrow W\langle\langle ii\,K=Q=0\,|\,\sigma_I(t)\rangle\rangle \tag{A29}
$$

and

$$
\int_0^t dt' \langle\langle ff\,K=Q=0\,|\,[M_0^{(2)p}(t,t')+M_0^{(2)R}(t,t')+M_0^{(2)pR}(t,t')]\,|\,ff\,K=Q=0\rangle\rangle\langle\langle ff\,K=Q=0\,|\,\sigma_I(t')\rangle\rangle \rightarrow \gamma\langle\langle ff\,K=Q=0\,|\,\sigma_I(t)\rangle\rangle . \tag{A30}
$$

We have assumed that $\langle\langle ff\,K=Q=0\,|\,\sigma_I(t)\rangle\rangle$ and $\langle\langle ii\,K=Q=0\,|\,\sigma_I(t)\rangle\rangle$ are slowly varying on the time scales τ_c and τ_{RAD}, which define the times of interests in the integrals of Eqs. (A29) and (A30), so that we can take $t\rightarrow\infty$ in the integrals (Markov approximation).[16,18] In the no-ground-state-interaction approximation [see Eq. (A23)] and for detunings that are not too large [see Eq. (A24)], we obtain the quantities W and γ of Eqs. (13a) and (15a). In the evaluation of γ

we have also used the fact that the correlation time of the spontaneous modes $\tau_{\mathrm{RAD}} \ll \tau_c$, so that strong collisions are unimportant during this time interval, i.e., $U_1^c(t,t')\rightarrow 1$. It is straightforward to evaluate all other matrix elements in an analogous way. So we finally arrive at the density matrix equations (12).

APPENDIX B

In this appendix we show that the collisionally induced spontaneous decay rate from the final-state manifold $|f\alpha\rangle$ of the radiator does not depend on whether we use the dipole approximation with an atom—spontaneous-mode interaction of the form $\boldsymbol{\mu}\cdot\hat{\mathbf{E}}_s$ or $\mathbf{p}\cdot\hat{\mathbf{A}}_s$.

According to Fermi's golden rule, the collisionally induced spontaneous decay rate due to the radiator collisionally interacting with a single perturber that is initially in the ground state $|g\rangle$ is given by

$$\gamma_{\mathrm{sp}}=\frac{1}{2j_f+1}\sum_{\alpha}\sum_{\mathbf{k},\lambda}\int d^3p_1\int d^3p_2\rho(\mathbf{p}_2)\frac{2\pi}{\hbar}\,|\langle\mathbf{k}\lambda|\langle F|\mathscr{D}|I\alpha\rangle|\{0\}\rangle|^2\delta(E_I-E_F-\hbar\omega_k)\;. \tag{B1}$$

The initial and final states $|I\alpha\rangle$ and $|F\rangle$ are scattering states of the radiator-perturber complex that fulfill the appropriate boundary conditions, i.e.,

$$|I\alpha\rangle=|f\alpha g\mathbf{p}_2\rangle+\frac{1}{E_I-H+i\epsilon}V(|\mathbf{x}_1|)|f\alpha g\mathbf{p}_2\rangle\;,$$
$$|F\rangle=|ig\mathbf{p}_1\rangle+\frac{1}{E_F-H-i\epsilon}V(|\mathbf{x}_1|)|ig\mathbf{p}_1\rangle\;, \tag{B2a}$$

and

$$H=H_R+H(1)+\frac{\hat{\mathbf{p}}_1^2}{2M}+V(|\mathbf{x}_1|)$$

and $\mathbf{x}_R=0$. They are eigenfunctions of H with eigenvalues

$$E_I=E_f+E_g+\frac{\mathbf{p}_2^2}{2M}\;, \tag{B2b}$$

$$E_F=E_i+E_g+\frac{\mathbf{p}_1^2}{2M}\;. \tag{B2c}$$

In the dipole approximation the interaction operator is given by

$$\mathscr{D}=-\boldsymbol{\mu}_R\cdot\hat{\mathbf{E}}_s(\mathbf{x}_R)-\boldsymbol{\mu}_1\cdot\hat{\mathbf{E}}_s(\mathbf{x}_1) \tag{B3a}$$

in the $\boldsymbol{\mu}\cdot\hat{\mathbf{E}}_s$ form of the laser-atom interaction and by

$$\mathscr{D}=-\frac{e}{m_e}[\tilde{\mathbf{p}}_R\cdot\hat{\mathbf{A}}_s(\mathbf{x}_R)+\tilde{\mathbf{p}}_1\cdot\hat{\mathbf{A}}(\mathbf{x}_1)] \tag{B3b}$$

in the $\mathbf{p}\cdot\hat{\mathbf{A}}_s$ form. We assume in the following that $|\mathbf{k}\cdot(\mathbf{x}_R-\mathbf{x}_1)|\ll 1$ for the important contribution to (B1) so that $\mathscr{D}$ does not influence the center-of-mass motion of the perturber. As we are considering a dipole-forbidden transition and the collisional interaction is short range, this condition is well satisfied. $\tilde{\mathbf{p}}_R$ and $\tilde{\mathbf{p}}_1$ in Eq. (B3b) are the internal momenta of radiator and perturber and m_e is the electron mass. The vector potential is given by

