Two-photon collisional redistribution of radiation

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We study collisional redistribution in the presence of two weakly exciting laser fields, including the effects due to degeneracy of the radiator states. A general expression for the total redistributed intensity is derived valid for arbitrary detunings and polarizations of the exciting laser fields. In particular, this expression contains all single- and sequential-collisional contributions, which are equally important under certain circumstances. We also point out the similarities and differences between the redistributed intensity as calculated in this paper and collisionally aided radiative excitation cross sections, which have been studied previously.

I. INTRODUCTION

Scattering of light by atoms undergoing collisions with a dilute foreign gas is an important tool for studying interatomic interactions.[1–3] In the binary-collision regime, where the duration of a strong collision τ_c is much smaller than the time interval between different collisions, the spectrum of the low-intensity scattered light from an atomic transition in a two-level system is centered around two different frequencies: (a) Rayleigh peak, centered at the frequency of the laser field, ω_L, which is scattered; (b) redistributed peak, centered around the atomic transition frequency ω_0. The redistributed peak, which vanishes in the absence of collisions when the lower state is a ground state, contains information about the interatomic interaction between the laser excited atom and a perturber atom from the dilute foreign gas. We can distinguish between two limiting cases. In the first case, $|\omega_L-\omega_0|\tau_c \ll 1$ (impact limit), the redistributed peak contains global information about the collision processes in the form of S-matrix elements, which determine the frequency-independent collision rates. This is due to the fact that the collision between the atom and a perturber occurs instantaneously in comparison with the time scale characterizing the laser excitation process of the atom. Each collision is therefore completed. The other limit is realized in the far wing, where $|\omega_L-\omega_0|\tau_c \gg 1$ (quasistatic limit). Now the time scale of the excitation of the atom by the laser field is much smaller than the duration of a collision and the redistributed intensity contains detailed information about the collisional process.

For a nondegenerate two-level system we can distinguish between two limiting cases in the quasistatic region.[4] In the first case, $|\omega_L-\omega_0| \ll kT/\hbar$, the perturber motion is unaffected by the presence of the laser excited atom. In a classical path treatment the perturber may be described by a straight-line trajectory and the total redistributed intensity is proportional to the dressed state excitation rate. These rates have been calculated in the context of collisionally aided radiative excitation (CARE) by Yeh and Berman[5] or Light and Szöke.[6] However, in the other limiting case, $|\omega_L-\omega_0| \gtrsim kT/\hbar$, the perturber motion is affected by the presence of the radiatively excited atom and field-dependent contributions to the collision operator (correlated events) significantly influence the redistributed intensity, as has been shown by Burnett *et al.*[4] They lead to factors like $\exp[-\hbar(\omega_L-\omega_0)/kT]$. In this situation, the simple CARE cross section and the corresponding rate as calculated by Yeh and Berman[5] may no longer give an adequate description of redistribution.

Considering the more realistic case of degenerate atomic levels the field-dependent corrections to the collision operator (correlation effects) even become important as soon as we go outside the impact region as has been shown by Burnett and Cooper.[7] This is due to the fact that the orientation or alignment of atom and perturber are more strongly correlated than their translational states. These types of correlations determine, for example, the degree of polarization of the redistributed intensity. These effects can be sometimes simply modeled within a simple reorientation model.[8,9]

The study of CARE cross sections has been generalized to two-photon excitation in weak fields by Yeh and Berman.[10] In particular, they investigated a nondegenerate three-level atom undergoing collisions with a perturber and calculated the two-photon excitation cross section for various dynamical cases. The perturber was assumed to move on a straight-line trajectory. In a light scattering experiment, where two laser fields excite an atom in the presence of collisions and the fluorescence radiation from the final to the intermediate atomic state is observed, the two-photon excitation cross section is proportional to the total scattered intensity including Rayleigh scattering and redistribution in the one-perturber limit.

In this paper, we study such a two-photon light scattering experiment and focus our attention on the calculation of the redistributed intensity associated with the transition of the excited atom from its final state to the intermediate state. In particular, we shall consider a realistic atom and consider a $J=0\rightarrow J=1\rightarrow J=0$ type two-photon excitation (e.g., in an alkaline-earth atom) in the presence of collisions including all effects due to the degeneracy of the intermediate state. Our treatment therefore contains correlation effects due to reorientation of the atom-perturber system, which manifest themselves in the dependence of the redistributed intensity on the polarizations of the exciting laser fields and which cannot adequately be described within a nondegenerate three-level system. Using the methods of Burnett *et al.*[4,7] we derive a general expression for the redistributed intensity valid for arbitrary detunings of the laser fields from their atomic transition frequencies in comparison with the collision time τ_c. In our treatment we also include contributions to the redistributed intensity due not just to a single collision but also subsequent collisions. Our general expressions are not limited to detunings less than $kT/\hbar$ and are therefore, in principle, able to describe situations where the classical path straight-line trajectory approximation breaks down. However, we shall restrict our discussion to weak laser fields in the sense that the ground state of the atom remains undepleted and the one-photon Rabi frequencies are much smaller than the inverse duration of a collision.

The paper is organized as follows. In Sec. II we present the problem under consideration together with a discussion of all approximations used for further treatment. We focus in particular on the reduced density matrix of the radiator and represent finally the stationary solutions. They are the input needed for the calculation of the redistributed intensity, which is the main object of Sec. III. There we outline the calculation of the two-photon excitation spectrum in general terms and finally give a general expression for the redistributed intensity, which is the primary goal of this paper. The discussion of different dynamical cases, which are all included in this formulation, is given in Sec. IV. Sections II–IV focus on the physics involved in the two-photon laser excitation in the presence of collisions. Technical details of our calculation together with the definition of the collisional correlation terms and estimates of their orders of magnitude are given in Appendixes A–F. Appendix G deals with the connection between the total redistributed intensity we calculated in Sec. III and dressed-state CARE cross sections.

II. THE DENSITY-MATRIX EQUATIONS

We study a system as schematically shown in Fig. 1. A neutral atom (radiator) is excited (for convenience) by a classical electromagnetic field consisting of two laser fields. The coupling of the atom to the other modes of the electromagnetic field, which do not carry photons, causes spontaneous decay and level shifts, which may be absorbed in redefined atomic energies. The radiator is surrounded by N neutral perturbers, which collide with the radiator. These perturbers, often noble-gas atoms, are supposed to have such high excitation energies in comparison with the radiator, that they can neither be directly excited by a collision process nor by photon excitation and their internal structure may therefore be neglected.

Let us first of all consider the interaction of the radiator with the classical electromagnetic field

$$\mathbf{E}(t)=\sum_{j=1}^{2}\mathbf{e}_j\mathscr{E}_j e^{-i\omega_j t}+\text{c.c.}\ , \tag{1}$$

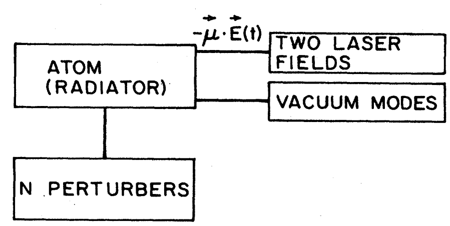

FIG. 1. Schematic representation of the dynamical system.

where $\mathbf{e}_j$, $j=1,2$ are the polarization vectors of two (continuous wave) coherent laser pulses of frequencies ω_1 and ω_2. In particular, we study an excitation process schematically shown in Fig. 2. The first laser $(\omega_1,\mathbf{e}_1)$ excites the radiator (e.g., an alkaline-earth atom) from its ground state $|g\rangle$ with energy E_g, and total angular momentum $J=0$ to a manifold of degenerate states $\{|e_i\rangle\}$, $i=1,2,3$ with energies E_e and $J=1$. The subscript i thereby indicates the different magnetic quantum numbers m_J. The second laser $(\omega_2,\mathbf{e}_2)$ induces a transition to the final state $|f\rangle$ with energy E_f, which for simplicity, is assumed to be nondegenerate $(J=0)$. In addition, the atom may be excited to $|f\rangle$ directly from $|g\rangle$. As long as the detunings of both lasers from their atomic transition frequencies are much smaller than the corresponding detunings associated with all other atomic states, the dynamics of the radiator due to the electromagnetic field may be described by an effective Hamiltonian H_{eff} for the degenerate three-level system $|g\rangle,\{|\bar{e}_i\rangle\},|\bar{f}\rangle$. Treating the interaction of the atom with the laser fields in the dipole approximation we find

$$\begin{aligned}H_{\text{eff}}=E_g\,|g\rangle\langle g\,|+\sum_{i=1}^{3}(E_g-\hbar\Delta_1)\,|\bar{e}_i\rangle\langle\bar{e}_i\,|\\
+(E_g-\hbar\Delta_1-\hbar\Delta_2)\,|\bar{f}\rangle\langle\bar{f}\,|-\frac{\hbar}{2}\sum_{i=1}^{3}\Omega^*_{fe_i}\,|\bar{e}_i\rangle\langle\bar{f}\,|\\
-\frac{\hbar}{2}\sum_{i=1}^{3}\Omega_{fe_i}\,|\bar{f}\rangle\langle\bar{e}_i\,|-\frac{\hbar}{2}\sum_{i=1}^{3}\Omega^*_{e_ig}\,|g\rangle\langle\bar{e}_i\,|\\
-\frac{\hbar}{2}\sum_{i=1}^{3}\Omega_{e_ig}\,|\bar{e}_i\rangle\langle g\,|\ ,\end{aligned} \tag{2a}$$

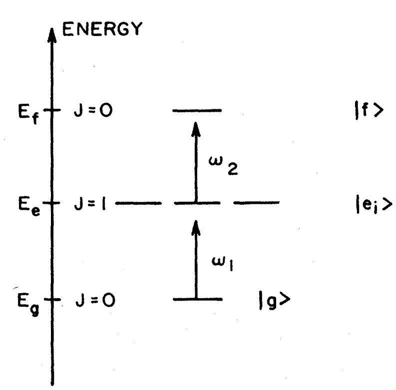

FIG. 2. Atomic configuration.

$$\Delta_1=(E_g+\hbar\omega_1-E_e)/\hbar \ ,$$
$$\Delta_2=(E_e+\hbar\omega_2-E_f)/\hbar \ , \tag{2b}$$

are the detunings from resonance and

$$\Omega_{e_i g}=\frac{2}{\hbar}\langle e_i\,|\,\boldsymbol{\mu}\cdot\mathbf{e}_1\,|\,g\,\rangle\mathscr{E}_1 \ ,$$
$$\Omega_{fe_i}=\frac{2}{\hbar}\langle f\,|\,\boldsymbol{\mu}\cdot\mathbf{e}_2\,|\,e_i\,\rangle\mathscr{E}_2 \ , \tag{2c}$$

are the Rabi frequencies for the transitions $|\,g\,\rangle\rightarrow|\,e_i\,\rangle$ and $|\,e_i\,\rangle\rightarrow|\,f\,\rangle$, and

$$|\,\bar{e}_i\,\rangle=|\,e_i\,\rangle e^{-i\omega_1 t} \ ,$$
$$|\,\bar{f}\,\rangle=|\,f\,\rangle e^{-i(\omega_1+\omega_2)t} \ , \tag{2d}$$

are rotating atomic states. In this effective Hamiltonian the influence of the two laser fields on the atomic dynamics has been taken into account in lowest-order perturbation theory in the laser fields (rotating-wave approximation). Quadratic Stark shifts due to the laser fields and the direct coupling between the ground state $|\,g\,\rangle$ and the final state $|\,f\,\rangle$ via all other (nonresonant) intermediate states have therefore been neglected as they are of second order in the fields and would give negligibly small contributions under the conditions in which we are interested. We further neglected ionization assuming that the continuum cannot be directly reached from $|\,f\,\rangle$ by absorption of a photon $(\omega_1,\mathbf{e}_1)$ or $(\omega_2,\mathbf{e}_2)$.

The coupling of the radiator with the vacuum modes of the electromagnetic field may be treated within the Markov approximation giving rise to constant spontaneous decay rates. This requires that all times characterizing the evolution of the atom—laser-fields—perturber system are much larger than the correlation time τ_V associated with the vacuum modes. As τ_V is typically the time for a photon to cross the atom and is of the order of 10^{-18} s, this is not a severe restriction.[4] For the density operator $\rho(t)$ of the combined system consisting of the radiator (interacting with both laser fields, which are turned on simultaneously at $t=0$) and N perturbers the equation of motion is then given by

$$\frac{d}{dt}\rho(t)=(L_{\text{eff}}+L_{p_N}+V_N+\Gamma)\rho(t) \ , \quad t>0 \tag{3}$$

with

$$L_{\text{eff}}\cdots=\frac{1}{i\hbar}[H_{\text{eff}},\cdots] \ ,$$
$$L_{p_N}\cdots=\frac{1}{i\hbar}\sum_{j=1}^{N}[\hat{\mathbf{p}}_j^2/2M \ ,\cdots] \ ,$$
$$V_N\cdots=\frac{1}{i\hbar}\sum_{j=1}^{N}[V_R(j),\cdots] \ .$$

$\hat{\mathbf{p}}_j$ is the kinetic momentum operator of the jth perturber and M its mass. $V_R(j)$ is the interaction potential between the radiator and the jth perturber. Γ is the (time-independent) spontaneous decay damping operator and acts only within the radiator subspace. For our degenerate three-level system under consideration, the relevant tetradic matrix elements of Γ are given in Appendix B [Eqs. (B4)]. The turn-on time for the field is unimportant since we will only be interested in the long-time solution of Eq. (3). In Eq. (3) the motion of the radiator has been neglected (i.e., we do not use the hydrodynamic derivative $d/dt\rightarrow\partial/\partial t+\mathbf{v}\cdot\boldsymbol{\nabla}$).

We want to derive an equation of motion for the reduced density operator of the radiator $\sigma(t)=\text{Tr}_{\text{perturbers}}\{\rho(t)\}$, which allows us to calculate all one-time averages of radiator observables. However, we are not allowed to eliminate the perturbers within the Markov (impact) approximation as we are interested in situations with arbitrary relative time scales between radiator and perturbers. In order to reduce the complicated $(N+1)$-body problem of Eq. (3) we shall make the binary-collision approximation (BCA).[4] Thereby we assume that strong collisions, which may not be treated by perturbation theory and are characterized by the (strong) collision time τ_c ($\approx 10^{-12}$ s for a typical van der Waals broadening collision), are well separated in time.[11] This implies that

$$\tau_c \ll \frac{1}{\gamma_c} \ , \tag{4}$$

where γ_c is a collisional dephasing or decay rate in the impact limit, whose inverse characterizes the time between different collisions. Within this approximation, the solution of the $(N+1)$-body problem is reduced to the solution of a two-body problem: the collision of the radiator in the presence of the laser fields with a single perturber. We stress, however, that sequences of such binary collisions are fully accounted for in our formulation.

For convenience we can define a projection operator $\mathscr{P}\ldots=\rho_N\text{Tr}_{\text{perturbers}}\{\cdots\}$. ρ_N is thereby the equilibrium (but not necessarily thermal equilibrium) density operator of the N (noninteracting) perturbers in the absence of the radiator atom with the normalization $\text{Tr}_{\text{perturbers}}\{\rho_N\}=1$. $\mathscr{P}\rho(t)$ then represents the "factorized" part of the full density operator of the radiator-perturber system. Starting from Eq. (3), we can derive with the help of the methods described by Burnett *et al.*[4] the equation of motion for the reduced density operator $\sigma(t)=\text{Tr}_{\text{perturbers}}\{\rho(t)\}$, which is given by

$$\frac{d}{dt}\sigma(t)=[L_{\text{eff}}+\Gamma+N\,\text{Tr}_P(\rho_P V_1)]\sigma(t) + \int_0^t dt'\,M(t-t')\sigma(t') \ . \tag{5}$$

This equation is valid as long as $t\gg\tau_c$, because effects due to initial correlations of the radiator-perturber system [i.e., $(1-\mathscr{P})\rho(t=0)\neq 0$], which decay on a time scale of order τ_c, may then be neglected. Within the BCA the memory kernel $M(\tau)$ is given by

$$M(\tau)=N\,\text{Tr}_P\{V_1 G_1(\tau)V_1\rho_P\} \ , \tag{6a}$$

where the two-body (tetradic) time-development operator $G_1(\tau)$ fulfills the equation of motion

$$\frac{d}{d\tau}G_1(\tau)=(L_{\text{eff}}+L_P+V_1+\Gamma)G_1(\tau)\ ,\quad \tau>0$$
$$G_1(\tau=0)=1\ . \tag{6b}$$

L_P and V_1 represent now the free motion and the interaction potential for one perturber. The N perturbers have been assumed to be statistically independent and each one may be described by a density operator ρ_P. Tr_P is now the trace over the states of one perturber. In the following, we shall neglect inelastic collisions. V_1 therefore represents an effective interaction which couples only degenerate radiator states and is brought about by virtual transitions to all other (radiator) states. In addition, we shall assume a spherically symmetric collisional environment for the radiator, which will, by use of rotational invariance properties, simplify our analysis considerably. Further, we shall for simplicity assume that the ground state of the radiator is not affected by collisions, i.e.,

$$V_1\,|g,g\rangle\rangle=0\ . \tag{7}$$

This can only be valid as long as small separations between radiator and perturber, where they certainly start to repel each other and invalidate Eq. (7), do not significantly influence the collisional quantities of interest, i.e., the excited state should be much more polarizable.

As far as the laser intensities are concerned, we shall in this paper restrict our study to the case of weak fields, i.e.,

$$|\Omega_{e_ig}|\,\tau_c,\ |\Omega_{fe_i}|\,\tau_c \ll 1\ , \tag{8a}$$

$$|\Omega_{e_ig}| \ll \max\{\,|\Delta_1|,\ \text{all damping rates}\}\ , \tag{8b}$$

$$|\Omega_{fe_i}| \ll \max\{\,|\Delta_2|,\ \text{all damping rates}\}\ . \tag{8c}$$

The first condition [Eq. (8a)] allows us to calculate the full time-evolution operator $G_1(\tau)$ in perturbation theory in the laser fields [see Appendix A, Eq. (A3a)]. The memory kernel $M(\tau)$ is now expressible in terms of the (zero-order) time-evolution operator for the collision between radiator and perturber [see Eq. (A3b)]

$$G_0(\tau)=\frac{1}{2\pi}\lim_{\epsilon\to 0}\left[\int_{-\infty}^{+\infty}dx\,e^{-ix\tau}\frac{i}{x-i(L_R+L_P+V_1+\Gamma)+i\epsilon}\right] \tag{9}$$

or $(d/d\tau)G_0(\tau)=(L_R+L_P+V_1+\Gamma)G_0(\tau)$ and it is no longer necessary to calculate the collisional dynamics *in* the presence of the laser fields. Note that $G_0(\tau)$ contains the effects due to spontaneous decay represented by Γ. As τ_c is of the order of 10^{-12} s, Eq. (8a) is not a very severe restriction for laser intensities often used in multiphoton experiments. The second and third conditions, Eqs. (8b), and (8c), allow us to calculate the density operator, Eq. (5), also perturbatively in the laser fields. But we shall allow for arbitrary values of Δ_1, Δ_2, and $\Delta_1+\Delta_2$ in comparison with $1/\tau_c$. It is the case where the detunings Δ_1, Δ_2, or $\Delta_1+\Delta_2$ become larger than $1/\tau_c$, which is of most interest in our study. Under these conditions, the characteristic time scale of the radiator evolution in the laser fields becomes shorter than the collision time τ_c and we become able to investigate details of the intracollisional evolution process.

Under the conditions stated above, Eqs. (4), (7), and (8), we find for the stationary ($t\to\infty$) reduced density-matrix elements of the radiator the expressions

$$\sigma_Q^1(\bar{e}g)=-\frac{\frac{1}{\sqrt{3}}(e_Q^{(1)})^*\hbar^{-1}\langle j_e||\mu||j_g\rangle\mathscr{E}_1}{\Delta_1+i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}\ ,$$

$$\sigma_Q^K(\bar{e}\,\bar{e})=\sum_{q_1,q_2}(e_{q_1}^{(1)})^*e_{-q_2}^{(1)}(-1)^{q_1}[K]^{1/2}\begin{pmatrix}1 & 1 & K\\ q_2 & q_1 & -Q\end{pmatrix}\begin{Bmatrix}1 & 1 & K\\ 1 & 1 & 0\end{Bmatrix}$$
$$\times\frac{2\,|\hbar^{-1}\langle j_e||\mu||j_g\rangle|^2\,|\mathscr{E}_1|^2}{\gamma_e+\gamma^K}\,\mathrm{Im}\left[\frac{1+C(K,eeeg,z=0)}{\Delta_1+i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}\right]\ ,$$

$$\sigma_0^0(\bar{f}g)=-[\mathbf{e}^{(1)}\cdot\mathbf{e}^{(2)*}]^*\frac{1}{3}\frac{\hbar^{-1}\langle j_f||\mu||j_e\rangle\mathscr{E}_2}{\Delta_1+\Delta_2+i[(\gamma_f/2+\gamma_{fg}(\Delta_1+\Delta_2)]}\frac{\hbar^{-1}\langle j_e||\mu||j_g\rangle\mathscr{E}_1}{\Delta_1+i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}[1+C(fgeg,z=0)]\ , \tag{10}$$

$$\sigma_Q^1(\bar{f}\,\bar{e})=\sum_{\substack{q_1,q_2,q_3,\\K_1,Q_1}}e_{-q_3}^{(1)}(-1)^{Q}(e_{-q_1}^{(2)})^*(e_{q_2}^{(1)})^*(-1)^{q_2}\left[\frac{1}{\sqrt{3}}\frac{1}{\hbar}\right]^3\langle j_f||\mu||j_e\rangle\mathscr{E}_2$$
$$\times|\langle j_e||\mu||j_g\rangle\mathscr{E}_1|^2[K_1]\begin{pmatrix}1 & 1 & K_1\\ Q & q_1 & Q_1\end{pmatrix}\begin{pmatrix}1 & 1 & K_1\\ q_3 & q_2 & Q_1\end{pmatrix}\frac{1}{\Delta_2+i[(\gamma_e+\gamma_f)/2+\gamma_{fe}(\Delta_2)]}$$
$$\times\left[2\frac{1+C(K_1,feee,z=0)}{\gamma_e+\gamma^{K_1}}\mathrm{Im}\left[\frac{1+C(K_1,eeeg,z=0)}{\Delta_1+i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}\right]\right.$$

$$+\frac{1+C(fefg,z=0)}{\Delta_1+\Delta_2+i[\gamma_f/2+\gamma_{fg}(\Delta_1+\Delta_2)]}\,\frac{1+C(fgeg,z=0)}{\Delta_1+i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}$$

$$\left.-i\frac{D_1(K_1,feeg,z=0)+D_2(K_1,feeg,z=0)}{\Delta_1+i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}+i\frac{D_3(K_1,fege,z=0)}{\Delta_1-i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}\right]\,,$$

$$\sigma_0^0(\bar{f}\bar{f})=\sum_{\substack{q_1,q_2,q_3,q_4\\K_1,Q_1}} e_{q_4}^{(2)}e_{-q_3}^{(1)}(-1)^{q_4}(e_{-q_1}^{(2)})^*(e_{q_2}^{(1)})^*(-1)^{q_2}\frac{1}{9}\frac{1}{\hbar^4}\,|\langle j_f||\mu||j_e\rangle\mathscr{E}_2|^2$$

$$\times|\langle j_e||\mu||j_g\rangle\mathscr{E}_1|^2[K_1]\begin{bmatrix}1 & 1 & K_1\\ q_4 & q_1 & Q_1\end{bmatrix}\begin{bmatrix}1 & 1 & K_1\\ q_3 & q_2 & Q_1\end{bmatrix}\frac{2}{\gamma_f}$$

$$\times\mathrm{Im}\left\{\frac{1}{\Delta_2+i[(\gamma_e+\gamma_f)/2+\gamma_{fe}(\Delta_2)]}\right.$$

$$\times\left[2\frac{1+C(K_1,feee,z=0)}{\gamma_e+\gamma^{K_1}}\mathrm{Im}\left[\frac{1+C(K_1,eeeg,z=0)}{\Delta_1+i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}\right]\right.$$

$$+\frac{1+C(fefg,z=0)}{\Delta_1+\Delta_2+i[\gamma_f/2+\gamma_{fg}(\Delta_1+\Delta_2)]}\,\frac{1+C(fgeg,z=0)}{\Delta_1+i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}$$

$$\left.\left.-i\frac{D_1(K_1,feeg,z=0)+D_2(K_1,feeg,z=0)}{\Delta_1+i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}+i\frac{D_3(K_1,fege,z=0)}{\Delta_1-i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}\right]\right\}\,.$$

with

$$\sigma_Q^K(\bar{l}\,\bar{m})=\langle\langle \bar{j}_l\bar{j}_m KQ\,|\,\sigma(t\to\infty)\rangle\rangle\ ,\quad l,m=g,e,f\ .$$

The bars above the angular momentum labels indicate the rotating states of Eq. (2d). The details of the derivation are outlined in the Appendixes A—C. $\langle j_f||\mu||j_e\rangle$ and $\langle j_e||\mu||j_g\rangle$ are reduced dipole matrix elements [see Eq. (B6)]. γ_e and γ_f are the spontaneous decay rates of the populations of the radiator manifolds $\{|e_i\rangle\}$ and $|f\rangle$ (see Appendix B). $\gamma_{eg}(\Delta_1)$, $\gamma_{fe}(\Delta_2)$, and $\gamma_{fg}(\Delta_1+\Delta_2)$ are collisional dephasing (destruction of optical coherence) rates of the radiator coherences indicated by the subscripts. γ^K is a collision rate acting within the excited-state manifold $\{|e_i\rangle\}$ and is not dependent on any detuning. The first-order field corrections of the collisional influence of the perturbers on the radiator are described by $C(K_1,feee,z=0)$, $C(K_1,eeeg,z=0)$, $C(fefg,z=0)$ and $C(fgeg,z=0)$. The arguments thereby indicate the tetradic elements which they couple. $D_1(K_1,feeg,z=0)$, $D_2(K_1,feeg,z=0)$, and $D_3(K_1,fege,z=0)$ represent the second-order field corrections to the memory kernel $M(\tau)$. All these collisional quantities are defined in Appendix C.

III. REDISTRIBUTED RADIATION

In this section, we study the spectrum of the spontaneously emitted radiation corresponding to the transition $|f\rangle\to|e_i\rangle$ of the radiator. For weak laser fields, this spectrum will consist of three lines (see Fig. 3): A line centered at frequency (a) $\omega=E_g/\hbar+\omega_1+\omega_2-E_e/\hbar$ due to two-photon Raman scattering from the ground state, a line centered at (b) $\omega=\omega_2$ due to "collisional-induced Rayleigh" scattering from a collisional component of the excited-state population, and a "redistributed" line at frequency (c) $\omega=(E_f-E_e)/\hbar$. Peaks (b) and (c) can only occur in the presence of collisions. The widths of these lines are determined by the spontaneous decay and collisional damping rates. The quantity in which we are particularly interested is the total redistributed intensity, which is obtained by integrating the redistributed peak (c) over a frequency range much larger than the width of this peak. The other peaks in this paper will be assumed to be well separated from peak (c).

Again, as in Sec. II, we consider the radiator atom,

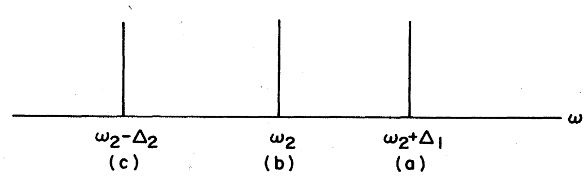

FIG. 3. General structure of the (weak-field) spectrum corresponding to the spontaneous decay $|f\rangle\to|e_i\rangle$.

which is excited by the two laser fields $(\omega_1,\mathbf{e}_1)$ and $(\omega_2,\mathbf{e}_2)$ and interacts with N perturbers and the vacuum modes of the electromagnetic field (see Figs. 1 and 2). The stationary (time-independent) spectrum of the spontaneously emitted radiation corresponding to the transition $|f\rangle \to \{|e_i\rangle\}$ of the radiator $I(\omega,\boldsymbol{\epsilon})$ is given by[7,12]

$$I(\omega,\boldsymbol{\epsilon}) \propto 2\mathrm{Re}\left[\int_0^\infty d\tau\, e^{i\omega\tau} C(\tau)\right] \tag{11a}$$

with

$$C(\tau)=\mathrm{Tr}_R\{d^- G(\tau)\}\ , \tag{11b}$$

$$G(\tau)=\mathrm{Tr}_{\text{perturbers}}\{U(\tau)[\rho(t\to\infty)d^+]\} \tag{11c}$$

and

$$d^-=\sum_{i=1}^{3}\langle e_i|\boldsymbol{\mu}\cdot\boldsymbol{\epsilon}^*|f\rangle\ |e_i\rangle\langle f|\ ,$$
$$d^+=(d^-)^\dagger=\sum_{i=1}^{3}\langle e_i|\boldsymbol{\mu}\cdot\boldsymbol{\epsilon}^*|f\rangle^*\ |f\rangle\langle e_i|\ . \tag{11d}$$

ω and $\boldsymbol{\epsilon}$ are the frequency and polarization of the spontaneously emitted photon and d^-,d^+ are the corresponding dipole transition operators. $U(\tau)$ is the (tetradic) time-development operator of the whole system. Treating the spontaneous decay again, as in Sec. II, in the Markov approximation, $U(\tau)$ obeys the equation of motion

$$\frac{d}{d\tau}U(\tau)=(L_{\text{eff}}+L_{p_N}+V_N+\Gamma)U(\tau)\ ,\quad \tau>0$$

with $U(\tau=0)=1$. Tr_R indicates the trace over all radiator states, i.e., $\{|f\rangle,|e_i\rangle\}$ due to the dipole transition operators of Eq. (11d). $\rho(t)$ is the density operator of the whole system [see Eq. (3)].

Using the projection-operator technique outlined in Burnett *et al.*[7] we find within the BCA the equation of motion

$$\frac{d}{d\tau}G(\tau)=[L_{\text{eff}}+\Gamma+N\,\mathrm{Tr}_P(\rho_P V_1)]G(\tau)$$
$$+\int_0^\tau dt'\,M(\tau-t')G(t')+N\,\mathrm{Tr}_P\left\{\rho_P V_1 G_1(\tau)\lim_{t\to\infty}\left[\int_0^t dt' G_1(t-t')V_1\sigma(t')d^+\right]\right\} \tag{12a}$$

with the memory kernel $M(\tau-t')$ and time-evolution operator $G_1(t-t')$ of Eqs. (6). This equation has to be solved with the initial condition

$$G(\tau=0)=\sigma(t\to\infty)d^+ \tag{12b}$$

as may be seen from Eq. (11c) under the assumption that the dipole transition operator acts only within the radiator subspace. The last term in Eq. (12a) represents the contribution to the spectrum, which is caused by spontaneous emission during a collision between radiator and perturber and corresponds to the D terms calculated by Burnett and Cooper.[7] In addition to the Markov approximation for the spontaneous decay and the BCA [see Eq. (4)] for our further treatment we shall make the same assumptions as in Sec II: neglect of inelastic collisions, spherically symmetric collisional environment of the radiator, no ground-state interaction, and weak fields as characterized by Eqs. (8).

From Eq. (11a) we find the spectrum

$$I(\omega,\boldsymbol{\epsilon})\propto 2\,\mathrm{Re}\left[\int_0^\infty d\tau\, e^{i(\omega-\omega_2)\tau}\sum_{i=1}^{3}\langle e_i|d^-|f\rangle\langle\bar f|G(\tau)|\bar e_i\rangle\right]$$
$$=\frac{2}{\sqrt{3}}\sum_q \mathrm{Re}[\epsilon_q\langle j_f||\mu||j_e\rangle^*\langle\langle \bar j_f\bar j_e 1q\,|\,G(z=\omega-\omega_2)\rangle\rangle]\ . \tag{13}$$

In the last line, $\boldsymbol{\epsilon}$ has thereby been decomposed into spherical components $\boldsymbol{\epsilon}=\sum_q \epsilon_q \boldsymbol{\epsilon}_q$ (see Appendix B) and relation (B6) has been used. The bars associated with the angular momentum labels again indicate the rotating states of Eq. (2d);

$$G(z)=\int_0^\infty d\tau\, e^{iz\tau}G(\tau) \tag{14a}$$

is the Laplace transform of the correlation function $G(\tau)$ and obeys the equation [see Eq. (12a)]

$$\{z-i[L_{\text{eff}}+\Gamma+M(z)]\}G(z)=J(z) \tag{14b}$$

with

$$J(z)=i\sigma(t\to\infty)d^+$$
$$+N\,\mathrm{Tr}_P\{\rho_P V_1 G_1(z)G_1(z=0)V_1 i\sigma(t\to\infty)d^+\}\ , \tag{14c}$$

where $G_1(z)$ is defined in Appendix A. This equation determines the tetradic elements

$$\langle\langle \bar j_f\bar j_e 1q\,|\,G(z=\omega-\omega_2)\rangle\rangle\ ,$$

which are needed for the evaluation of the spectrum of the emitted light.

Our primary interest will be the evaluation of the spectrum around the redistributed peak ($z=\omega-\omega_2\approx-\Delta_2$). Using the methods of Appendixes D and F for estimating the orders of magnitude of the collisional quantities $M_1(\tau)$, $M_2(\tau)$, and the last term in Eq. (14c), it turns out that these contributions are at most of order $\gamma_c\tau_c$ in comparison with unity and are therefore negligible in the BCA.