$$\hat{\mathbf{A}}_s(\mathbf{x})=\sum_{\mathbf{k},\lambda}[\hat{\mathbf{A}}_{k,\lambda}(\mathbf{x})+\mathrm{H.c.}]\;,$$
$$\hat{\mathbf{A}}_{k,\lambda}(\mathbf{x})=\frac{1}{i\omega_k}\hat{\mathbf{E}}_{k,\lambda}(\mathbf{x}) \tag{B3c}$$

in the Coulomb gauge.[21] Both interaction forms, i.e., Eqs. (B3a) and (B3b), are related through a unitary transformation.[28] For the matrix elements of Eq. (B1) we find

$$|\langle k\lambda|\langle F|\mathscr{D}|I\alpha\rangle|\{0\}\rangle|^2=|\langle F|(\boldsymbol{\mu}_R+\boldsymbol{\mu}_1)\cdot\boldsymbol{\varepsilon}^*_{k,\lambda}|I\alpha\rangle|^2\frac{\hbar\omega_k}{2\epsilon_0\bar{V}} \tag{B4a}$$

for the interaction operator of Eq. (B3a) and

$$|\langle\mathbf{k}\lambda|\langle F|\mathscr{D}|I\alpha\rangle|\{0\}\rangle|^2=\left|\left\langle F\left|\frac{e}{m_e}(\tilde{\mathbf{p}}_R+\tilde{\mathbf{p}}_1)\cdot\boldsymbol{\varepsilon}^*_{k,\lambda}\right|I\alpha\right\rangle\right|^2\frac{\hbar}{\omega_k 2\epsilon_0\bar{V}} \tag{B4b}$$

for the interaction operator of Eq. (B3b). Using the relation[21]

$$\frac{1}{i\hbar}[(\mathbf{x}_R+\mathbf{x}_1),H]=\frac{\tilde{\mathbf{p}}_R+\tilde{\mathbf{p}}_1}{m_e} \tag{B5}$$

and taking matrix elements we find

$$\frac{1}{i\hbar}\langle F|(\mathbf{x}_R+\mathbf{x}_1)|I\alpha\rangle(E_I-E_F)=\frac{1}{m_e}\langle F|(\tilde{\mathbf{p}}_R+\tilde{\mathbf{p}}_1)|I\alpha\rangle\;. \tag{B6}$$

Inserting this equation into (B4a) and (B4b) and into Eq. (B1), thereby using the fact that $E_I-E_F=\hbar\omega_k$ due to the δ function, we find that both interaction forms, i.e., Eqs. (B3a) and (B3b), yield the same result. In particular, if we take into account that the transition $|i\rangle\rightarrow|f\alpha\rangle$ is dipole forbidden, neglect $V(|\mathbf{x}_1|)$ in the denominators of Eqs. (B2a), and consider only terms of first order in $V(|\mathbf{x}_1|)$, Eq. (B1) finally gives rise to the collisionally induced spontaneous decay rate of Eq. (15a), i.e., $\gamma=N\gamma_{\mathrm{sp}}$. If we start from this approximate expression instead of Eq. (B1), it is crucial to keep *both* contributions to the dipole matrix element in Eq. (15b) in order to obtain identical results for both interaction forms, i.e., Eqs. (B3a) and (B3b). If we keep only the second term of Eq. (15b), which would correspond to the "resonant" term due to an allowed transition, for example, we fail to obtain identical results. In particular, if the implicit sum over all intermediate states in the second term of Eq. (15b) were restricted to the electronic radiator-perturber state $|kl\rangle$, which is energetically closest to $|fg\rangle$, the results would differ by a factor of

$$\left[\frac{E_k+E_l-E_i-E_g}{E_f+E_g-E_i-E_g}\right]^2 ,$$

which can be very significant (~ 12 for Ca $^1D_2$ perturbed by Xe).

APPENDIX C

In this appendix we perform the BCA on the various matrix elements of Eq. (26). For this purpose we expand the propagator $G'(t,t')$ of Eq. (24c) perturbatively in terms of $L_{k\lambda}^{(j)}$ and $L_c^{(j)}$, i.e.,

$$G'(t,t')=\overline{G}_c(t,t')+\int_{t'}^{t}dt_1\overline{G}_c(t,t_1)\mathscr{J}(t_1)\overline{G}_c(t_1,t')+\int_{t'}^{t}dt_1\int_{t'}^{t_1}dt_2\overline{G}_c(t,t_1)\mathscr{J}(t_1)\overline{G}_c(t_1,t_2)\times\mathscr{J}(t_2)\overline{G}_c(t_2,t')+\cdots \tag{C1}$$

with

$$\mathscr{J}(t)=\sum_{j=1}^{N}[L_c^{(j)}(t)+(1-\mathscr{B})L_{k\lambda}^{(j)}(t)] .$$

Inserting this expansion into the definition of $\mathscr{N}(t,t')$ in Eq. (24b), keeping terms up to second order in $L_{k\lambda}^{(j)}$ and $L_c^{(j)}$, and approximating $\overline{G}_c(t,t')$ of Eq. (A2b) by its BCA form given in Eq. (A3a), we find the terms $\mathscr{N}_i^{(n)}(t,t')$ of Eq. (25). In the following we reduce these quantities within the BCA and discuss the various matrix elements that are important according to Eq. (26).