The total redistributed intensity $I_{\rm red}(\epsilon)$ is well defined as long as the peak in the spectrum centered around $\omega\approx\omega_2-\Delta_2$ is well separated from the Rayleigh and Raman peaks, which requires

$$|\Delta_1+\Delta_2|, |\Delta_2| \gg \gamma_e,\gamma_f,\gamma_c \ . \tag{15}$$

Under these conditions, we may define

$$I_{\rm red}(\epsilon)=\int_{\omega_2-\Delta_2-\eta}^{\omega_2-\Delta_2+\eta} d\omega\, I(\omega,\epsilon) \ , \tag{16a}$$

where the range of integration is determined by η with

$$\gamma_e,\gamma_f,\gamma_c \ll \eta \ll |\Delta_2|, |\Delta_1+\Delta_2| \ . \tag{16b}$$

If condition (15) is violated, redistribution of radiation, Rayleigh and Raman scattering become indistinguishable and start to interfere with one another. The integrations are, however, quite straightforward if we wish to put together both Rayleigh and redistributed components. In fact, if all three peaks overlap, because $|\Delta_1+\Delta_2|, |\Delta_2| \lesssim \max\{\gamma_e,\gamma_f,\gamma_c\}$, in the weak-field limit the above-defined quantity will become equal to the total scattered intensity [as may be seen from Eq. (14b)]

$$I_{\rm red}(\epsilon)\rightarrow\int_{-\infty}^{\infty} d\omega\, I(\omega,\epsilon)\propto\frac{2\pi}{3}|\langle j_f||\mu||j_e\rangle|^2\sigma_0^0(ff) \tag{17}$$

and the concept of a redistributed component becomes physically meaningless. However, we shall not at this stage pursue these cases and shall restrict further discussion on situations where condition (15) is fulfilled. From Eqs. (13), (14b), (14c), (10), and Appendix B together with the relation

$$\int_{-\eta}^{\eta} dx\frac{1}{x+i\alpha}\rightarrow -i\pi \quad \text{as } \alpha/\eta\rightarrow 0$$

we find after a tedious but straightforward calculation for the redistributed intensity

$$
\begin{aligned}
I_{\rm red}(\epsilon) &\propto \frac{2\pi}{3}|\langle j_f||\mu||j_e\rangle|^2\tfrac{1}{9}|\langle j_f||\mu||j_e\rangle\mathscr{E}_2|^2\,|\langle j_e||\mu||j_g\rangle\mathscr{E}_1|^2\frac{1}{\hbar^4}\\
&\times\sum_{\substack{q_1,q_2,q_3,q_4,\\K,Q}}(e^{(2)}_{q_4})^*(e^{(1)}_{-q_3})^*(-1)^{q_4}e^{(2)}_{-q_1}e^{(1)}_{q_2}(-1)^{q_2}[K]\begin{pmatrix}1&1&K\\q_4&q_1&Q\end{pmatrix}\begin{pmatrix}1&1&K\\q_3&q_2&Q\end{pmatrix}\\
&\times\Bigg\{\frac{1}{\Delta_2-i[(\gamma_e+\gamma_f)/2+\gamma_{fe}(\Delta_2)]}\frac{1}{\Delta_2}\\
&\quad\times\Bigg[-\frac{1+C^*(K,feee,z=0)}{\gamma_e+\gamma^K}\,\frac{\gamma_e+2\gamma_{eg}(\Delta_1)-2\Delta_1{\rm Im}C(K,eeeg,z=0)}{\Delta_1^2+[\gamma_e/2+\gamma_{eg}(\Delta_1)]^2}\\
&\qquad+\frac{1+C^*(fefg,z=0)}{\Delta_1-i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}\,\frac{1+C^*(fgeg,z=0)}{\Delta_1+\Delta_2-i[\gamma_f/2+\gamma_{fg}(\Delta_1+\Delta_2)]}\\
&\qquad+\frac{iD_1^*(K,feeg,z=0)+iD_2^*(K,feeg,z=0)}{\Delta_1-i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}-\frac{iD_3^*(K,fege,z=0)}{\Delta_1+i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}\Bigg]\\
&\quad+\frac{2}{\gamma_f}{\rm Im}\Bigg[\frac{1}{\Delta_2+i[(\gamma_e+\gamma_f)/2+\gamma_{fe}(\Delta_2)]}\\
&\qquad\times\Bigg[-\frac{1+C(K,feee,z=0)}{\gamma_e+\gamma^K}\,\frac{\gamma_e+2\gamma_{eg}(\Delta_1)-2\Delta_1{\rm Im}C(K,eeeg,z=0)}{\Delta_1^2+[\gamma_e/2+\gamma_{eg}(\Delta_1)]^2}\\
&\qquad\quad+\frac{1+C(fefg,z=0)}{\Delta_1+i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}\,\frac{1+C(fgeg,z=0)}{\Delta_1+\Delta_2+i[\gamma_f/2+\gamma_{fg}(\Delta_1+\Delta_2)]}\\
&\qquad\quad-\frac{iD_1(K,feeg,z=0)+iD_2(K,feeg,z=0)}{\Delta_1+i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}+\frac{iD_3(K,fege,z=0)}{\Delta_1-i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}\Bigg]\Bigg]\\
&\quad+\frac{1}{\Delta_1-i[\gamma_e/2+\gamma_{eg}(\Delta_1)]}\,\frac{1+C^*(fgeg,z=0)}{\Delta_1+\Delta_2-i[\gamma_f/2+\gamma_{fg}(\Delta_1+\Delta_2)]}\,\frac{1}{\Delta_1+\Delta_2}\Bigg\}\ .
\end{aligned}\tag{18}
$$

This complicated expression is the main result of our paper and will be discussed and simplified in Sec. IV. As a general feature we observe that the redistributed intensity is independent of the polarization of the emitted photon ϵ, which is due to two facts: The $J=0$ symmetry of the state $|f\rangle$ and the negligible contribution of spontaneous emission during a collision [represented by the second term of Eq. (14c)] to the redistributed intensity. If we had studied the spectrum of the spontaneously emitted radiation corresponding to the transition from $|f\rangle$ to a different unexcited state manifold $\{|e_i'\rangle\}$ with energy $E_{e'}$, the redistributed peak would have been centered around frequency $\omega \approx (E_f - E_{e'})/\hbar$. Equation (18) would still describe the total redistributed intensity under the conditions of Eq. (15) provided we made the replacement $(2\pi/3)|\langle j_f||\mu||j_e\rangle|^2 \rightarrow (2\pi/3)|\langle j_f||\mu||j_{e'}\rangle|^2$.

IV. DISCUSSION

The expression for the redistributed intensity [Eq. (18)] is valid for arbitrary relative values of Δ_1, Δ_2, $\Delta_1+\Delta_2$, and the inverse collision duration τ_c as long as a redistributed intensity is well defined and condition (15) is fulfilled so that Rayleigh, Raman, and redistributed components are well separated. To get some insight into the different dynamical situations Eq. (18) describes, we shall now study three limiting cases.

A. $|\Delta_1|\tau_c \gg 1$, $|\Delta_2|\tau_c \ll 1$

Using the estimates of Appendix D for the collisional quantities and assuming $\gamma_e\tau_c \ll 1$, we see that the redistributed intensity of Eq. (18) reduces to

$$I_{\text{red}}(\epsilon) \propto \frac{2\pi}{3}|\langle j_f||\mu||j_e\rangle|^2 \frac{1}{9}|\langle j_f||\mu||j_e\rangle \mathscr{E}_2|^2 |\langle j_e||\mu||j_g\rangle \mathscr{E}_1|^2 \frac{1}{\hbar^4}$$
$$\times \sum_{\substack{q_1,q_2,q_3,q_4,\\ K,Q}} (e_{q_4}^{(2)})^*(e_{-q_3}^{(1)})^*(-1)^{q_4} e_{-q_1}^{(2)} e_{q_2}^{(1)} (-1)^{q_2}[K] \begin{bmatrix} 1 & 1 & K \\ q_4 & q_1 & Q \end{bmatrix} \begin{bmatrix} 1 & 1 & K \\ q_3 & q_2 & Q \end{bmatrix}$$
$$\times \frac{1}{\gamma_f} \frac{\gamma_e + 2\gamma_{fe}(\Delta_2)}{\Delta_2^2} \frac{2\gamma_{eg}(\Delta_1) - \gamma^K - 2\Delta_1 \mathrm{Im}C(K, eeeg, z=0)}{(\gamma_e+\gamma^K)\Delta_1^2} . \tag{19}$$

Thereby we have rationalized the denominators in Eq. (18) using

$$\frac{1}{\Delta \pm i\gamma} = \frac{1}{\Delta} \mp i\frac{\gamma}{\Delta^2} + \cdots \tag{20}$$

and neglecting higher orders in $(\gamma/|\Delta|)$ according to condition (15).

Due to the short time of interest associated with the absorption of the first laser photon $(\omega_1, \mathbf{e}_1)$, i.e., $1/|\Delta_1| \ll \tau_c$, the redistributed intensity contains detailed information about the radiator-perturber collision through $\gamma_{eg}(\Delta_1)$ and $\mathrm{Im}C(K, eeeg, z=0)$. As the laser photon $(\omega_1, \mathbf{e}_1)$ is absorbed instantaneously due to the Franck-Condon principle (at internuclear separations R_S between radiator and perturber, at which a stationary phase point occurs and where the interatomic potential can make up the energy difference $\hbar\Delta_1$), $\gamma_{eg}(\Delta_1)$ is determined by the behavior of the interatomic potential around R_S (see discussion in Appendix E). $\mathrm{Im}C(K, eeeg, z=0)$ describes the influence of the first-order field correction of the collision operator on the redistributed intensity. Burnett and Cooper[7] defined

$$\Gamma_{eg}^K(\Delta_1) = 2\gamma_{eg}(\Delta_1) - 2\Delta_1 \mathrm{Im}C(K, eeeg, z=0) , \tag{21}$$

which describes quasistatic absorption of the laser photon $(\omega_1, \mathbf{e}_1)$ at the internuclear distance R_S followed by the propagation of the radiator- (in the excited-state manifold $\{|e_i\rangle\}$) perturber system *to the end of the collision.* In the case of a degenerate excited-state manifold $\{|e_i\rangle\}$, this completion of the collision is associated with a reorientation of the radiator-perturber complex and $\mathrm{Im}C(K, eeeg, z=0)$ is of crucial importance. In particular, in the antistatic wing of Δ_1, where [Eq. (F3)]

$$2\Delta_1 \mathrm{Im}C(K, eeeg, z=0) \rightarrow -\gamma^K ,$$
$$\gamma_{eg}(\Delta_1) \rightarrow 0 ,$$

the redistributed intensity therefore goes to zero. Without the term $\mathrm{Im}C(K, eeeg, z=0)$, $I_{\text{red}}(\epsilon)$ would become negative in this limit.[7] For a nondegenerate excited state, $\mathrm{Im}C(eeeg, z=0)=0$, which reflects the fact that no reorientation occurs and m_J-state mixing during the completion of the collision after the absorption is therefore unimportant.

As the time of interest associated with the absorption of the second photon $(\omega_2, \mathbf{e}_2)$ is quite large in the sense $1/|\Delta_2| \gg \tau_c$ (i.e., we are in the impact limit), no detailed information (beyond that contained in completed collision S-matrix elements) about the internuclear difference potential between the manifolds $\{|f\rangle\}$ and $\{|e_i\rangle\}$ enters the redistributed intensity. $\gamma_{fe}(\Delta_2)$ is (to order $|\Delta_2|\tau_c$) independent of Δ_2 under this condition and contains only global information about the internuclear difference potential in the form of S-matrix elements.[13]

Equation (19) may be interpreted as the result of a two-step process. First,

$$\sum_{q_3,q_2} (e^{(1)}_{-q_3})^* e^{(1)}_{q_2}(-1)^{q_2}[K]^{1/2} \begin{bmatrix} 1 & 1 & K \\ q_3 & q_2 & Q \end{bmatrix} \times \frac{1}{3}\frac{1}{\hbar^2} |\langle j_e||\mu||j_g\rangle \mathscr{E}_1|^2 \frac{\Gamma^K_{eg}(\Delta_1)-\gamma^K}{\Delta_1^2} \tag{19'}$$

is the rate of creating a multipole component K of the excited state due to the absorption of a photon $(\omega_1,\mathbf{e}_1)$. [Emission from this excited state should give rise to a redistributed photon of frequency $\omega \approx (E_e - E_g)/\hbar$.] Then, in the second step,

$$\frac{W_F}{\gamma_e+\gamma^K} \tag{19''}$$

is the probability of creating a redistributed photon of frequency $\omega \approx (E_f - E_e)/\hbar$ by absorption of a laser photon $(\omega_2,\mathbf{e}_2)$ before the multipole is destroyed by spontaneous decay or subsequent collisions;

$$W_F = W\frac{\gamma_e+2\gamma_{fe}(\Delta_2)}{\gamma_e+\gamma_f+2\gamma_{fe}(\Delta_2)} \tag{19'''}$$

is the rate for creating this redistributed photon with the total transition rate W from the K-multipole of $\{|e_i\rangle\}$ to $|f\rangle$ given by

$$W=\sum_{q_1,q_4} (e^*_{q_4}) e^{(2)}_{-q_1}(-1)^{q_4}[K]^{1/2} \begin{bmatrix} 1 & 1 & K \\ q_4 & q_1 & Q \end{bmatrix} \frac{1}{3}\frac{1}{\hbar^2} |\langle j_f||\mu||j_e\rangle \mathscr{E}_2|^2 \frac{\gamma_e+\gamma_f+2\gamma_{fe}(\Delta_2)}{\Delta_2^2+[(\gamma_e+\gamma_f)/2+\gamma_{fe}(\Delta_2)]^2} .$$

Note that in Eq. (19''') the rate of creating a Rayleigh scattered photon at frequency $\omega \approx \omega_2$ has been subtracted from the total transition rate W [see condition (15)]. If $|\Delta_2|$ were less or of the order of $[(\gamma_e+\gamma_f)/2]+\gamma_{fe}(\Delta_2)$, Rayleigh scattering and redistribution around $\omega \approx (E_f-E_e)/\hbar$ would become indistinguishable, because peaks (b) and (c) in Fig. 3 would overlap. Under this condition, the quantity defined in Eq. (16a) would still be given by expression (19) provided we replaced the redistribution rate W_F of Eq. (19'') by the total transition rate W from $\{|e_i\rangle\}$ to $|f\rangle$. The redistributed intensity is then proportional to $\sigma_0^0(ff)$, because the contribution of the Raman peak (a) is of higher order in $\gamma/|\Delta_1|$. Thus the factor $\{[\gamma_e+2\gamma_{fe}(\Delta_2)]/[\gamma_e+\gamma_f+2\gamma_{fe}(\Delta_2)]\}$ in Eq. (19''') represents the branching ratio for redistributed radiation, but with redistribution also occurring due to the decay γ_e of the lower level.[14]

B. $|\Delta_2|\tau_c \gg 1$, $|\Delta_1|\tau_c \ll 1$

With the help of the estimates of Appendix D with $\gamma_e\tau_c \ll 1$ and relation (20), the redistributed intensity reduces in this case to the expression

$$\begin{aligned} I_{\text{red}}(\epsilon) \propto{}& \frac{2\pi}{3}|\langle j_f||\mu||j_e\rangle|^2 \tfrac{1}{9} |\langle j_f||\mu||j_e\rangle \mathscr{E}_2|^2 |\langle j_e||\mu||j_g\rangle \mathscr{E}_1|^2 \frac{1}{\hbar^4} \\ &\times \sum_{\substack{q_1,q_2,q_3,q_4,\\ K,Q}} (e^{(2)}_{q_4})^*(e^{(1)}_{-q_3})^*(-1)^{q_4} e^{(2)}_{-q_1} e^{(1)}_{q_2}(-1)^{q_2}[K] \begin{bmatrix} 1 & 1 & K \\ q_4 & q_1 & Q \end{bmatrix} \begin{bmatrix} 1 & 1 & K \\ q_3 & q_2 & Q \end{bmatrix} \\ &\times \frac{1}{\gamma_f} \frac{\gamma_e+2\gamma_{eg}(\Delta_1)}{(\gamma_e+\gamma^K)\{\Delta_1^2+[\gamma_e/2+\gamma_{eg}(\Delta_1)]^2\}} \frac{2\gamma_{fe}(\Delta_2)-\gamma^K-2\Delta_2 \text{Im}C(K,feee,z=0)}{\Delta_2^2} . \end{aligned} \tag{22}$$

Now the laser photon $(\omega_2,\mathbf{e}_2)$ is absorbed instantaneously at a certain internuclear separation, whereas the laser photon $(\omega_1,\mathbf{e}_1)$ is absorbed during a time much larger than the duration of a collision. The redistributed intensity therefore contains detailed information about the internuclear difference potential between the manifolds $\{|f\rangle\}$ and $\{|e_i\rangle\}$ through $\gamma_{fe}(\Delta_2)$ and $\text{Im}C(K,feee,z=0)$ but only global information about the difference potential between the states $\{|e_i\rangle\}$ and $\{|g\rangle\}$ in the form of S-matrix elements as $\gamma_{eg}(\Delta_1)$ is evaluated in the impact limit. $\gamma_{fe}(\Delta_2)$ is determined by the properties of the internuclear difference potential in the region of the internuclear separations R_S, at which the absorption of the laser photon $(\omega_2,\mathbf{e}_2)$ occurs. The quantity

$$\Gamma^K_{fe}(\Delta_2)=2\gamma_{fe}(\Delta_2)-2\Delta_2\text{Im}C(K,feee,z=0) \tag{23}$$

describes a collision with the radiator in the excited-state manifold, which is interrupted by the absorption of the laser photon $(\omega_2,\mathbf{e}_2)$ at the internuclear separation R_S. In Appendix C we have pointed out that $C(K=0,feee,z=0)=0$, which implies that this kind of collisional quantity is unimportant in the case of a nondegenerate excited-state manifold $\{|e_i\rangle\}$. In the case of a degenerate excited-state manifold its importance may be seen most drastically by considering an antistatic detuning Δ_2. In this case, we have (see Appendix F)

$$2\Delta_2 \mathrm{Im}C(K,feee,z=0) \to -\gamma^K ,$$
$$\gamma_{fe}(\Delta_2) \to 0$$

and the redistributed intensity goes to zero. Without the collisional quantities $\mathrm{Im}C(K,feee,z=0)$, it would become negative in this limit.

Equation (22) may also be interpreted in terms of a two-step process. First,

$$\sum_{q_2,q_3} (e^{(1)}_{-q_3})^* e^{(1)}_{q_2} (-1)^{q_2} [K]^{1/2} \begin{bmatrix} 1 & 1 & K \\ q_3 & q_2 & Q \end{bmatrix} \times \frac{1}{3}\frac{1}{\hbar^2} |\langle j_e||\mu||j_g\rangle \mathscr{E}_1|^2 \frac{\gamma_e + 2\gamma_{eg}(\Delta_1)}{\Delta_1^2 + [\gamma_e/2 + \gamma_{eg}(\Delta_1)]^2} \tag{22$'$}$$

is the rate of absorbing a photon $(\omega_1, \mathbf{e}_1)$ and creating thereby an excited-state population with a multipole K. Then,

$$\frac{W^{(K)}}{\gamma_e + \gamma^K} \tag{22$''$}$$

is the probability of absorbing a photon $(\omega_2, \mathbf{e}_2)$ from this excited multipole and giving rise to a redistributed photon of frequency $\omega \approx (E_f - E_e)/\hbar$ before the multipole is destroyed by spontaneous decay or subsequent collisions;

$$W^{(K)} = \sum_{q_1,q_4} (e^{(2)}_{q_4})^* e^{(2)}_{-q_1} (-1)^{q_4} [K]^{1/2} \begin{bmatrix} 1 & 1 & K \\ q_4 & q_1 & Q \end{bmatrix} \times \frac{1}{3}\frac{1}{\hbar^2} |\langle j_f||\mu||j_e\rangle \mathscr{E}_2|^2 \frac{\Gamma^K_{fe}(\Delta_2) - \gamma^K}{\Delta_2^2} \tag{22$'''$}$$

is the rate of creating this redistributed photon.

C. $|\Delta_1|\tau_c \gg 1$, $|\Delta_2|\tau_c \gg 1$, $|\Delta_1+\Delta_2|\tau_c \gg 1$

Rationalizing all denominators in Eq. (18) by using Eq. (20), we find for the redistributed intensity the expression

$$\begin{aligned} I_{\mathrm{red}}(\epsilon) \propto{} & \frac{2\pi}{3} |\langle j_f||\mu||j_e\rangle|^2 \tfrac{1}{9} |\langle j_f||\mu||j_e\rangle \mathscr{E}_2|^2 |\langle j_e||\mu||j_g\rangle \mathscr{E}_1|^2 \frac{1}{\hbar^4} \\ & \times \sum_{\substack{q_1,q_2,q_3,q_4 \\ K,Q}} (e^{(2)}_{q_4})^* (e^{(1)}_{-q_3})^* (-1)^{q_4} e^{(2)}_{-q_1} e^{(1)}_{q_2} (-1)^{q_2} [K] \begin{bmatrix} 1 & 1 & K \\ q_4 & q_1 & Q \end{bmatrix} \begin{bmatrix} 1 & 1 & K \\ q_3 & q_2 & Q \end{bmatrix} \\ & \times \frac{1}{\gamma_f} \Bigg[\frac{1}{\gamma_e + \gamma^K} \frac{\Gamma^K_{eg}(\Delta_1) - \gamma^K}{\Delta_1^2} \frac{\Gamma^K_{fe}(\Delta_2) - \gamma^K}{\Delta_2^2} \\ & \quad + \Bigg[\frac{\Gamma^K_{eg}(\Delta_1) + \Gamma^K_{fe}(\Delta_2) - \gamma^K}{\Delta_1^2 \Delta_2^2} - \frac{2\gamma_{fe}(\Delta_2)}{\Delta_1 \Delta_2^2 (\Delta_1+\Delta_2)} - \frac{2\gamma_{eg}(\Delta_1)}{\Delta_1^2 \Delta_2 (\Delta_1+\Delta_2)} - \frac{2\gamma_{fg}(\Delta_1+\Delta_2)}{\Delta_1 \Delta_2 (\Delta_1+\Delta_2)^2} \\ & \quad + \frac{2\,\mathrm{Im}C(fefg,z=0) + 2\,\mathrm{Im}C(fgeg,z=0)}{\Delta_1 \Delta_2 (\Delta_1+\Delta_2)} \\ & \quad + \frac{2\,\mathrm{Re}D_1(K,feeg,z=0)}{\Delta_1\Delta_2} - \frac{2\,\mathrm{Re}D_2(K,feeg,z=0) - 2\,\mathrm{Re}D_3(K,fege,z=0)}{\Delta_1\Delta_2} \Bigg] \Bigg] , \end{aligned} \tag{24}$$

which reduces to Eqs. (19) and (22) in the corresponding limits.

According to our estimates for the collisional quantities in Appendix D we now have to keep the contributions of the second-order collisional quantities. As the structure of Eq. (24) is quite complicated we may gain some additional insight by also considering the calculation of the redistributed intensity in a dressed-state formulation.[15] Using the results of Appendix G the total redistributed intensity of Eq. (24) is proportional to the stationary dressed-state population in state $|\mathrm{III}\rangle$, which is given by

$$\sigma_{\mathrm{III,III}}(t\to\infty) = \frac{1}{\gamma_f} \frac{N}{V} 4\pi \int_0^\infty dv\, v^2 f(v) v \int \frac{d\Omega_v}{4\pi} 2\pi \int_0^\infty db\, b \sum_{\substack{|i\rangle \\ =\{|\mathrm{I}\rangle, |\mathrm{II}_1\rangle, |\mathrm{II}_2\rangle, |\mathrm{II}_3\rangle\}}} |\langle \mathrm{III}|X\rangle^{(i)}_{t\to\infty}|^2 \sigma_{ii}(t\to\infty) . \tag{25}$$

This expression is valid for weak fields in the classical path approximation with straight-line trajectories. $\langle \mathrm{III}|X\rangle^{(i)}_{t\to\infty}$ is thereby an optical collision (CARE) S-matrix element between the dressed states $|i\rangle$ and $|\mathrm{III}\rangle$. The redistributed intensity of Eq. (24) contains, therefore, two different types of contributions.

(a) Sequential-collisional contributions: First, a dressed-state population $\sigma_{ii}(t\to\infty)$ $(i \neq \mathrm{I})$ is created by an optical collision and a subsequent collision excites the radiator perturber system from $|i\rangle$ to $|\mathrm{III}\rangle$. These types of contributions are represented by the first term in Eq. (24).

(b) Single-collisional contribution: Within one single collision, the radiator is excited from the ground state to the dressed state $|\,\mathrm{III}\rangle$ and gives rise to a redistributed photon. This process is described by an S-matrix element $\langle \mathrm{III}\,|\,X\rangle^{(\mathrm{I})}_{t\to\infty}$ and corresponds to the terms in large parentheses in the last three lines of Eq. (24). It is interesting to note that $|\langle \mathrm{III}\,|\,X\rangle^{(\mathrm{I})}_{t\to\infty}|^2$ describes absorption during a collision, propagation in the excited electronic state and further absorption [second term of Eq. (G6)] as well as direct two-photon absorption [first term in Eq. (G6)] plus interferences between both events.

The dressed-state formulation of the redistribution problem has a possible advantage over the procedure we used in this paper when both detunings are large, as long as all radiator states are nondegenerate and the integration over the directions of the perturber velocity is trivial, i.e., $\int (d\Omega_v/4\pi)=1$. In this case, we simply have to evaluate S-matrix elements, which is alot easier than the calculation of the nested integrals of Eq. (E1). However, as soon as radiator states are degenerate (which is unavoidable) the averaging over the velocity directions of the perturber has to be performed and this simplicity is lost.

Let us now study Eq. (24) in different limiting cases to get some feeling for the relative importance of various terms.

(1) All detunings antistatic. The times of interest for all transitions in the radiator, i.e., $|g\rangle\to\{|e_i\rangle\}$, $\{|e_i\rangle\}\to|f\rangle$, and $|g\rangle\to|f\rangle$ are much shorter than the collision time τ_c, but in this case there does not exist any stationary phase point associated with any of these transitions. As outlined in Appendix F, this implies that the dominant contribution to the collisional quantities comes from weak collisions, which allows us to get some simple relations between them. Inserting the expressions of Appendix F [Eqs. (F2) and (F3)] into Eq. (24) we find that

$$I_{\mathrm{red}}(\epsilon)\to 0\ . \tag{26}$$

The main feature we observe is that

$$\mathrm{Re}D_2(K,feeg,z=0)-\mathrm{Re}D_3(K,fege,z=0)\ ,$$

$$C(K,feee,z=0)\ ,$$

$$C(K,eeeg,z=0)\ ,$$

and

$$\gamma^K$$

contribute equally to the redistributed intensity and lead to the cancellations necessary to achieve this result.

(2) Δ_1,Δ_2 quasistatically and $\Delta_1+\Delta_2$ antistatically detuned. Again, all characteristic times associated with the various transitions of the radiator are short in comparison with the duration of a collision but the transitions $|g\rangle\to\{|e_i\rangle\}$ and $\{|e_i\rangle\}\to|f\rangle$ now occur at a certain internuclear separation, whereas the transition $|g\rangle\to|f\rangle$ does not have a stationary phase point. In Appendix E we briefly discuss the quasistatic picture of absorption at a certain internuclear separation and also give an estimate for $\mathrm{Re}(D_2-D_3)$ in the quasistatic limit in the case of a nondegenerate intermediate state for simplicity. This estimate together with Eq. (D9) and the discussion of Appendix G shows that for an antistatic detuning of $\Delta_1+\Delta_2$, $\mathrm{Re}D_2-\mathrm{Re}D_3$ gives the dominant contribution to the total redistributed intensity provided all detunings are sufficiently large, i.e., $|\Delta\tau_c|^{-5/6}\ll 1$ for a R^{-6} radiator-perturber interaction. For quasistatic detunings of Δ_1 and Δ_2 we can therefore write

$$\begin{aligned} I_{\mathrm{red}}(\epsilon)\to{}&\frac{2\pi}{3}\,|\langle j_f||\mu||j_e\rangle|^2\tfrac{1}{9}\,|\langle j_f||\mu||j_e\rangle\mathscr{E}_2|^2\,|\langle j_e||\mu||j_g\rangle\mathscr{E}_1|^2\frac{1}{\hbar^4}\\ &\times\sum_{\substack{q_1,q_2,q_3,q_4,\\K,Q}}(e^{(2)}_{q_4})^*(e^{(1)}_{-q_3})^*(-1)^{q_4}e^{(2)}_{-q_1}e^{(1)}_{q_2}(-1)^{q_2}[K]\begin{Bmatrix}1&1&K\\q_4&q_1&Q\end{Bmatrix}\begin{Bmatrix}1&1&K\\q_3&q_2&Q\end{Bmatrix}\\ &\times(-1)\frac{1}{\gamma_f}\,\frac{2\,\mathrm{Re}D_2(K,feeg,z=0)-2\,\mathrm{Re}D_3(K,fege,z=0)}{\Delta_1\Delta_2}\ , \end{aligned}\tag{27}$$

as long as $\Delta_1+\Delta_2$ is antistatically detuned. This expression represents the picture of a single-collision quasimolecular two-step absorption:[16] The laser photon $(\omega_1,\mathbf{e}_1)$ is absorbed at the internuclear separation R_{S_1}, the radiator- (in the excited-state manifold $\{|e_i\rangle\}$) perturber system subsequently evolves until the internuclear separation R_{S_2} is reached, where the second laser photon $(\omega_2,\mathbf{e}_2)$ is absorbed.

In Eq. (27) we have neglected the subsequent collision contribution in comparison with the single-collisional contribution. This is certainly no problem as long as

$$\gamma_e\gg\gamma^K\ , \tag{28}$$

which is the case for sufficiently low perturber densities. But in the opposite limit, where

$$\frac{1}{\tau_c}\gg\gamma^K\gg\gamma_e \tag{29}$$

this is no longer obvious. Using the estimate of Cooper[17] we find that the ratio $[\Gamma^K_{eg}(\Delta_1)]/\gamma^K$ varies as $(|\Delta_1|\tau_c)^{1/2}$ for a van der Waals potential, whereas Eq. (E16) shows that

$$-\frac{2\,\mathrm{Re}D_2(K,feeg,z=0)-2\,\mathrm{Re}D_3(K,fege,z=0)}{\Delta_1\Delta_2}$$

roughly increases like $(|\Delta_1|\tau_c)^{5/6}$. For sufficiently large detunings $|\Delta_1|\tau_c\gg 1$, $|\Delta_2|\tau_c\gg 1$ the subsequent-collision contribution [first term in Eq. (24)] is therefore indeed negligible in comparison with the single-collision quantities.

(3) All detunings quasistatic. If there is also a stationary phase point associated with $\Delta_1+\Delta_2$ a redistributed photon of frequency $\omega \approx (E_f - E_e)/\hbar$ can also be generated by the direct absorption of both photons $(\omega_1, \mathbf{e}_1)$ and $(\omega_2, \mathbf{e}_2)$ during a single collision [first term in Eq. (G6)]. In general the single-collision contribution to the redistributed intensity contains now information about this direct two-photon process, the two-step process of Eq. (27), and interferences between the amplitudes of both these processes. Qualitative insight into the relative importance of the various contributions may be obtained by considering the case of a nondegenerate intermediate state as discussed in Appendix G. Equation (G6) in particular shows that as long as points of stationary phase are well separated, the two-step contribution dominates for large detunings such that for a R^{-6} interaction $|\Delta_{\tau_c}|^{-5/12} \ll 1$ (which is the ratio between the interference and the two-step term). The direct two-photon contribution is consequently smaller by $\sim |\Delta\tau_c|^{-5/6}$. For these large detunings the subsequent-collision contribution [first term in Eq. (24)] is also negligible, as has been shown above, and the total redistributed intensity is again given by Eq. (27).

(4) Other cases. An asymptotic evaluation of the second-order collisional quantities becomes quite complicated in other cases where some detunings are antistatic and others quasistatic. However, we can get some qualitative insight by considering the CARE transition probability $|\langle \mathrm{III} | X \rangle^{(\mathrm{I})}_{t\to\infty}|^2$ for a nondegenerate three-level system in the weak-field limit as given in Eq. (G6). This expression shows that the total redistributed intensity goes to zero as soon as $\Delta_1+\Delta_2$ and Δ_1 or $\Delta_1+\Delta_2$ and Δ_2 are antistatically detuned due to the fact that the sequential-collisional contributions also vanish in this case.

V. CONCLUSIONS

We have studied collisional redistribution of radiation in an atom, which is excited by two weak laser fields via a degenerate intermediate state and undergoes collisions with a bath of structureless perturbers. In particular, we have investigated the total redistributed intensity corresponding to the atomic transition from the final to an intermediate state. Our general expression for the redistributed intensity is valid for arbitrary polarizations of the exciting laser fields and arbitrary detunings of the laser frequencies from the atomic transition frequencies and contains information about different kinds of collisional events. If Δ_2 is in the impact region and Δ_1 quasistatically detuned, it measures a process where a photon $(\omega_1, \mathbf{e}_1)$ is absorbed at a certain internuclear distance and the subsequent completion of the collision causes a reorientation of the radiator-perturber system. This type of process has also been studied in one-photon collisional redistribution by investigating the polarization of the emitted photon.[1,6–9] If, on the other hand, Δ_1 is in the impact limit and Δ_2 is quasistatically detuned, the total redistributed intensity contains information about a collision with the radiator in the excited-state manifold $\{ |e_i\rangle \}$, which is interrupted by the instantaneous absorption of a photon $(\omega_2, \mathbf{e}_2)$.

If all detunings are larger than the inverse collision time, new types of collisional quantities, which cannot be studied by one-photon collisional redistribution, become important. If Δ_1 and Δ_2 are quasistatically detuned, all points of stationary phase well separated and all detunings sufficiently large, the redistributed intensity is dominantly determined by a "molecular" two-step process. The photon $(\omega_1, \mathbf{e}_2)$ is absorbed at a certain internuclear separation and the radiator-perturber system subsequently evolves with the radiator in the excited-state manifold $\{ |e_i\rangle \}$ until the second photon $(\omega_2, \mathbf{e}_2)$ is absorbed at that internuclear separation, which matches the corresponding difference potential. As soon as, in addition to $\Delta_1+\Delta_2$, Δ_1 or Δ_2 are also antistatically detuned, the redistributed intensity becomes vanishingly small. If all three detunings are quasistatic and points of stationary phase not well separated or detunings not sufficiently large, the situation is quite complicated, because interferences between the transition amplitudes associated with the molecular two-step process and the direct two-photon excitation may become important.