1. Zeroth-order quantities

Let us first consider the couplings arising from the zeroth-order approximation with respect to the laser field, i.e., $\mathscr{N}_0^{(1)}(t,t')$ and $\mathscr{N}_0^{(2)}(t,t')$.

For the term of first order in $L_{k\lambda}^{(j)}$ we obtain

$$\mathscr{N}_0^{(1)}(t,t')=\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[L_{k\lambda}^{(j)}(t)\overline{G}_c(t,t')\sum_{i=1}^{N}(1-\mathscr{B})V_i(t')\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\left.\right\rangle\rho(\mathbf{p}_m)\right] . \tag{C2}$$

Inserting Eq. (A3a) for the collisional propagator, we obtain terms such as

$$\mathscr{B}L_{k\lambda}^{(j)}G_j\prod_{l<j}G_l(1-\mathscr{B})V_i\mathscr{B} , \tag{C3a}$$

where we have used the fact that due to $\mathrm{Tr}_R\mathscr{B}$ acting on the very left in Eq. (24a) the leftmost collision has to refer to perturber j. If $i\neq j$ expression (C3a) reduces to

$$\mathscr{B}L_{k\lambda}^{(j)}G_j\mathscr{B}\prod_{l<j}G_l(1-\mathscr{B})V_i\mathscr{B}=\mathscr{B}L_{k\lambda}^{(j)}G_j\mathscr{B}(1-\mathscr{B})V_i\mathscr{B}=0 \tag{C3b}$$

by using Eq. (A4b). So we find in the thermodynamic limit within the BCA

$$\mathscr{N}_0^{(1)}(t,t')=N\,\mathrm{Tr}_1[L_{k\lambda}^{(1)}(t)U_1(t,t')V_1(t')\,|g,g\rangle\!\rangle\rho(\mathbf{p}_1)] . \tag{C2'}$$

For the term second order in $L_{k\lambda}^{(j)}$ we find

$$\mathscr{N}_0^{(2)}(t,t')=\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[L_{k\lambda}^{(j)}(t)\overline{G}_c(t,t')\sum_{i=1}^{N}L_{k\lambda}^{(i)}(t')\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\left.\right\rangle\rho(\mathbf{p}_m)\right]+\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[L_{k\lambda}^{(j)}(t)\int_{t'}^{t}dt_1\overline{G}_c(t,t_1)\sum_{i=1}^{N}(1-\mathscr{B})L_{k\lambda}^{(i)}(t_1)\overline{G}_c(t_1,t')\sum_{k=1}^{N}(1-\mathscr{B})V_k(t')\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\left.\right\rangle\rho(\mathbf{p}_m)\right] . \tag{C4a}$$

Again we insert Eq. (A3a) for $\overline{G}_c(t,t')$. The first term is only nonzero if $i=j$ because of $p_iL_{k\lambda}^{(i)}p_i=0$, Eq. (A4b), and the fact that the leftmost collision refers to perturber j due to $\mathrm{Tr}_R\mathscr{B}$ at the very left. As the time of interest is small, i.e., $|t-t'|\approx 1/\omega \ll \tau_c$, because the spontaneous photon of interest is off resonant with respect to all perturber transitions, we may again put $\prod_{l<j}G_l\rightarrow 1$ and the first term of Eq. (C4a) reduces to a one-perturber average. Due to $\mathrm{Tr}_R\mathscr{B}$ at the very left, the leftmost collision of the second term in Eq. (C4a) also has to refer to perturber j. Using again the same type of arguments as for the first term, it is straightforward to show that it is only nonzero within the BCA if $k=j$, which implies that all perturber indices have to refer to perturber j. So we find, in the thermodynamic limit,

$$\mathcal{N}_0^{(2)}(t,t')=N\,\mathrm{Tr}_1[L_{k\lambda}^{(1)}(t)U_1(t,t')L_{k\lambda}^{(1)}(t')\,|\,g,g\,\rangle\!\rangle\rho(\mathbf{p}_1)]$$
$$+N\,\mathrm{Tr}_1\left[L_{k\lambda}^{(1)}(t)\int_{t'}^{t}dt_1\,U_1(t,t_1)L_{k\lambda}^{(1)}(t_1)U_1(t_1,t')V_1(t')\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_1)\right]. \tag{C4b}$$

The first two terms in Eq. (26) involve matrix elements of the form

$$\langle\!\langle nn\,K=Q=0\,|\,\mathcal{N}_0^{(1)}(t,t')\,|\,if\,K'=2Q'\,\rangle\!\rangle$$

or

$$\langle\!\langle nn\,K=Q=0\,|\,\mathcal{N}_0^{(1)}(t,t')\,|\,fi\,K'=2Q'\,\rangle\!\rangle \tag{C5}$$

due to Tr_R. Thus n indicates an arbitrary radiator state. It has been shown in Appendix A 2 [see Eq. (A16a)] that matrix elements of this form vanish identically in the case of a spherically symmetric collision environment of the radiator.