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APPENDIX A: EVALUATION OF THE STATIONARY REDUCED DENSITY-MATRIX ELEMENTS

We start from the equation for the reduced density operator $\sigma(t)$ [Eq. (5)], where the BCA has already been made and perform the Laplace transformation

$$\sigma(z) = \int_0^\infty dt\, e^{izt}\sigma(t)\ , \quad \mathrm{Im} z > 0 \tag{A1a}$$

with the inverse

$$\sigma(t) = \frac{1}{2\pi} \lim_{\epsilon\to 0} \left[\int_{-\infty}^{\infty} dx\, e^{-ixt}\sigma(x+i\epsilon) \right] . \tag{A1b}$$

This yields

$$[z - i(L_{\mathrm{eff}} + \Gamma)]\sigma(z) = i\sigma(t=0) + iM(z)\sigma(z) \tag{A2}$$

with

$$[z - i(L_{\mathrm{eff}} + L_P + V_1 + \Gamma)]G_1(z) = i1$$

and

$$M(z) = N\, \mathrm{Tr}_P\{[V_1 G_1(z) V_1 + V_1]\rho_P\} .$$

According to the weak-field conditions [Eq. (8a)], we may write up to second-order perturbation theory in the electromagnetic field

$$G_1(z) = G_0(z) + G_0(z)L_E G_0(z) + G_0(z)L_E G_0(z) L_E G_0(z) + \cdots \tag{A3a}$$

with the unperturbed propagator

$$G_0(z)=\frac{i}{z-i(L_R+L_P+V_1+\Gamma)} . \tag{A3b}$$

Thereby, we defined

$$L_{\text{eff}}=L_R+L_E , \tag{A3c}$$

where L_R is the diagonal part of L_{eff} and L_E contains the nondiagonal part due to the laser fields of amplitudes $\mathscr{E}_1$ and $\mathscr{E}_2$. Up to second-order perturbation theory in the laser fields, we find for the Laplace-transformed collision kernel

$$M(z)=M_0(z)+M_1(z)+M_2(z) \tag{A4}$$

with

$$M_0(z)=N\,\mathrm{Tr}_P\{[V_1G_0(z)V_1+V_1]\rho_P\} ,$$

$$M_1(z)=N\,\mathrm{Tr}\{V_1G_0(z)L_EG_0(z)V_1\rho_P\} ,$$

and

$$M_2(z)=N\,\mathrm{Tr}_P\{V_1G_0(z)L_EG_0(z)L_EG_0(z)V_1\rho_P\} .$$

The subscripts indicate the order in the electromagnetic field. The stationary solution of the reduced density operator is then given by

$$\sigma(t\to\infty)=\lim_{z\to 0}\left[\frac{z}{i}\sigma(z)\right] . \tag{A5}$$

Evaluating the tetradic matrix elements in Eq. (A2) with the help of the relations of Appendixes B and C finally yields in lowest-order perturbation theory in the laser fields $\mathscr{E}_1$ and $\mathscr{E}_2$ for $t\to\infty$ the stationary density-matrix elements of Eq. (10).

APPENDIX B: TETRADIC VECTORS AND THEIR MATRIX ELEMENTS

In order to exploit the spherical symmetry of the distribution of the perturbers around the radiator, we represent the reduced density matrix of the radiator in an irreducible tetradic basis with respect to the rotation group, which is defined by[7]

$$|j_1j_2KQ\rangle\!\rangle=\sum_{m_1,m_2}|j_1m_1,j_2m_2\rangle\!\rangle(-1)^{j_1-m_2-Q}\times\begin{pmatrix} j_1 & j_2 & K\\ m_1 & -m_2 & -Q\end{pmatrix}[K]^{1/2} , \tag{B1}$$

with $[K]=2K+1$. The operator

$$|j_1m_1,j_2m_2\rangle\!\rangle=|j_1m_1\rangle\langle j_2m_2| \tag{B2}$$

is called a tetradic vector and is defined in terms of the radiator states $|j_im_i\rangle$ with total angular momentum j_i and magnetic quantum number m_i. If $L\ldots=(1/i\hbar)[0,\cdots]$ is a Liouville space operator, corresponding to a Hilbert space operator O, its matrix elements with respect to two tetradic vectors are given by[4,18]

$$\langle\!\langle ab\,|\,L\,|\,cd\rangle\!\rangle=\frac{1}{i\hbar}(\langle a\,|\,O\,|\,c\rangle\langle b\,|\,d\rangle^* -\langle a\,|\,c\rangle\langle b\,|\,O^\dagger\,|\,d\rangle^*) . \tag{B3}$$

Treating the coupling of the radiator atom to the vacuum modes in Markov approximation and lowest-order perturbation theory, thereby neglecting the atomic motion, the tetradic matrix elements of Γ are given by[4,19]

$$\langle\!\langle j_1j_2KQ\,|\,\Gamma\,|\,j_1j_2K'Q'\rangle\!\rangle=-\delta_{KK'}\delta_{QQ'}(\tfrac{1}{2}\gamma_1+\tfrac{1}{2}\gamma_2) \tag{B4a}$$

and

$$\langle\!\langle j_1j_1KQ\,|\,\Gamma\,|\,j_2j_2K'Q'\rangle\!\rangle =(-1)^{1+K+j_1+j_2}\begin{Bmatrix} j_2 & j_2 & K\\ j_1 & j_1 & 1\end{Bmatrix}[j_2]\gamma_{2\to 1}\delta_{QQ'}\delta_{KK'} . \tag{B4b}$$

$\gamma_{i\to k}$ is the spontaneous decay rate from state $|i\rangle$ with angular momentum j_i to state $|k\rangle$. In the dipole approximation it is given by

$$\gamma_{i\to k}=|\langle j_i||r||j_k\rangle|^2\frac{4\omega^3\alpha}{3c^2(2j_i+1)}\bigg|_{\hbar\omega=E_i-E_k>0} \tag{B4c}$$

with the fine-structure constant α, the speed of light c, and the position operator of the electrons r. $\gamma_i=\sum_k\gamma_{i\to k}$ is the total spontaneous decay rate from state $|i\rangle$.

Matrix elements of the dipole Liouville operators L_j which describe the coupling due to the laser field $\mathscr{E}_j$ are evaluated using the relation

$$i\hbar\langle\!\langle j_1j_2KQ\,|\,L_j\,|\,j_3j_4K'Q'\rangle\!\rangle=-\sum_q(e_q^{(j)})^*(-1)^q(-1)^{j_3-j_4}\delta_{j_2j_4}\langle j_1||\mu||j_3\rangle\mathscr{E}_j\;{}^{q}_{j_1j_4j_3}G^{K'K}_{Q'Q} +\sum_q e_q^{(j)}(-1)^{j_3-j_4}(-1)^{1+K+K'}\delta_{j_1j_3}\langle j_4||\mu||j_2\rangle\mathscr{E}_j^*\;{}^{-q}_{j_2j_3j_4}G^{K'K}_{Q'Q} \tag{B5}$$

with $E_1,E_2\geq E_3,E_4$ and

$${}^{q}_{j_1j_4j_3}G^{K'K}_{Q'Q}=(-1)^{j_1+j_3+Q'}[K]^{1/2}[K']^{1/2}\begin{pmatrix} K' & 1 & K\\ Q' & q & -Q\end{pmatrix}\begin{Bmatrix} K' & 1 & K\\ j_1 & j_4 & j_3\end{Bmatrix} .$$

The polarization and dipole operator are thereby decomposed into their spherical components (i.e., $\mathbf{e}_j=\sum_q e_q^{(j)}\boldsymbol{\epsilon}_q$ and $\boldsymbol{\mu}=\sum_q \mu_q \boldsymbol{\epsilon}_q$ with $\boldsymbol{\epsilon}_q$ defined in Brink and Satchler[20] [formula (4.37)]). The reduced dipole matrix elements are defined by

$$\langle j_1 m_1 | \mu_q | j_2 m_2 \rangle = (-1)^{j_1-m_1} \begin{pmatrix} j_1 & 1 & j_2 \\ -m_1 & q & m_2 \end{pmatrix} \langle j_1 || \mu || j_2 \rangle \; . \tag{B6}$$

APPENDIX C: DEFINITION OF THE COLLISION OPERATORS

In this appendix, we shall perform the angular integration over the directions of the perturber velocities and simplify thereby the tetradic matrix elements of the collision operators of Eq. (A4). In the negligible ground-state interaction approximation [Eq. (7)] all matrix elements with $V_1 | j_g j_g 00 \rangle\rangle$ on the right-hand side vanish. On the other hand, all collisional matrix elements with $\langle\langle j_f j_f 00 | V_1$ on the left-hand side also vanish if we neglect inelastic collisions even if the final state is perturbed. As has been shown by Burnett *et al.*[4] (in their Appendix C) this is related to the fact that $|f\rangle$ is nondegenerate and is valid as long as the influence of bound states of the radiator-perturber system on the collisional quantities is negligible. In the following, we shall assume that this is the case. Let us now discuss the remaining collisional quantities determining the dynamics of the radiator in the laser fields.

1. Zero-order collisional quantities

Assuming that the equilibrium density operator of an ensemble of perturbers and the interaction between radiator and perturber are rotationally invariant, we can simplify the tetradic matrix elements of the collision operators of Eq. (A4) considerably. For these purposes we define new collision-frame (tetradic) vectors by

$$\begin{aligned} | j_1 j_2 K q \rangle\rangle &= \sum_Q | j_1 j_2 K Q \rangle\rangle \mathscr{D}^K_{Qq}(\Omega) \; , \\ | j_1 j_2 K Q \rangle\rangle &= \sum_q [\mathscr{D}^K_{Qq}(\Omega)]^* \, | j_1 j_2 K q \rangle\rangle \; . \end{aligned} \tag{C1}$$

The new basis $|j_1 j_2 K q\rangle\rangle$ is obtained from the laboratory-fixed basis $|j_1 j_2 K Q\rangle\rangle$ by a rotation of the coordinate system such that the new z axis, for example, is always directed antiparallel to $\mathbf{p}$ (the kinetic momentum of the perturber in a classical path approximation) and the orthogonal directions are defined in an arbitrary way.[9] Ω here indicates the three Euler angles necessary for describing the rotation.[20] Neglecting inelastic collisions the tetradic matrix elements of the zero-order collision operators of interest are of the form

$$\begin{aligned} \langle\langle \bar{j}_1 \bar{j}_2 K Q | M_0(z) | \bar{j}_1 \bar{j}_2 K' Q' \rangle\rangle &= N \int d\Omega_{\mathbf{p}} \int dp\, p^2 \langle\langle \bar{j}_1 \bar{j}_2 K Q | \; \langle\langle \mathbf{pp} | [V_1 G_0(z) V_1 + V_1] \rho_P | \bar{j}_1 \bar{j}_2 K' Q' \rangle\rangle \\ &= \sum_{q,q'} N \int dp\, p^2 \langle\langle \bar{j}_1 \bar{j}_2 K q | \; \langle\langle \mathbf{pp} | [V_1 G_0(z) V_1 + V_1] \rho_P | \bar{j}_1 \bar{j}_2 K' q' \rangle\rangle \\ &\quad \times \frac{1}{2\pi} \int d\Omega\, \mathscr{D}^K_{Qq}(\Omega) [\mathscr{D}^{K'}_{Q'q'}(\Omega)]^* = \delta_{KK'} \delta_{QQ'} \, {}^{j_1 j_2}_{j_1 j_2} M^K(z) \; . \end{aligned} \tag{C2}$$

In the second line we have thereby used the assumption of rotational symmetry of the collisional environment of the radiator. $\int d\Omega$ denotes the integral over all possible orientations of the collision frame (Euler angles) and is given by Brink and Satchler[20] (Appendix V). The bars over the quantities j indicate the rotating states of Eq. (2d) (with $|\bar{g}\rangle = |g\rangle$). $M_0(z)$ is therefore diagonal in K and independent of Q. Using relation (B1) we find (for integer j_1, j_2)

$$\begin{aligned} {}^{j_1 j_2}_{j_1 j_2} M^K(z) = \sum_{\substack{\mu_1,\mu_2,\mu_3,\mu_4, \\ q}} (-1)^{\mu_2+\mu_4} \begin{pmatrix} j_1 & j_2 & K \\ -\mu_1 & \mu_2 & q \end{pmatrix} \begin{pmatrix} j_1 & j_2 & K \\ -\mu_3 & \mu_4 & q \end{pmatrix} \\ \times N \int d^3p_1 d^3p_2 \langle\langle \bar{j}_1 \mu_1 \mathbf{p}_1, \bar{j}_2 \mu_2 \mathbf{p}_1 | V_1 G_0(z) V_1 + V_1 | \bar{j}_1 \mu_3 \mathbf{p}_2, \bar{j}_2 \mu_4 \mathbf{p}_2 \rangle\rangle \rho(p_2) \end{aligned} \tag{C3}$$

with the radiator states in the collision frame $|j\mu\rangle$. Thereby, we have assumed ρ_P to be diagonal in the momentum states $|\mathbf{p}\rangle$ with $\rho(p_2) = \langle \mathbf{p}_2 | \rho_P | \mathbf{p}_2 \rangle$ and the normalization $4\pi \int dp\, p^2 \rho(p) = 1$.

The collisional decay rates in the reduced density-matrix equations of the radiator are then given by

$$\begin{aligned} \gamma_{eg}(\Delta_1) &= -\mathrm{Re}[{}^{eg}_{eg} M^1(z=0)] \; , \\ \gamma_{fe}(\Delta_2) &= -\mathrm{Re}[{}^{fe}_{fe} M^1(z=0)] \; , \\ \gamma_{fg}(\Delta_1+\Delta_2) &= -\mathrm{Re}[{}^{fg}_{fg} M^0(z=0)] \; , \\ \gamma^K &= -\mathrm{Re}[{}^{ee}_{ee} M^K(z=0)] \; . \end{aligned} \tag{C4}$$

It is thereby understood that the imaginary parts (shifts) have been absorbed in redefined atomic energies. Using the relation

$${}^{j_1 j_2}_{j_1 j_2} M^K(z) = [{}^{j_2 j_1}_{j_2 j_1} M^K(-z)]^* \tag{C5}$$

we immediately recognize that ${}^{j_1 j_1}_{j_1 j_1} M^K(z=0)$ is purely real. Neglecting inelastic collisions, each of the atomic manifolds $|f\rangle$, $\{|e_i\rangle\}$, and $|g\rangle$ is complete (as long as scattering states are complete and bound radiator-perturber states may be neglected) and $\gamma^{K=0}$ as well as the quantities ${}^{ff}_{ff} M^0(z=0)$ and ${}^{gg}_{gg} M^0(z=0)$ vanish.[4]

2. First-order collision quantities

Assuming no-ground-state interaction and neglecting inelastic collisions (and also bound and quasibound states), in lowest-order perturbation theory in the laser fields only four first-order collisional quantities enter the reduced density-matrix equations [Eq. (5)]. We shall now discuss them and perform the average over perturber directions under the same assumptions as in Appendix C 1.

Let us consider first the quantity

$$\langle\langle \bar{j}_e\bar{j}_e KQ \mid M_1(z) \mid \bar{j}_e j_g 1Q' \rangle\rangle = \sum_{\substack{q_1,q_2,q_3,q_4,\\ K_2,Q_2,Q_3}} N\,\mathrm{Tr}_P\{\langle\langle \bar{j}_e\bar{j}_e Kq_1 \mid V_1 G_0(z) \mid \bar{j}_e\bar{j}_e K_2 q_2\rangle\rangle \langle\langle \bar{j}_e\bar{j}_e K_2 Q_2 \mid L_1 \mid \bar{j}_e j_g 1Q_3\rangle\rangle \langle\langle \bar{j}_e j_g 1q_3 \mid G_0(z) V_1 \mid \bar{j}_e j_g 1q_4\rangle\rangle \rho_P\}$$
$$\times \mathscr{D}^{K}_{Qq_1}(\Omega)[\mathscr{D}^{K_2}_{Q_2q_2}(\Omega)]^* \mathscr{D}^{1}_{Q_3q_3}(\Omega)[\mathscr{D}^{1}_{Q'q_4}(\Omega)]^* \ . \tag{C6}$$

Thereby we have neglected inelastic collisions and have transformed to collision frame (tetradic) states $|j_1j_2Kq\rangle\rangle$ using the relations of Eq. (C1). Taking into account the contraction formula for rotation matrices as given by Brink and Satchler[20] (Appendix V) and performing the integration over all Euler angles as in Appendix C 1 we find with the help of relation (B5)

$$\langle\langle \bar{j}_e\bar{j}_e KQ \mid M_1(z) \mid \bar{j}_e j_g 1Q' \rangle\rangle = \langle\langle \bar{j}_e\bar{j}_e KQ \mid L_1 \mid \bar{j}_e j_g 1Q' \rangle\rangle C(K,eeeg,z) \tag{C7a}$$

with

$$C(K,eeeg,z) = \sum_{\mu_1,\mu_2,\ldots,\mu_5,Q} (-1)^{\mu_2+\mu_4} \begin{bmatrix} 1 & 1 & K \\ \mu_1 & -\mu_2 & Q \end{bmatrix} \begin{bmatrix} 1 & 1 & K \\ \mu_3 & -\mu_4 & Q \end{bmatrix}$$
$$\times N \int d^3p_1 d^3p_2 d^3p_3 d^3p_4 \langle\langle \bar{j}_e\mu_1\mathbf{p}_1, \bar{j}_e\mu_2\mathbf{p}_1 \mid V_1 G_0(z) \mid \bar{j}_e\mu_5\mathbf{p}_2, \bar{j}_e\mu_4\mathbf{p}_3\rangle\rangle$$
$$\times \langle\langle \bar{j}_e\mu_5\mathbf{p}_2, j_g 0\mathbf{p}_3 \mid G_0(z) V_1 \mid \bar{j}_e\mu_3\mathbf{p}_4, j_g 0\mathbf{p}_4\rangle\rangle \rho(p_4) \ . \tag{C7b}$$