Let us now consider the matrix element of the fifth term in Eq. (26). In the absence of collisions, this term vanishes because

$$\int_0^t dt'\langle\!\langle 1,1\,|\,\langle\!\langle l_1,l_1\,|\,L_{k\lambda}^{(1)}(t)L_{k\lambda}^{(1)}(t')\,|\,g,g\,\rangle\!\rangle\,|\,0,0\,\rangle\!\rangle\to 0 \quad \text{as } \omega\,|\,t-t'\,|\to\infty\ . \tag{C6a}$$

Taking into account that the dominant contribution to Eq. (C4b) involves a long-time propagation in the electronic radiator-perturber tetradic state $|\,fl_1,il_1'\,\rangle\!\rangle$ or $|\,il_1,fl_1'\,\rangle\!\rangle$, we can adiabatically eliminate off-resonant electronic radiator-perturber states by using Eq. (A6). Then we find

$$\mathrm{Tr}_R\,\langle\!\langle 1,1\,|\,\mathcal{N}_0^{(2)}(t,t')\,|\,0,0\,\rangle\!\rangle\,|\,ig,ig\,\rangle\!\rangle=0\ , \tag{C6b}$$

$$\frac{\overline{V}}{(2\pi)^3}\frac{\omega_k^2}{c^3}\sum_{K,Q}\int_0^t dt'\,\mathrm{Tr}_R\,\langle\!\langle 1,1\,|\,\mathcal{N}_0^{(2)}(t,t')\,|\,0,0\,\rangle\!\rangle\,|\,ff\,KQ\,\rangle\!\rangle\langle\!\langle ff\,KQ\,|\,\sigma_I(t')\,\rangle\!\rangle\to\Gamma_{SS}(\omega_k,\varepsilon,t)\ . \tag{C6c}$$

2. First-order quantities

According to Eq. (26) the important contribution to $\mathcal{N}(t,t')$ of first order in $L_c^{(j)}$ is

$$\mathcal{N}_1^{(1)}(t,t')=\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[L_{k\lambda}^{(j)}(t)\overline{G}_c(t,t')\sum_{i=1}^{N}L_c^{(i)}(t')\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_m)\right]$$
$$+\mathrm{Tr}_{\{p\}}\sum_{j=1}^{N}\left[L_{k\lambda}^{(j)}(t)\int_{t'}^{t}dt_1\,\overline{G}_c(t,t_1)\sum_{i=1}^{N}L_c^{(i)}(t_1)\overline{G}_c(t_1,t')\sum_{k=1}^{N}(1-\mathscr{B})V_k(t')\prod_{m=1}^{N}\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_m)\right]. \tag{C7}$$

If $i\neq j$ in the first term of Eq. (C7) then $L_c^{(i)}$ has to be next to a collisional propagator G_i. This is due to the fact that the time of interest associated with a perturber-dipole excitation is of order $1/\omega\ll\tau_c$ and the perturber has to be deexcited again because of $\mathrm{Tr}_{\{p\}}$ at the very left. Equation (A4b) and $p_iL_i^{(c)}=0$ then imply that the first term vanishes. If $i=j$ then the short time of interest associated with a perturber-dipole excitation implies that only a collision between perturber j and the radiator is possible during the time interval (t,t'). So the first term of Eq. (C7) reduces to a one-perturber average.

The second term of Eq. (C7) is nonzero only if $i=j$, by the same argument as used above. If $i=j$, the short time of interest associated with a perturber-dipole excitation and Eq. (A4b) implies that all perturber indices have to be equal to j. So we find for Eq. (C7) within the BCA the expression

$$\mathcal{N}_1^{(1)}(t,t')=N\,\mathrm{Tr}_1\left[L_{k\lambda}^{(1)}(t)\left[1+\int_{t'}^{t}dt_1\,U_1(t,t_1)V_1(t_1)\right]L_c^{(1)}(t')\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_1)\right]$$
$$+N\,\mathrm{Tr}_1\left[L_{k\lambda}^{(1)}(t)\int_{t'}^{t}dt_1\,U_1(t,t_1)L_c^{(1)}(t_1)U_1(t_1,t')V_1(t')\left|g,g\right\rangle\!\!\right\rangle\rho(\mathbf{p}_1)\right], \tag{C7'}$$

where we have used Eq. (A6) in the first term of Eq. (C7). The first term of Eq. (C7′) vanishes in the thermodynamic limit because

$$\int d^3p\,\langle\mathbf{p}\,|\,e^{i(\mathbf{k}-\mathbf{k}_c)\mathbf{x}_1}\,|\,\mathbf{p}\rangle\rho(\mathbf{p})\to 0 \quad \text{as } V\to\infty \tag{C7''}$$