Similarly, we obtain for the other tetradic matrix elements of interest the expressions

$$\begin{aligned} &\langle\langle \bar{j}_f j_g 00 \mid M_1(z) \mid \bar{j}_e j_g 1Q'\rangle\rangle = \langle\langle \bar{j}_f j_g 00 \mid L_2 \mid \bar{j}_e j_g 1Q'\rangle\rangle C(fgeg,z) \ ,\\ &\langle\langle \bar{j}_f \bar{j}_e 1Q \mid M_1(z) \mid \bar{j}_f j_g 00\rangle\rangle = \langle\langle \bar{j}_f\bar{j}_e 1Q \mid L_1 \mid \bar{j}_f j_g 00\rangle\rangle C(fefg,z) \ ,\\ &\langle\langle \bar{j}_f\bar{j}_e 1Q \mid M_1(z) \mid \bar{j}_e\bar{j}_e K'Q'\rangle\rangle = \langle\langle \bar{j}_f\bar{j}_e 1Q \mid L_2 \mid \bar{j}_e\bar{j}_e K'Q'\rangle\rangle C(K',feee,z) \end{aligned} \tag{C8a}$$

with

$$C(fgeg,z) = \sum_{\mu} \tfrac{1}{3} N \int d^3p_1 d^3p_2 d^3p_3 d^3p_4 \langle\langle \bar{j}_f 0\mathbf{p}_1, j_g 0\mathbf{p}_1 \mid V_1 G_0(z) \mid \bar{j}_f 0\mathbf{p}_2, j_g 0\mathbf{p}_3\rangle\rangle$$
$$\times \langle\langle \bar{j}_e\mu\mathbf{p}_2, j_g 0\mathbf{p}_3 \mid G_0(z) V_1 \mid \bar{j}_e\mu\mathbf{p}_4, j_g 0\mathbf{p}_4\rangle\rangle \rho(p_4) \ ,$$

$$C(fefg,z) = \sum_{\mu} \tfrac{1}{3} N \int d^3p_1 d^3p_2 d^3p_3 d^3p_4 \langle\langle \bar{j}_f 0\mathbf{p}_1, \bar{j}_e\mu\mathbf{p}_1 \mid V_1 G_0(z) \mid \bar{j}_f 0\mathbf{p}_2, \bar{j}_e\mu\mathbf{p}_3\rangle\rangle$$
$$\times \langle\langle \bar{j}_f 0\mathbf{p}_2, j_g 0\mathbf{p}_3 \mid G_0(z) V_1 \mid \bar{j}_f 0\mathbf{p}_4, j_g 0\mathbf{p}_4\rangle\rangle \rho(p_4) \ , \tag{C8b}$$

and

$$C(K',feee,z) = \sum_{\mu_1,\mu_2,\ldots,\mu_5,Q'} (-1)^{\mu_2+\mu_4} \begin{bmatrix} 1 & 1 & K' \\ \mu_1 & -\mu_2 & Q' \end{bmatrix} \begin{bmatrix} 1 & 1 & K' \\ \mu_3 & -\mu_4 & Q' \end{bmatrix}$$
$$\times N \int d^3p_1 d^3p_2 d^3p_3 d^3p_4 \langle\langle \bar{j}_f 0\mathbf{p}_1, \bar{j}_e\mu_2\mathbf{p}_1 \mid V_1 G_0(z) \mid \bar{j}_f 0\mathbf{p}_2, \bar{j}_e\mu_5\mathbf{p}_3\rangle\rangle$$
$$\times \langle\langle \bar{j}_e\mu_1\mathbf{p}_2, \bar{j}_e\mu_5\mathbf{p}_3 \mid G_0(z) V_1 \mid \bar{j}_e\mu_3\mathbf{p}_4, \bar{j}_e\mu_4\mathbf{p}_4\rangle\rangle \rho(p_4) \ .$$

Using again the arguments of Burnett *et al.*[4] (i.e., neglecting inelastic collisions and bound radiator-perturber states) implies $C(K=0, feee, z=0) = C(K=0, eeeg, z=0) = 0$.

3. Second-order collisional quantities

Similarly, as in Appendix C 2, we find for the second-order collisional quantities, which determine the dynamics of the reduced density matrix of the radiator in the weak-field limit, the expressions

$$\langle\langle \bar{j}_f\bar{j}_e 1Q \mid M_2(z) \mid \bar{j}_e j_g 1Q' \rangle\rangle = \sum_{\substack{q_1,q_2,\\K_1,Q_1}} e^{(1)}_{q_1}(e^{(2)}_{q_2})^*(-1)^{q_1+q_2} \begin{bmatrix} 1 & 1 & K_1 \\ -q_2 & Q & -Q_1 \end{bmatrix} \begin{bmatrix} 1 & 1 & K_1 \\ Q' & -q_1 & -Q_1 \end{bmatrix}$$
$$\times [K_1]\frac{1}{\hbar^2}\frac{1}{3}\langle j_f||\mu||j_e\rangle\langle j_e||\mu||j_g\rangle^*\mathscr{E}_1^*\mathscr{E}_2[D_1(K_1,feeg,z)+D_2(K_1,feeg,z)\,, \tag{C9a}$$

$$\langle\langle \bar{j}_f\bar{j}_e 1Q \mid M_2(z) \mid j_g\bar{j}_e 1Q' \rangle\rangle = \sum_{\substack{q_1,q_2,\\K_1,Q_1}} (e^{(1)}_{q_1})^*(e^{(2)}_{q_2})^*(-1)^{q_2}[K_1] \begin{bmatrix} 1 & 1 & K_1 \\ -Q & q_2 & Q_1 \end{bmatrix} \begin{bmatrix} 1 & 1 & K_1 \\ q_1 & Q' & -Q_1 \end{bmatrix}$$
$$\times \frac{1}{\hbar^2}\frac{1}{3}\langle j_f||\mu||j_e\rangle\langle j_e||\mu||j_g\rangle\mathscr{E}_1\mathscr{E}_2 D_3(K_1,fege,z)$$

with

$$D_1(K_1,feeg,z)= \sum_{\substack{\mu_1,\mu_2,\mu_3,\mu_4,\\Q_1}} (-1)^{\mu_2+\mu_4} \begin{bmatrix} 1 & 1 & K_1 \\ -\mu_4 & \mu_3 & Q_1 \end{bmatrix} \begin{bmatrix} 1 & 1 & K_1 \\ -\mu_2 & \mu_1 & Q_1 \end{bmatrix}$$
$$\times N\int d^3p_1\cdots d^3p_6\langle\langle \bar{j}_f0\mathbf{p}_1,\bar{j}_e\mu_2\mathbf{p}_1 \mid V_1G_0(z) \mid \bar{j}_f0\mathbf{p}_2,\bar{j}_e\mu_4\mathbf{p}_3\rangle\rangle$$
$$\times\langle\langle \bar{j}_f0\mathbf{p}_2,j_g0\mathbf{p}_3 \mid G_0(z) \mid \bar{j}_f0\mathbf{p}_4,j_g0\mathbf{p}_5\rangle\rangle\langle\langle \bar{j}_e\mu_1\mathbf{p}_4,j_g0\mathbf{p}_5 \mid G_0(z)V_1 \mid \bar{j}_e\mu_3\mathbf{p}_6,j_g0\mathbf{p}_6\rangle\rangle\rho(p_6)\,,$$

$$D_2(K_1,feeg,z)= \sum_{\substack{\mu_2,\mu_3,\ldots,\mu_7,\\Q_1}} (-1)^{\mu_3+\mu_7} \begin{bmatrix} 1 & 1 & K_1 \\ \mu_3 & -\mu_2 & Q_1 \end{bmatrix} \begin{bmatrix} 1 & 1 & K_1 \\ \mu_7 & -\mu_6 & Q_1 \end{bmatrix}$$
$$\times N\int d^3p_1\cdots d^3p_6\langle\langle \bar{j}_f0\mathbf{p}_1,\bar{j}_e\mu_2\mathbf{p}_1 \mid V_1G_0(z) \mid \bar{j}_f0\mathbf{p}_2,\bar{j}_e\mu_4\mathbf{p}_3\rangle\rangle$$
$$\times\langle\langle \bar{j}_e\mu_3\mathbf{p}_2,\bar{j}_e\mu_4\mathbf{p}_3 \mid G_0(z) \mid \bar{j}_e\mu_5\mathbf{p}_4,\bar{j}_e\mu_6\mathbf{p}_5\rangle\rangle$$
$$\times\langle\langle \bar{j}_e\mu_5\mathbf{p}_4,j_g0\mathbf{p}_5 \mid G_0(z)V_1 \mid \bar{j}_e\mu_7\mathbf{p}_6,j_g0\mathbf{p}_6\rangle\rangle\rho(p_6)\,, \tag{C9b}$$

$$D_3(K_1,fege,z)= \sum_{\substack{\mu_2,\mu_3,\ldots,\mu_7,\\Q_1}} (-1)^{\mu_3+\mu_5} \begin{bmatrix} 1 & 1 & K_1 \\ \mu_3 & -\mu_2 & Q_1 \end{bmatrix} \begin{bmatrix} 1 & 1 & K_1 \\ \mu_5 & -\mu_7 & Q_1 \end{bmatrix}$$
$$\times N\int d^3p_1\cdots d^3p_6\langle\langle \bar{j}_f0\mathbf{p}_1,\bar{j}_e\mu_2\mathbf{p}_1 \mid V_1G_0(z) \mid \bar{j}_f0\mathbf{p}_2,\bar{j}_e\mu_4\mathbf{p}_3\rangle\rangle$$
$$\times\langle\langle \bar{j}_e\mu_3\mathbf{p}_2,\bar{j}_e\mu_4\mathbf{p}_3 \mid G_0(z) \mid \bar{j}_e\mu_5\mathbf{p}_4,\bar{j}_e\mu_6\mathbf{p}_5\rangle\rangle$$
$$\times\langle\langle j_g0\mathbf{p}_4,\bar{j}_e\mu_6\mathbf{p}_5 \mid G_0(z)V_1 \mid j_g0\mathbf{p}_6,\bar{j}_e\mu_7\mathbf{p}_6\rangle\rangle\rho(p_6)\,.$$

APPENDIX D: COLLISIONAL QUANTITIES IN THE INTERACTION PICTURE

We now discuss the time-dependent form of the collisional quantities and give estimates for their magnitudes. For convenience, we shall write them down in an interaction picture, defined by the time-development operator

$$U_I(t_1,t_2)=U_0^\dagger(t_1,t_2)U_S(t_1,t_2) \tag{D1a}$$

and the interaction potential

$$V_1^I(t_1,t_2)=U_0^\dagger(t_1,t_2)V_1U_0(t_1,t_2)\ , \tag{D1b}$$

where

$$U_0(t_1,t_2)=e^{(L_R+L_P)(t_1-t_2)}$$

is the unperturbed (tetradic) time-development operator and

$$U_S(t_1,t_2)=e^{(L_R+L_P+V_1)(t_1-t_2)}$$

is the time-development operator for the interacting radiator-perturber system. The tetradic matrix elements of these time-evolution operators are defined in terms of Hilbert space matrix elements in the usual way,[4,18] e.g.,

$$\langle\langle ab\,|\,U_0(t_1,t_2)\,|\,cd\rangle\rangle = \langle a\,|\,\bar U_0(t_1,t_2)\,|\,c\rangle\langle b\,|\,\bar U_0(t_1,t_2)\,|\,d\rangle^* \tag{D2}$$

with the Hilbert space time-development operator

$$\bar U_0(t_1,t_2)=\exp\left[\frac{1}{i\hbar}(H_R+H_P)(t_1-t_2)\right]$$

and the Hamilton operators H_R and H_P are for radiator and perturber, respectively. The interaction-picture time-development operator is a solution of the equation of motion

$$\frac{d}{dt_1}U_I(t_1,t_2)=V_1^I(t_1,t_2)U_I(t_1,t_2)\ ,\quad t_1>t_2 \tag{D3a}$$

or

$$\frac{d}{dt_2}U_I^\dagger(t_1,t_2)=U_I^\dagger(t_1,t_2)V_1^I(t_1,t_2) \tag{D3b}$$

with the initial condition $U_I(t_2,t_2)=1$.

Transforming the expressions for the collisional quantities of Appendix C to the time domain using Eq. (A1a) and the definition of the interaction-picture time-development operator in Eq. (D1a) we find

$$\begin{aligned}
\gamma_{fe}(\Delta_2)&=\sum_\mu \tfrac{1}{3}N\int d^3p_1d^3p_2\rho(p_2)\mathrm{Re}\Big[i[\Delta_2+\tfrac{1}{2}i(\gamma_e+\gamma_f)]\int_0^\infty d\tau\exp\{i[\Delta_2+\tfrac{1}{2}i(\gamma_e+\gamma_f)]\tau\}\\
&\qquad\times\langle\langle j_f0\mathbf{p}_1,j_e\mu\mathbf{p}_1\,|\,U_I(\tau,0)V_1^I(0,0)\,|\,j_f0\mathbf{p}_2,j_e\mu\mathbf{p}_2\rangle\rangle\Big]\ ,\\
\gamma_{fg}(\Delta_1+\Delta_2)&=N\int d^3p_1d^3p_2\rho(p_2)\mathrm{Re}\Big[i(\Delta_1+\Delta_2+\tfrac{1}{2}i\gamma_f)\int_0^\infty d\tau\exp[i(\Delta_1+\Delta_2+\tfrac{1}{2}i\gamma_f)\tau]\\
&\qquad\times\langle\langle j_f0\mathbf{p}_1,j_g0\mathbf{p}_1\,|\,U_I(\tau,0)V_1^I(0,0)\,|\,j_f0\mathbf{p}_2,j_g0\mathbf{p}_2\rangle\rangle\Big]\ ,\\
\gamma_{eg}(\Delta_1)&=\sum_\mu \tfrac{1}{3}N\int d^3p_1d^3p_2\rho(p_2)\mathrm{Re}\Big[i(\Delta_1+\tfrac{1}{2}i\gamma_e)\int_0^\infty d\tau\exp[i(\Delta_1+\tfrac{1}{2}i\gamma_e)\tau]\\
&\qquad\times\langle\langle j_e\mu\mathbf{p}_1,j_g0\mathbf{p}_1\,|\,U_I(\tau,0)V_1^I(0,0)\,|\,j_e\mu\mathbf{p}_2,j_g0\mathbf{p}_2\rangle\rangle\Big]\ ,
\end{aligned} \tag{D4}$$

$$\begin{aligned}
\gamma^K&=-\sum_{\substack{\mu_1,\mu_2,\mu_3,\mu_4,\\ Q}}(-1)^{\mu_2+\mu_4}\begin{bmatrix}1&1&K\\-\mu_1&\mu_2&Q\end{bmatrix}\begin{bmatrix}1&1&K\\-\mu_3&\mu_4&Q\end{bmatrix}\\
&\quad\times N\int d^3p_1d^3p_2\rho(p_2)\mathrm{Re}\Big[\int_0^\infty d\tau e^{-\gamma_e\tau}\langle\langle j_e\mu_1\mathbf{p}_1,j_e\mu_2\mathbf{p}_1\,|\,V_1^I(\tau,0)U_I(\tau,0)V_1^I(0,0)\,|\,j_e\mu_3\mathbf{p}_2,j_e\mu_4\mathbf{p}_2\rangle\rangle\Big]\ ,\\
C(fefg,z)&=\sum_\mu\tfrac{1}{3}N\int d^3p_1d^3p_2d^3p_3d^3p_4\rho(p_4)\\
&\quad\times\int_0^\infty d\tau_1\exp\{i[\Delta_2+z+\tfrac{1}{2}i(\gamma_e+\gamma_f)]\tau_1\}\langle\langle j_f0\mathbf{p}_1,j_e\mu\mathbf{p}_1\,|\,V_1^I(\tau_1,0)U_I(\tau_1,0)\,|\,j_f0\mathbf{p}_2,j_e\mu\mathbf{p}_3\rangle\rangle\\
&\quad\times\int_0^\infty d\tau_2\exp(i\{\Delta_1+\Delta_2+z+[E(\mathbf{p}_3)-E(\mathbf{p}_2)]/\hbar+\tfrac{1}{2}i\gamma_f\}\tau_2)\\
&\quad\times\langle\langle j_f0\mathbf{p}_2,j_g0\mathbf{p}_3\,|\,U_I(\tau_2,0)V_1^I(0,0)\,|\,j_f0\mathbf{p}_4,j_g0\mathbf{p}_4\rangle\rangle\ ,
\end{aligned} \tag{D5}$$

$$
\begin{aligned}
C(fgeg,z)=\sum_{\mu}\tfrac{1}{3}N\int d^3p_1 d^3p_2 d^3p_3 d^3p_4\rho(p_4)
&\times\int_0^\infty d\tau_1 \exp[i(\Delta_1+\Delta_2+z+\tfrac{1}{2}i\gamma_f)\tau_1]\langle\langle j_f0\mathbf{p}_1,j_g0\mathbf{p}_1\,|\,V_1^I(\tau_1,0)U_I(\tau_1,0)\,|\,j_f0\mathbf{p}_2,j_g0\mathbf{p}_3\rangle\rangle\\
&\times\int_0^\infty d\tau_2 \exp(i\{\Delta_1+z+[E(\mathbf{p}_3)-E(\mathbf{p}_2)]/\hbar+\tfrac{1}{2}i\gamma_e\}\tau_2)\\
&\times\langle\langle j_e\mu\mathbf{p}_2,j_f0\mathbf{p}_3\,|\,U_I(\tau_2,0)V_1^I(0,0)\,|\,j_e\mu\mathbf{p}_4,j_g0\mathbf{p}_4\rangle\rangle\ ,
\end{aligned}
$$