for $\mathbf{k}\neq\mathbf{k}_c$ (we are not interested in coherent effects in the forward direction). The dominant contribution to the second and third terms involves an intermediate propagation in the tetradic state $|\,fl_1,il_1'\,\rangle\!\rangle$ or $|\,il_1,fl_1'\,\rangle\!\rangle$ and $\mathcal{N}_1^{(1)}(t,t')$ vanishes in the absence of collisions. From Eq. (26) we see that the contribution to $\Gamma_{k,\lambda}$ of the terms proportional to $\mathcal{N}_1^{(1)}(t,t')$ involves a long intermediate propagation before time t', which is not restricted by τ_c, just as in the case of Rayleigh scattering [compare with Eq. (C12)]. These contributions can therefore be important only in the same frequency domain where Rayleigh scattering is significant. Furthermore, they involve two averages over perturber coordinates [the second average comes from the coupling between $\langle\langle n_1,n_1' \mid \langle\langle 1,0 \mid \Sigma(t')\rangle\rangle$, $\langle\langle n_1,n_1' \mid \langle\langle 0,1 \mid \Sigma(t')\rangle\rangle$ and $\langle\langle i,i \mid \sigma_I(t'')\rangle\rangle]$, whereas Rayleigh scattering involves only one average over the perturber coordinates. If we assume that the matrix elements within these averages are roughly the same for Rayleigh scattering and the contributions due to the third and fourth terms in Eq. (26), we can obtain an upper bound for the relative importance of both types of contributions. According to Eq. (28) N/N_R (N_R is the number of radiators in volume V; in our case $N_R=1$) perturbers contribute to Rayleigh scattering, i.e., $\mathrm{Tr}_1 \to N/N_R$, whereas only those perturbers can contribute to the terms proportional to $\mathcal{N}_1^{(1)}(t,t')$ in Eq. (26) that are within a sphere of radius b_w around a radiator, i.e., $\mathrm{Tr}_1 \to (N/V)\pi b_w^3$ [because both $\mathcal{N}_1^{(1)}(t,t')$ and $\langle\langle n_1,n_1' \mid \langle\langle 1,0 \mid \Sigma(t')\rangle\rangle, \langle\langle n_1,n_1' \mid \langle\langle 0,1 \mid \Sigma(t')\rangle\rangle$ vanish in the absence of collisions]. b_w is the Weisskopf (strong-collision) radius, which is approximately related to the duration of a collision τ_c and a typical (impact) collision rate γ_c by[14]

$$\gamma_c \tau_c \approx \frac{N}{V}\pi b_w^3 \ . \tag{C8}$$

It is therefore assumed that the collisional interaction is short range and only nonzero for $|\mathbf{x}_R - \mathbf{x}_1| \lesssim b_w$. From these simple considerations we find within the BCA, the ratio between the contributions to the spectrum due to the third and fourth terms in Eq. (26) and pure Rayleigh scattering

$$\frac{\left[\dfrac{N}{V}\pi b_w^3\right]^2}{N/N_R} \ll 1 \ , \tag{C7'''}$$

indicating that Rayleigh scattering is definitely dominant. The effects of radiators associated with different volumes V, of course, add incoherently.

3. Second-order quantities

For the important contribution to $\mathcal{N}(t,t')$, which is second order in $L_c^{(j)}$, we obtain

$$\begin{aligned}
\mathcal{N}_2^{(2)}(t,t') = {} & \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[L_{k\lambda}^{(j)}(t) \int_{t'}^{t} dt_1 \int_{t'}^{t_1} dt_2 \bar{G}_c(t,t_1) \sum_{i=1}^{N} L_c^{(i)}(t_1)\bar{G}_c(t_1,t_2) \right.\\
& \left. \times \sum_{k=1}^{N} L_c^{(k)}(t_2)\bar{G}_c(t_2,t') \sum_{l=1}^{N} L_{k\lambda}^{(l)}(t') \prod_{m=1}^{N} \Big| g,g \Big\rangle\!\Big\rangle \rho(\mathbf{p}_m) \right]\\
& + \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[L_{k\lambda}^{(j)}(t) \int_{t'}^{t} dt_1 \int_{t'}^{t_1} dt_2 \bar{G}_c(t,t_1) \sum_{i=1}^{N} L_c^{(i)}(t_1)\bar{G}_c(t_1,t_2) \right.\\
& \left. \times \sum_{k=1}^{N} (1-\mathscr{B}) L_{k\lambda}^{(k)}(t_2)\bar{G}_c(t_2,t') \sum_{l=1}^{N} L_c^{(l)}(t') \prod_{m=1}^{N} \Big| g,g \Big\rangle\!\Big\rangle \rho(\mathbf{p}_m) \right]\\
& + \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[L_{k\lambda}^{(j)}(t) \int_{t'}^{t} dt_1 \int_{t'}^{t_1} dt_2 \bar{G}_c(t,t_1) \sum_{i=1}^{N} (1-\mathscr{B}) L_{k\lambda}^{(i)}(t_1)\bar{G}_c(t_1,t_2) \right.\\
& \left. \times \sum_{k=1}^{N} L_c^{(k)}(t_2)\bar{G}_c(t_2,t') \sum_{l=1}^{N} L_c^{(l)}(t') \prod_{m=1}^{N} \Big| g,g \Big\rangle\!\Big\rangle \rho(\mathbf{p}_m) \right]\\
& + \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[L_{k\lambda}^{(j)}(t) \int_{t'}^{t} dt_1 \int_{t'}^{t_1} dt_2 \int_{t'}^{t_2} dt_3 \bar{G}_c(t,t_1) \sum_{i=1}^{N} L_c^{(i)}(t_1)\bar{G}_c(t_1,t_2) \sum_{k=1}^{N} L_c^{(k)}(t_2)\bar{G}_c(t_2,t_3) \right.\\
& \left. \times \sum_{l=1}^{N} (1-\mathscr{B}) L_{k\lambda}^{(l)}(t_3)\bar{G}_c(t_3,t') \sum_{n=1}^{N} (1-\mathscr{B}) V_n(t') \prod_{m=1}^{N} \Big| g,g \Big\rangle\!\Big\rangle \rho(\mathbf{p}_m) \right]\\
& + \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[L_{k\lambda}^{(j)}(t) \int_{t'}^{t} dt_1 \int_{t'}^{t_1} dt_2 \int_{t'}^{t_2} dt_3 \bar{G}_c(t,t_1) \sum_{i=1}^{N} L_c^{(i)}(t_1)\bar{G}_c(t_1,t_2) \sum_{i=1}^{N} (1-\mathscr{B}) L_{k\lambda}^{(k)}(t_2)\bar{G}_c(t_2,t_3) \right.\\
& \left. \times \sum_{l=1}^{N} L_c^{(l)}(t_3)\bar{G}_c(t_3,t') \sum_{n=1}^{N} (1-\mathscr{B}) V_n(t') \prod_{m=1}^{N} \Big| g,g \Big\rangle\!\Big\rangle \rho(\mathbf{p}_m) \right]\\
& + \mathrm{Tr}_{\{p\}} \sum_{j=1}^{N} \left[L_{k\lambda}^{(j)}(t) \int_{t'}^{t} dt_1 \int_{t'}^{t_1} dt_2 \int_{t'}^{t_2} dt_3 \bar{G}_c(t,t_1) \sum_{i=1}^{N} (1-\mathscr{B}) L_{k\lambda}^{(i)}(t_1)\bar{G}_c(t_1,t_2) \sum_{k=1}^{N} L_c^{(k)}(t_2)\bar{G}_c(t_2,t_3) \right.\\
& \left. \times \sum_{l=1}^{N} L_c^{(l)}(t_3)\bar{G}_c(t_3,t') \sum_{n=1}^{N} (1-\mathscr{B}) V_n(t') \prod_{m=1}^{N} \Big| g,g \Big\rangle\!\Big\rangle \rho(\mathbf{p}_m) \right] .
\end{aligned} \tag{C9}$$