$$
\begin{aligned}
C(K,feee,z)=\sum_{\substack{\mu_1,\mu_2,\ldots,\mu_5,\\ Q}}(-1)^{\mu_1+\mu_3}\begin{bmatrix}1&1&K\\ \mu_3&-\mu_4&Q\end{bmatrix}\begin{bmatrix}1&1&K\\ \mu_1&-\mu_2&Q\end{bmatrix}
&\times N\int d^3p_1 d^3p_2 d^3p_3 d^3p_4\rho(p_4)\\
&\times\int_0^\infty d\tau_1 \exp\{i[\Delta_2+z+\tfrac{1}{2}i(\gamma_e+\gamma_f)]\tau_1\}\\
&\times\langle\langle j_f0\mathbf{p}_1,j_e\mu_2\mathbf{p}_1\,|\,V_1^I(\tau_1,0)U_I(\tau_1,0)\,|\,j_f0\mathbf{p}_2,j_e\mu_5\mathbf{p}_3\rangle\rangle\\
&\times\int_0^\infty d\tau_2 \exp(i\{z+[E(\mathbf{p}_3)-E(\mathbf{p}_2)]/\hbar+i\gamma_e\}\tau_2)\\
&\times\langle\langle j_e\mu_1\mathbf{p}_2,j_e\mu_5\mathbf{p}_3\,|\,U_I(\tau_2,0)V_1^I(0,0)\,|\,j_e\mu_3\mathbf{p}_4,j_e\mu_4\mathbf{p}_4\rangle\rangle\ ,
\end{aligned}
$$

$$
\begin{aligned}
C(K,eeeg,z)=\sum_{\substack{\mu_1,\mu_2,\ldots,\mu_5,\\ Q}}(-1)^{\mu_2+\mu_4}\begin{bmatrix}1&1&K\\ \mu_2&-\mu_1&Q\end{bmatrix}\begin{bmatrix}1&1&K\\ \mu_4&-\mu_3&Q\end{bmatrix}
&\times N\int d^3p_1 d^3p_2 d^3p_3 d^3p_4\rho(p_4)\\
&\times\int_0^\infty d\tau_1 \exp[i(z+i\gamma_e)\tau_1]\langle\langle j_e\mu_1\mathbf{p}_1,j_e\mu_2\mathbf{p}_1\,|\,V_1^I(\tau_1,0)U_I(\tau_1,0)\,|\,j_e\mu_5\mathbf{p}_2,j_e\mu_4\mathbf{p}_3\rangle\rangle\\
&\times\int_0^\infty d\tau_2 \exp(i\{\Delta_1+z+[E(\mathbf{p}_3)-E(\mathbf{p}_2)]/\hbar+\tfrac{1}{2}i\gamma_3\}\tau_2)\\
&\times\langle\langle j_e\mu_5\mathbf{p}_2,j_g0\mathbf{p}_3\,|\,U_I(\tau_2,0)V_1^I(0,0)\,|\,j_e\mu_3\mathbf{p}_4,j_g0\mathbf{p}_4\rangle\rangle\ ,
\end{aligned}
$$

$$
\begin{aligned}
D_1(K,feeg,z)=\sum_{\substack{\mu_1,\mu_2,\mu_3,\mu_4,\\ Q}}(-1)^{\mu_1+\mu_2}\begin{bmatrix}1&1&K\\ -\mu_1&\mu_4&Q\end{bmatrix}\begin{bmatrix}1&1&K\\ -\mu_2&\mu_3&Q\end{bmatrix}
&\times N\int d^3p_1\cdots d^3p_6\rho(p_6)\\
&\times\int_0^\infty d\tau_1 \exp\{i[\Delta_2+z+\tfrac{1}{2}i(\gamma_e+\gamma_f)]\tau_1\}\\
&\times\langle\langle j_f0\mathbf{p}_1,j_e\mu_2\mathbf{p}_1\,|\,V_1^I(\tau_1,0)U_I(\tau_1,0)\,|\,j_f0\mathbf{p}_2,j_e\mu_1\mathbf{p}_3\rangle\rangle\\
&\times\int_0^\infty d\tau_2 \exp(i\{\Delta_1+\Delta_2+z+[E(\mathbf{p}_3)-E(\mathbf{p}_2)]/\hbar+\tfrac{1}{2}i\gamma_f\}\tau_2)\\
&\times\langle\langle j_f0\mathbf{p}_2,j_g0\mathbf{p}_3\,|\,U_I(\tau_2,0)\,|\,j_f0\mathbf{p}_4,j_g0\mathbf{p}_5\rangle\rangle\\
&\times\int_0^\infty d\tau_3 \exp(i\{\Delta_1+z+[E(\mathbf{p}_5)-E(\mathbf{p}_4)]/\hbar+\tfrac{1}{2}i\gamma_e\}\tau_3)\\
&\times\langle\langle j_e\mu_3\mathbf{p}_4,j_g0\mathbf{p}_5\,|\,U_I(\tau_3,0)V_1^I(0,0)\,|\,j_e\mu_4\mathbf{p}_6,j_g0\mathbf{p}_6\rangle\rangle\ ,
\end{aligned}
\qquad \text{(D6)}
$$

$$D_2(K,feeg,z)=\sum_{\substack{\mu_1,\mu_2,\ldots,\mu_6,\\ Q}}(-1)^{\mu_1+\mu_2}\begin{bmatrix}1 & 1 & K\\ -\mu_1 & \mu_4 & Q\end{bmatrix}\begin{bmatrix}1 & 1 & K\\ -\mu_2 & \mu_3 & Q\end{bmatrix}$$

$$\times N\int d^3p_1\cdots d^3p_6\rho(p_6)$$

$$\times\int_0^\infty d\tau_1 \exp\{i[\Delta_2+z+\tfrac{1}{2}i(\gamma_e+\gamma_f)]\tau_1\}$$

$$\times\langle\langle j_f 0\mathbf{p}_1, j_e\mu_2\mathbf{p}_1 \,|\, V_1^I(\tau_1,0)U_I(\tau_1,0)\,|\, j_f 0\mathbf{p}_2, j_e\mu_5\mathbf{p}_3\rangle\rangle$$

$$\times\int_0^\infty d\tau_2 \exp(i\{z+[E(\mathbf{p}_3)-E(\mathbf{p}_2)]/\hbar+i\gamma_e\}\tau_2)$$

$$\times\langle\langle j_e\mu_3\mathbf{p}_2, j_e\mu_5\mathbf{p}_3 \,|\, U_I(\tau_2,0)\,|\, j_e\mu_6\mathbf{p}_4, j_e\mu_1\mathbf{p}_5\rangle\rangle$$

$$\times\int_0^\infty d\tau_3 \exp(i\{\Delta_1+z+[E(\mathbf{p}_5)-E(\mathbf{p}_4)]/\hbar+\tfrac{1}{2}i\gamma_e\}\tau_3)$$

$$\times\langle\langle j_e\mu_6\mathbf{p}_4, j_g 0\mathbf{p}_5 \,|\, U_I(\tau_3,0)V_1^I(0,0)\,|\, j_e\mu_4\mathbf{p}_6, j_g 0\mathbf{p}_6\rangle\rangle\ ,$$

$$D_3(K,fege,z)=\sum_{\substack{\mu_1,\mu_2,\ldots,\mu_6,\\ Q}}(-1)^{\mu_1+\mu_2}\begin{bmatrix}1 & 1 & K\\ -\mu_1 & \mu_4 & Q\end{bmatrix}\begin{bmatrix}1 & 1 & K\\ -\mu_2 & \mu_3 & Q\end{bmatrix}$$

$$\times N\int d^3p_1\cdots d^3p_6\rho(p_6)$$

$$\times\int_0^\infty d\tau_1 \exp\{i[\Delta_2+z+\tfrac{1}{2}i(\gamma_e+\gamma_f)]\tau_1\}$$

$$\times\langle\langle j_f 0\mathbf{p}_1, j_e\mu_2\mathbf{p}_1 \,|\, V_1^I(\tau_1,0)U_I(\tau_1,0)\,|\, j_f 0\mathbf{p}_2, j_e\mu_5\mathbf{p}_3\rangle\rangle$$

$$\times\int_0^\infty d\tau_2 \exp(i\{z+[E(\mathbf{p}_3)-E(\mathbf{p}_2)]/\hbar+i\gamma_e\}\tau_2)$$

$$\times\langle\langle j_e\mu_3\mathbf{p}_2, j_e\mu_5\mathbf{p}_3 \,|\, U_I(\tau_2,0)\,|\, j_e\mu_4\mathbf{p}_5, j_e\mu_6\mathbf{p}_4\rangle\rangle$$

$$\times\int_0^\infty d\tau_3 \exp(i\{-\Delta_1+z+[E(\mathbf{p}_4)-E(\mathbf{p}_5)]/\hbar+\tfrac{1}{2}i\gamma_e\}\tau_3)$$

$$\times\langle\langle j_g 0\mathbf{p}_5, j_e\mu_6\mathbf{p}_4 \,|\, U_I(\tau_3,0)V_1^I(0,0)\,|\, j_g 0\mathbf{p}_6, j_e\mu_1\mathbf{p}_6\rangle\rangle\ ,$$

with $E(\mathbf{p})=\mathbf{p}^2/2M$. In Eqs. (D4) we also performed a partial integration using the equation of motion Eq. (D3a). For γ^K we used formula (B8) of Ref. 7. These forms of the collisional quantities are very convenient for the transition to the classical path approximation and for estimates on their orders of magnitude.

A rough estimate of the second-order collisional quantities in the case where one time of interest is long (compared with the duration of a collision) may be obtained in the following way:[7] Let us consider the equation for $D_2(K,feeg,z)$. For an upper bound we may set $\tau_2=0$ in the integrand [i.e., $U_I(\tau_2=0,0)=1$] and perform the integration over τ_2, which gives rise to a factor $\min\{\tau_c,1/|z|\}$ (for $\gamma_e\tau_c \ll 1$) as τ_2 cannot exceed τ_c without making the integrand vanishingly small. If one time of interest is large (e.g., $|z+\Delta_2|\tau_c \ll 1$) we next perform the integration over τ_1 using the equation of motion for the time-development operator [Eq. (D3a)]. This gives us a factor $[U_I(\infty,0)-1]$, whose maximum modulus is 2. The remaining integral can be estimated by $\max\{\gamma_{eg}(0),\gamma_{eg}(z+\Delta_1)\}/|z+\Delta_1+(i\gamma_e/2)|$. With the help of these procedures, we find the following estimates:

$$|D_2(K,feeg,z)| \to 2\min\{\tau_c,1/|z|\}\times\begin{cases}\dfrac{\max\{\gamma_{eg}(z+\Delta_1),\gamma_{eg}(0)\}}{|z+\Delta_1+\frac{1}{2}i\gamma_e|} & \text{if } |z+\Delta_2|\tau_c \ll 1\\[2ex] \dfrac{\max\{\gamma_{fe}(z+\Delta_2),\gamma_{fe}(0)\}}{|z+\Delta_2+\frac{1}{2}i(\gamma_e+\gamma_f)|} & \text{if } |z+\Delta_1|\tau_c \ll 1\,,\end{cases}$$

$$|D_3(K,fege,z)| \to 2\min\{\tau_c,1/|z|\}\times\begin{cases}\dfrac{\max\{\gamma_{ge}(z-\Delta_1),\gamma_{ge}(0)\}}{|z-\Delta_1+\frac{1}{2}i\gamma_e|} & \text{if } |z+\Delta_2|\tau_c \ll 1\\[2ex] \dfrac{\max\{\gamma_{fe}(z+\Delta_2),\gamma_{fe}(0)\}}{|z+\Delta_2+\frac{1}{2}i(\gamma_e+\gamma_f)} & \text{if } |z-\Delta_1|\tau_c \ll 1\,,\end{cases} \tag{D7}$$

$$|D_1(K,feeg,z)| \to 2\min\{\tau_c,1/|z+\Delta_1+\Delta_2|\}\times\begin{cases}\dfrac{\max\{\gamma_{eg}(z+\Delta_1),\gamma_{eg}(0)\}}{|z+\Delta_1+\frac{1}{2}i\gamma_e|} & \text{if } |z+\Delta_2|\tau_c \ll 1\\[2ex] \dfrac{\max\{\gamma_{fe}(z+\Delta_2),\gamma_{fe}(0)\}}{|z+\Delta_2+\frac{1}{2}i(\gamma_e+\gamma_f)|} & \text{if } |z+\Delta_1|\tau_c \ll 1\,.\end{cases}$$

A crude upper bound for $D_2(K,feeg,z)$ and $D_3(K,fege,z)$ in the cases where $|\Delta_1+z|$ and $|\Delta_2+z|$ are both large in comparison with $1/\tau_c$ may thus be obtained by setting $\tau_1=0$ everywhere in the integrand and setting $U_I(\tau_2,0)=1$. The upper-bound estimates obtained in this way are

$$\left.\begin{matrix}|D_2(K,feeg,z)|\\ |D_3(K,fege,z)|\end{matrix}\right\} \to \max\{\gamma_{eg}(\Delta_1+z),\gamma_{eg}(0)\}\tau_c^2\,. \tag{D8a}$$

An upper-bound estimate for $D_1(K,feeg,z)$ is given by

$$|D_1(K,feeg,z) \to \max\{\gamma_{eg}(\Delta_1+z),\gamma_{eg}(0)\}\tau_c^2\,. \tag{D8b}$$

Thereby we estimated the whole integral over τ_2 by τ_c.

Similarly we find for $\gamma_e\tau_c \ll 1$

$$|C(fgeg,z)| \to \max\{\gamma_{eg}(\Delta_1+z),\gamma_{eg}(0)\}\times\begin{cases}\dfrac{1}{|\Delta_1+\Delta_2+z|} & \text{if } |\Delta_1+\Delta_2+z|\tau_c \gg 1 \text{ and antistatic}\\[2ex] \tau_c & \text{otherwise}\,,\end{cases}$$

$$|C(fefg,z)| \to \max\{\gamma_{fe}(\Delta_2+z),\gamma_{fe}(0)\}\times\begin{cases}\dfrac{1}{|\Delta_1+\Delta_2+z|} & \text{if } |\Delta_1+\Delta_2+z|\tau_c \gg 1 \text{ and antistatic}\\[2ex] \tau_c & \text{otherwise}\,.\end{cases} \tag{D9}$$

Note, antistatic means that there is no quasistatic (Franck-Condon) transition. Quantities like $\Gamma_{eg}^K(\Delta_1)$ or $\Gamma_{fe}^K(\Delta_2)$ of Eqs. (21) and (23) are of the order of $\max\{\gamma_{eg}(\Delta_1),\gamma^K\}$ or $\max\{\gamma_{fe}(\Delta_2),\gamma^K\}$ as has been shown by Cooper.[9]