We perform the BCA by inserting Eq. (A3a) into Eq. (C9). In Eq. (24a) we only need $\mathrm{Tr}_R \mathcal{N}_2^{(2)}(t,t')$, which implies that within the BCA the leftmost collision has to refer to perturber j. According to our resonance conditions (9) and (20) the dominant contribution to Eq. (C9) comes from long-time terms, which involve an intermediate propagation in the electronic radiator-perturber tetradic state $|k_1\{l_1\},k_1'\{l_1'\}\rangle\rangle$ during the time interval (t_1,t_2). k_1 and k_1' thereby indicate two degenerate radiator states, and $\{l_1\},\{l_1'\}$ are two N-perturber (internal) states with the same total energy. Depending on the type of propagation during the time intervals between the first and second and between the third and fourth perturber-dipole interactions, we can distinguish among three types of contributions to Eq. (C9).

(a) *Collisionally induced photon emission due to single collisions* is characterized by all the terms in Eq. (C9) which involve an intermediate propagation in the radiator-perturber tetradic $|f\{l_1\},i\{l_1'\}\rangle\rangle$ or $|i\{l_1\},f\{l_1'\}\rangle\rangle$ during the times between the first and second and between the third and fourth perturber-dipole interactions. Such intermediate propagations are only possible by the combined action of a perturber dipole and a collisional interaction referring to the same perturber. Therefore, a $L_{k\lambda}^{(j)}$ (or $L_c^{(j)}$) must always be next to a V_j. There is no possibility for other collisions occurring in between, because the off-resonant excitation and deexcitation occur during a short time of order $1/\omega \ll \tau_c$. This implies, e.g., for the first term in Eq. (C9),

$$\mathcal{B} L_{k\lambda}^{(j)}(1-p_j)V_j G_j \prod_{i<l<j} G_l G_i L_c^{(i)} \cdots \mathcal{B}$$

$$= \mathcal{B} L_{k\lambda}^{(j)}(1-p_j)V_j G_j \mathcal{B} L_c^{(1)} \cdots \mathcal{B}$$

$$=0 \, , \qquad \text{(C10)}$$

if $i \neq j$. Thus we need Eq. (A4b) and the fact that within the BCA the index j cannot appear again anywhere to the right of $L_c^{(i)}$. Using this argument repeatedly implies that all the perturber indices in Eq. (C9) have to be equal to j. So the particular part of $\mathcal{N}_2^{(2)}(t,t')$ that gives rise to collisionally induced photon emission due to single collisions, i.e., $\mathcal{N}_S(t,t')$, reduces to a one-perturber average. As $\mathcal{N}_S(t,t')$ is of second order in the laser fields, we only need to consider its coupling to $\langle\langle i,i\,|\,\sigma_I(t')\rangle\rangle$, because its coupling to $\langle\langle ffKQ\,|\,\sigma_I(t')\rangle\rangle$ is always negligible in comparison with $\mathcal{N}_0^{(2)}(t,t')$, which is of zeroth order in the laser field. A straightforward (but tedious) evaluation of the matrix elements shows that it is only possible to have $k_1=k_1'=i$ and $l_1=l_1'=g$. Adiabatically eliminating off-resonant electronic radiator-perturber states and taking into account condition (A23) we find in the thermodynamic limit

$$\frac{\overline{V}}{(2\pi)^3}\frac{\omega_k^2}{c^3}\int_0^t dt' \mathrm{Tr}_R \langle\langle 1,1\,|\,\mathcal{N}_S(t,t')\,|\,0,0\rangle\rangle\,|\,i,i\,\rangle\rangle\langle\langle i,i\,|\,\sigma_I(t')\rangle\rangle \to \Gamma_S(\omega_k,\boldsymbol{\varepsilon},t) \qquad \text{(C11)}$$

with $\Gamma_S(\omega_k,\boldsymbol{\varepsilon},t)$ given in Eq. (36).

(b) *Rayleigh scattering* is characterized by all the terms in Eq. (C9) that do not involve an intermediate propagation in the radiator-perturber tetradic $|f\{l_1\},i\{l_1'\}\rangle\rangle$ or $|i\{l_1\},f\{l_1'\}\rangle\rangle$ during the times between the first and second and between the third and fourth perturber-dipole interactions. This implies that these propagation times are of the order $1/\omega \ll \tau_c$ so that we may, as before, put $\overline{G}_c \to 1$ during these two time intervals. However, the collisional propagator $\overline{G}_c(t_1,t_2)$, which is associated with the "long" intermediate propagation in the radiator-perturber tetradic $|k_1,\{l_1\},k_1'\{l_1'\}\rangle\rangle$, is fully taken into account. A long propagation during the time interval (t_1,t_2) is now possible only if $i=j$ and $k=l$, which immediately implies that $i=j=k=l$ due to the projection operators involved. A straightforward evaluation of the matrix elements shows that we must have $l_1=l_1'=g$. Adiabatically eliminating off-resonant electronic radiator-perturber states in $\overline{G}_c(t_1,t_2)$, which is replaced by its BCA form (A3a), we find in the thermodynamic limit for the particular part of $\mathcal{N}_2^{(2)}(t,t')$ that describes Rayleigh scattering, i.e., $\mathcal{N}_R(t,t')$,

$$\begin{aligned}\int_0^t dt' \langle\langle 1,1\,|\,\mathcal{N}_R(t,t')\,|\,0,0\rangle\rangle \sigma_I(t') \\ = \frac{\hbar\omega_k}{2\epsilon_0\overline{V}}\frac{1}{\hbar^2} 2\,\mathrm{Re}\int_0^t dt' e^{i(\omega-\omega_k)(t-t')} N \int d^3p_1 \int \cdots \int d^3p_4 \rho(\mathbf{p}_4)\,|D_R|^2 \\ \times \langle \mathbf{p}_1\,|\,e^{-i(\mathbf{k}-\mathbf{k}_c)\mathbf{x}_1(t)}\,|\,\mathbf{p}_2\rangle^* \langle\langle g\mathbf{p}_1,g\mathbf{p}_2\,|\,U_1^e(t,t')\,|\,g\mathbf{p}_3,g\mathbf{p}_4\rangle\rangle \\ \times \langle \mathbf{p}_3\,|\,e^{-i(\mathbf{k}-\mathbf{k}_c)\mathbf{x}_1(t')}\,|\,\mathbf{p}_4\rangle \rho(\mathbf{p}_4) \\ \times \prod_{j\neq 1}\theta_0 \int d^3p\, d^3p' \langle\langle \mathbf{p}g,\mathbf{p}g\,|\,U_j^e(t,t')\,|\,\mathbf{p}'g,\mathbf{p}'g\rangle\rangle \rho(\mathbf{p}')\sigma_I(t') \, ,\end{aligned} \qquad \text{(C12)}$$

with D_R given by Eq. (28′).

The last factor in Eq. (C12) characterizes the influence of all other perturbers $j \neq 1$ on the Rayleigh scattering line shape and all collisions $j \neq 1$ occur before collision 1. Its effect can easily be demonstrated by neglecting the phase factors $e^{-i(\mathbf{k}-\mathbf{k}_c)\mathbf{x}_1}$, which corresponds to neglecting Doppler broadening. In Eq. (24a) we only need $\mathrm{Tr}_R \mathcal{N}_R(t,t')$, which implies that

$$\int d^3p_1 \langle\langle ff\, K=Q=0 \,|\, \langle\langle g\mathbf{p}_1, g\mathbf{p}_1 \,|\, U_1^e(t,t') \,|\, g\mathbf{p}_3, g\mathbf{p}_3 \rangle\rangle \,|\, ff\, K=Q=0 \rangle\rangle = 1 \,, \tag{C13}$$

due to unitarity (if inelastic collisions are neglected). Thereby we have also used the fact that $U_1^e(t,t')$ is diagonal in the radiator multipoles of Eq. (A9) in the case of a spherically symmetric collision environment. Using relations (26) and (27) of Ref. 14 we see that the last term of Eq. (C12) essentially introduces a factor $\exp[-\gamma^{(K=0)}(\omega-\omega_k)(t-t')]$ into Eq. (C12). $\gamma^{(K=0)}(\omega-\omega_k)$ is thereby a collisional decay rate of the total population of the radiator manifold under consideration, which depends on the frequency difference $\omega-\omega_k$. In the impact regime we have $\gamma^{(K=0)}(\omega-\omega_k) \to 0$ as $|\omega_k-\omega|\tau_c \to 0$ as we are neglecting inelastic collisions from the radiator manifolds $|f\alpha\rangle$ and $|i\rangle$. Taking this into account, Eq. (C12) finally reduces to the Rayleigh scattering contribution given by Eq. (28) in the classical path straight-line trajectory approximation. From Eq. (28) it is clear that the time interval $t-t'$ is at most the inverse of the Doppler width, so, since the decay of the intermediate state is at most γ_c (which is an inelastic decay rate and certainly much less than the Doppler width), neglect of this decay is justified.

(c) *Interference contributions* are obtained from Eq. (C9) if there is a propagation in the radiator-perturber tetradic state $|f\{l_1\}, i\{l_1'\}\rangle\rangle$ or $|i\{l_1\}, f\{l_2'\}\rangle\rangle$ during the time between the first and second but not between the third and fourth perturber-dipole interactions or vice versa. These terms describe interferences between Rayleigh scattering and collisionally induced photon emission due to single collisions. As in Rayleigh scattering, the propagation time t_1-t_2 is not restricted to τ_c, because there is only a collision at one end of the interval (t_1,t_2). These contributions can therefore be important only in the frequency domain of Rayleigh scattering. N/N_R perturbers contribute to Rayleigh scattering, whereas the only perturbers that contribute to the interferences are those within a sphere of radius b_w around a radiator, i.e., $(N/V)\pi b_w^3$ (see also Appendix C 2). The interference contributions are therefore less, by at least a factor of order $N_R[(N/V)\pi b_w^3]/N \ll 1$ in comparison with Rayleigh scattering, and are therefore negligible.

[1] J. R. Murray and C. K. Rhodes, J. Appl. Phys. **47**, 5041 (1976).
[2] K. Niemax, J. Quant. Spectrosc. Radiat. Transfer **17**, 125 (1977).
[3] G. Moe, A. C. Tam, and W. Happer, Phys. Rev. A **14**, 349 (1976).
[4] A. Gallagher and T. Holstein, Phys. Rev. A **16**, 2413 (1977).
[5] P. S. Julienne, J. Chem. Phys. **68**, 32 (1978).
[6] K. Ueda and K. Fukuda, J. Phys. Chem. **86**, 678 (1981).
[7] J. C. Lewis and J. Van Kranendonk, Can. J. Phys. **50**, 352 (1972).
[8] J. C. Lewis, Can. J. Phys. **50**, 2881 (1972).
[9] J. C. Lewis and J. Van Kranendonk, Can. J. Phys. **50**, 2902 (1972).
[10] J. C. Lewis and J. Van Kranendonk, Phys. Rev. Lett. **24**, 802 (1970).
[11] R. M. Herman, Phys. Rev. Lett. **42**, 1206 (1979).
[12] P. R. Berman, in *Advances in Atomic and Molecular Physics,* edited by D. R. Bates and B. Bederson (Academic, New York, 1977), Vol. 13, pp. 57–112.
[13] E. W. Smith, J. Cooper, and C. R. Vidal, Phys. Rev. **185**, 140 (1969).
[14] E. W. Smith, J. Cooper, and L. J. Roszman, J. Quant. Spectrosc. Radiat. Transfer **13**, 1523 (1973).
[15] J. Cooper and D. N. Stacey, Phys. Rev. A **12**, 2438 (1975).
[16] K. Burnett, J. Cooper, R. J. Ballagh, and E. W. Smith, Phys. Rev. A **22**, 2005 (1980).
[17] G. Alber and J. Cooper, Phys. Rev. A **31**, 3644 (1985).
[18] G. S. Agarwal, *Quantum Statistical Theories of Spontaneous Emission and Their Relation to Other Approaches* (Springer, Berlin, 1974).
[19] K. Burnett and J. Cooper, Phys. Rev. A **22**, 2027 (1980).
[20] S. G. Rautian, A. G. Rudavets, and A. M. Shalagin, Zh. Eksp. Teor. Fiz. **78**, 545 (1980) [Sov. Phys.—JETP **51**, 274 (1980)].
[21] W. H. Louisell, *Quantum Statistical Properties of Radiation* (Wiley, New York, 1973).
[22] J. Cooper, in *Spectral Line Shapes,* edited by K. Burnett (de Gruyter, Berlin, 1983), Vol. 2, p. 737.
[23] W. J. Alford, N. Andersen, K. Burnett, and J. Cooper, Phys. Rev. A **30**, 2366 (1984).
[24] B. R. Mollow, Phys. Rev. A **12**, 1919 (1975).
[25] A. Omont, E. W. Smith, and J. Cooper, Astrophys. J. **175**, 185 (1972).
[26] K. Burnett and J. Cooper, Phys. Rev. A **22**, 2044 (1980).
[27] D. M. Brink and G. R. Satchler, *Angular Momentum* (Clarendon, Oxford, 1968).
[28] J. R. Ackerhalt and P. W. Milonni, J. Opt. Soc. Am. B **1**, 116 (1984).