APPENDIX E: CLASSICAL PATH APPROXIMATION AND QUASISTATIC EXPRESSIONS FOR COLLISION QUANTITIES

Following the arguments of Smith *et al.*[21] we can immediately write down the collisional quantities of Appendix D in a classical path approximation. For the second-order quantities we find

$$D_1(K,feeg,z)=\sum_{\substack{\mu_1,\mu_2,\mu_3,\mu_4,\\ Q}}(-1)^{\mu_1+\mu_2}\begin{bmatrix}1 & 1 & K\\ -\mu_1 & \mu_4 & Q\end{bmatrix}\begin{bmatrix}1 & 1 & K\\ -\mu_2 & \mu_3 & Q\end{bmatrix}N/V$$
$$\times 4\pi\int_0^\infty dv\, v^2 f(v) 2\pi\int_0^\infty db\, bv\int_{-\infty}^{\infty}dt_0\int_0^\infty d\tau_1\int_0^\infty d\tau_2\int_0^\infty d\tau_3$$
$$\times\exp\{i[z+\Delta_2+\tfrac{1}{2}i(\gamma_e+\gamma_f)]\tau_3\}\exp[i(z+\Delta_1+\Delta_2+\tfrac{1}{2}i\gamma_f)\tau_2]\exp[i(z+\Delta_1+\tfrac{1}{2}i\gamma_e)\tau_1]$$
$$\times\langle\langle j_f0,j_e\mu_2\,|\,V_1^{(k)}(\tau_3+\tau_2+\tau_1)U^{(k)}(\tau_3+\tau_2+\tau_1,\tau_2+\tau_1)\,|\,j_f0,j_e\mu_1\rangle\rangle$$
$$\times\langle\langle j_f0,j_g0\,|\,U^{(k)}(\tau_2+\tau_1,\tau_1)\,|\,j_f0,j_g0\rangle\rangle\langle\langle j_e\mu_3,j_g0\,|\,U^{(k)}(\tau_1,0)V_1^{(k)}(0)\,|\,j_e\mu_4,j_g0\rangle\rangle\ ,$$

$$D_2(K,feeg,z)=\sum_{\substack{\mu_1,\mu_2,\ldots,\mu_6,\\ Q}}(-1)^{\mu_1+\mu_2}\begin{bmatrix}1 & 1 & K\\ -\mu_1 & \mu_4 & Q\end{bmatrix}\begin{bmatrix}1 & 1 & K\\ -\mu_2 & \mu_3 & Q\end{bmatrix}N/V$$
$$\times 4\pi\int_0^\infty dv\, v^2 f(v) 2\pi\int_0^\infty db\, bv\int_{-\infty}^{\infty}dt_0\int_0^\infty d\tau_1\int_0^\infty dt_2\int_0^\infty d\tau_3$$
$$\times\exp\{i[z+\Delta_2+\tfrac{1}{2}i(\gamma_e+\gamma_f)]\tau_3\}\exp[i(z+i\gamma_e)\tau_2]\exp[i(z+\Delta_1+\tfrac{1}{2}i\gamma_e)\tau_1]$$
$$\times\langle\langle j_f0,j_e\mu_2\,|\,V_1^{(k)}(\tau_3+\tau_2+\tau_1)U^{(k)}(\tau_3+\tau_2+\tau_1,\tau_2+\tau_1)\,|\,j_f0,j_e\mu_5\rangle\rangle$$
$$\times\langle\langle j_e\mu_3,j_e\mu_5\,|\,U^{(k)}(\tau_2+\tau_1,\tau_1)\,|\,j_e\mu_6,j_e\mu_1\rangle\rangle\langle\langle j_e\mu_6,j_g0\,|\,U^{(k)}(\tau_1,0)V_1^{(k)}(0)\,|\,j_e\mu_4,j_g0\rangle\rangle\ ,$$

$$D_3(K,fege,z)=\sum_{\substack{\mu_1,\mu_2,\ldots,\mu_6,\\ Q}}(-1)^{\mu_1+\mu_2}\begin{bmatrix}1 & 1 & K\\ -\mu_1 & \mu_4 & Q\end{bmatrix}\begin{bmatrix}1 & 1 & K\\ -\mu_2 & \mu_3 & Q\end{bmatrix}N/V$$
$$\times 4\pi\int_0^\infty dv\, v^2 f(v) 2\pi\int_0^\infty db\, bv\int_{-\infty}^{\infty}dt_0\int_0^\infty d\tau_1\int_0^\infty d\tau_2\int_0^\infty d\tau_3$$
$$\times\exp\{i[z+\Delta_2+\tfrac{1}{2}i(\gamma_e+\gamma_f)]\tau_3\}\exp[i(z+i\gamma_e)\tau_2]\exp[i(z-\Delta_1+\tfrac{1}{2}i\gamma_e)\tau_1]$$
$$\times\langle\langle j_f0,j_e\mu_2\,|\,V_1^{(k)}(\tau_3+\tau_2+\tau_1)U^{(k)}(\tau_3+\tau_2+\tau_1,\tau_2+\tau_1)\,|\,j_f0,j_e\mu_5\rangle\rangle$$
$$\times\langle\langle j_e\mu_3,j_e\mu_5\,|\,U^{(k)}(\tau_2+\tau_1,\tau_1)\,|\,j_e\mu_4,j_e\mu_6\rangle\rangle\langle\langle j_g0,j_e\mu_6\,|\,U^{(k)}(\tau_1,0)V_1^{(k)}(0)\,|\,j_g0,j_e\mu_1\rangle\rangle\ , \qquad \text{(E1)}$$

with the perturber density N/V. In an analogous way, one can easily obtain the classical path expressions for the other collisional quantities of Appendix D.

The classical path tetradic time-development operator is given by

$$U^{(k)}(t_1,t_2)=\bar{U}^{(k)}(t_1,t_2)\bar{U}^{(k)}(t_1,t_2)^* \tag{E2a}$$

in the sense that

$$\langle\langle 12 \mid U^{(k)}(t_1,t_2) \mid 34 \rangle\rangle = \langle 1 \mid \bar{U}^{(k)}(t_1,t_2) \mid 3 \rangle \langle 2 \mid \bar{U}^{(k)}(t_1,t_2) \mid 4 \rangle^*$$

with

$$i\hbar \frac{d}{dt_1}\bar{U}^{(k)}(t_1,t_2)=V^{(k)}(t_1)\bar{U}^{(k)}(t_1,t_2)\ , \quad t_1 \geq t_2 \tag{E2b}$$

and the initial condition $\bar{U}^{(k)}(t_2,t_2)=1$. $V_1^{(k)}(t)\cdots=1/i\hbar[V^{(k)}(t),\ldots]$ is the tetradic interaction operator. (k) indicates the dependence of the time-development operator and the potential on the parameters characterizing the initial state of the wave packet, which describes the perturber motion, i.e., $(k)\equiv\{b,v,t_0\}$ (see Fig. 4). In the case of a spherical symmetric potential between radiator and perturber, which we are for simplicity considering in this section, we have

$$V^{(k)}(t_1)\equiv\exp\left[-\frac{1}{i\hbar}H_R(t_1-t_2)\right]V(R(t_1)) \times\exp\left[\frac{1}{i\hbar}H_R(t_1-t_2)\right] \tag{E2c}$$

with

$$R^2(t_1)=b^2+[v(t_1+t_0)]^2\ ,$$

which describes the straight-line trajectory of the perturber. $V(R)$ in Eq. (E2c) is the interatomic potential at the internuclear distance R and is an operator acting within the electronic states of the radiator-perturber system.

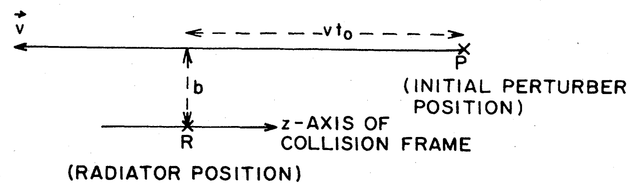

FIG. 4. Straight-line trajectory of a perturber (P) passing a radiator atom (R) showing the definition of impact parameter b and time of closest approach t_0.

The phase factors in Eq. (E2c) are unimportant in the case of elastic collisions we are considering in this paper. $\mathbf{v}$ is the velocity of the perturber with $v=|\mathbf{v}|$ and $f(v)$ the velocity distribution $[4\pi\int_0^\infty dv\, v^2 f(v)=1]$, b is the impact parameter. The straight-line trajectory assumption is certainly valid as long as $|V(R)| \ll (M/2)v^2$.[21] For short times of interest (large detunings Δ), where the collisional quantities are dominantly determined by contributions from stationary phase points $[\hbar\Delta=V(R)]$, this implies for a thermal distribution of the perturber $\hbar|\Delta| \ll kT$. As long as we are restricting ourselves to the near wings (i.e., all detunings $\ll kT/\hbar$), the above straight-line trajectory classical path expressions for the collisional quantities are good approximations. For even larger detunings, we have to go back to our original quantum-mechanical expressions of Appendix C and calculate these quantities with more sophisticated methods.[4]

Before we approximately evaluate the second-order collisional quantities in the quasistatic limit, let us first of all discuss the basic concepts involved by considering for simplicity a collisional dephasing rate, e.g., $\gamma_{eg}(\Delta_1)$. Its classical path expression in the no-ground-state interaction approximation is given by

$$\gamma_{eg}(\Delta_1)=\sum_\mu \frac{1}{3}\frac{N}{V}4\pi\int_0^\infty dv\, v^2 f(v) 2\pi \times\int_0^\infty db\, bv \int_{-\infty}^{\infty} dt_0 \mathrm{Re}\left[(\Delta_1+\tfrac{1}{2}i\gamma_e)\frac{1}{\hbar}\int_0^\infty d\tau \exp[i(\Delta_1+\tfrac{1}{2}i\gamma_e)\tau] \times\langle j_e\mu \mid \bar{U}^{(k)}(\tau,0)V^{(k)}(0) \mid j_e\mu\rangle\right]. \tag{E3}$$

The time-development operator is a solution of Eq. (E2b) with the interatomic potential operator $V^{(k)}(\tau)$ acting within the excited-state manifold $\{|e_i\rangle\}$ (within our approximation of neglecting inelastic collisions). For small interatomic separations R, this potential is approximately diagonalized by a Hund's case-(a) (Ref. 22) basis of electronic states. These states have total angular momentum $J=1$ (because our perturber is in an internal $J=0$ state) and a well-defined projection Λ in the direction defined by the positions of radiator and perturber. Figure 5 shows schematically typical diagonal matrix elements of the internuclear potential $V(R)$ in this basis. These potential curves only depend on $|\Lambda|$.[22]

On the other hand, for large internuclear separations, the radiator states with a well-defined space-fixed projection μ of the total angular momentum approximately diagonalize $V(R)$ [Hund's case (e), Ref. 22]. The time-development operator may in general be written as a time-ordered exponential, i.e.,

$$\bar{U}^{(k)}(\tau,0)=\mathscr{T}\exp\left[-\frac{i}{\hbar}\int_0^\tau dt\, V^{(k)}(t)\right]. \tag{E4}$$

As long as an adiabatic approximation is justified [i.e., $\bar{U}^{(k)}(\tau,0)$ is approximately diagonal in a particular basis] the time-ordering operator $\mathscr{T}$ is unimportant but becomes

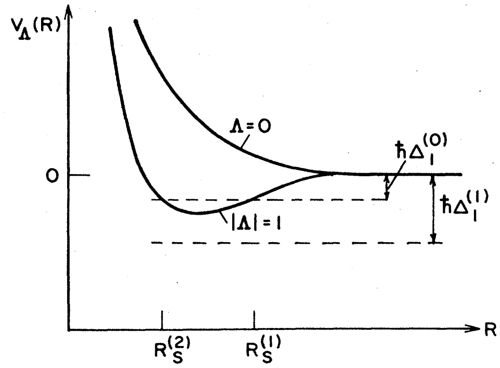

FIG. 5. Qualitative sketch of $V_\Lambda(R)=\langle j_e\Lambda \mid V(R) \mid j_e\Lambda\rangle$ as a function of the internuclear separation for Ba—rare-gas systems as given by Ref. 1. $\hbar\Delta_1^{(0)}$ is a quasistatic detuning with the two stationary phase points $R_S^{(1)}$, $R_S^{(2)}$, where the laser photon $(\omega_1,\mathbf{e}_1)$ is absorbed. $\hbar\Delta_1^{(1)}$ is an antistatic detuning, where no stationary phase point exists.

important as soon as such an adiabatic approximation breaks down.[23] For large detunings, the main contribution to $\gamma_{eg}(\Delta_1)$ will come from times τ with an associated phase which is stationary. Times larger than the time of interest τ_I about the stationary phase point (which is associated with a phase of order unity) give rise to large phase changes which should average to zero due to the integration over impact parameters b. Therefore, as long as the time of interest τ_I is small in comparison with the collision time τ_c (which is the characteristic time scale of the variation of the potential), i.e.,

$$\tau_I=\max\left\{\frac{1}{|\Delta_1|}\;,\;\left|\frac{1}{\hbar}\frac{dV^{(k=k_S)}(\tau)}{d\tau}\right|_{\tau=0}^{-1/2}\right\}\ll\tau_c\;, \tag{E5}$$

we may use the stationary phase approximation to approximately write

$$V^{(k)}(\tau)\rightarrow V^{(k)}(0) \tag{E6a}$$

and

$$\exp\left[i\int_0^\tau dt[\Delta_1-\hbar^{-1}V^{(k)}(t)]\right]\rightarrow\exp\{i[\Delta_1-\hbar^{-1}V^{(k)}(0)]\tau\}\;. \tag{E6b}$$

k_S indicates the particular set of parameters k such that the interatomic potential can match the detuning (stationary phase point)

$$\hbar\Delta_1=V^{(k=k_S)}(0)\;.$$

If the potential is monotonic, we have

$$\left|\frac{1}{\hbar}\frac{dV^{(k=k_S)}(\tau)}{d\tau}\right|_{\tau=0}\approx\frac{|\Delta_1|}{\tau_c}$$

and Eq. (E5) is roughly equivalent to

$$|\Delta_1|\tau_c\gg1\;. \tag{E7}$$

For the collisional dephasing rate we obtain in this stationary phase approximation together with $|\Delta_1|\gg\gamma_e$ the expression

$$\gamma_{eg}(\Delta_1)=\sum_\mu\frac{1}{3}\frac{N}{V}4\pi\int_0^\infty dv\,v^2f(v)2\pi\times\int_0^\infty db\,bv\int_{-\infty}^{\infty}dt_0\mathrm{Re}\left[\Delta_1\frac{1}{\hbar}\left\langle j_e\mu\right|\left[\pi\delta(\Delta_1-\hbar^{-1}V^{(k)}(0))+i\frac{\mathrm{P}}{\Delta_1-\hbar^{-1}V^{(k)}(0)}\right]V^{(k)}(0)\left|j_e\mu\right\rangle\right]\;. \tag{E8}$$

Thereby we used the identity

$$\int_0^\infty d\tau\exp\{i[\Delta_1-\hbar^{-1}V^{(k)}(0)]\tau\}=i\frac{\mathrm{P}}{\Delta_1-\hbar^{-1}V^{(k)}(0)}+\pi\delta(\Delta_1-\hbar^{-1}V^{(k)}(0))\;, \tag{E9}$$

where P indicates the Cauchy principal value.

Only the δ function contributes to the real part in Eq. (E8). There are two values of t_0, namely $t_0=\pm[(R_S^{(j)2}-b^2)^{1/2}/v]$ with $\hbar\Delta_1=V(R_S^{(j)})$, where the interatomic potential matches the detuning Δ_1. If in the region around $R_s^{(j)}$ the interatomic potential is approximately diagonalized by the Hund's case-(a) electronic states $|j_e\Lambda\rangle$ we find for the collisional dephasing rate

$$\gamma_{eg}(\Delta_1)=\frac{N}{V}\Delta_1^2\frac{2}{3}\pi^2\sum_j\frac{R_s^{(j)}}{\hbar^{-1}\left|\frac{dV_\Lambda(R)}{dR}\right|_{R=R_S^{(j)}}}2R_s^{(j)}\;, \tag{E10}$$

with $V_\Lambda(R)=\langle j_e\Lambda \mid V(R) \mid j_e\Lambda\rangle$. $|j_e\Lambda\rangle$ is the electronic state, which leads to a stationary phase point. Thereby we used the relation

$$\delta(f(x))=\sum_j\left|\frac{df}{dx}\right|_{x=x_j}^{-1}\delta(x-x_j)\;, \tag{E11}$$

where j indicates all zeros of $f(x)$, i.e., $f(x_j)=0$. Obviously, this relation is only valid as long as $|df/dx|_{x=x_j}\neq0$.

This expression is immediately recognized as the standard quasistatic result for the linewidth and explicitly shows that $\gamma_{eg}(\Delta_1)$ measures directly the derivative of the potential at a certain internuclear separation $R_S^{(j)}$, where the absorption occurs. It should be mentioned that in a case where

$$\left|\frac{1}{\hbar}\frac{dV^{(k=k_S)}(\tau)}{d\tau}\right|_{\tau=0}^{-1/2}\gtrsim\tau_c$$

(i.e., the two stationary phase points of Fig. 5 are very close) and Eq. (E5) is violated, the above quasistatic picture is still applicable as long as

$$\tau_I = \max\left\{ \frac{1}{|\Delta_1|}, \left| \frac{1}{\hbar} \frac{d^2 V^{(k=k_S)}(\tau)}{d\tau^2} \right|_{\tau=0}^{-1/3} \right\} \ll \tau_c . \tag{E12}$$

But in this case, the time-ordered exponential has to be evaluated asymptotically with the help of a transitional Airy approximation[24] giving rise to an oscillatory dependence of the collisional quantity on the detuning Δ_1, which is due to interference between the two stationary phase points. We also see that in the case of an antistatic detuning Δ_1 (i.e., no stationary phase point $R_S^{(j)}$ exists) $\gamma_{eg}(\Delta_1)$ becomes negligibly small (and in our asymptotic evaluation it is even zero).

Let us now consider the second-order collisional quantity $[\mathrm{Re}D_2(K,feeg,z=0)-\mathrm{Re}D_3(K,fege,z=0)]$ in the quasistatic limit, where $|\Delta_1|\tau_c \gg 1$ and $|\Delta_2|\tau_c \gg 1$ and stationary phase points exist for both transitions, i.e., $|g\rangle \rightarrow \{|e_i\rangle\}$ and $\{|e_i\rangle\} \rightarrow |f\rangle$. As we are here only interested in an order of magnitude estimate, we shall evaluate this quantity only under the assumption of a nondegenerate intermediate state $|j_e\rangle$. This simplifies our discussion and illustrates the basic physics, which this collisional quantity represents. The extension to the nondegenerate case is straightforward, but very tedious, since it requires the modulus squared of sums of products. As the times of interest for τ_1 and τ_3 are short in comparison with the collision time τ_c we may approximately write

$$\begin{aligned} &V_1^{(k)}(\tau_3+\tau_2) \rightarrow V_1^{(k)}(\tau_2) , \\ &V_1^{(k)}(-\tau_1) \rightarrow V_1^{(k)}(0) , \\ &U^{(k)}(0,-\tau_1) \rightarrow \exp[V_1^{(k)}(0)\tau_1] , \\ &U^{(k)}(\tau_3+\tau_2,\tau_2) \rightarrow \exp[V_1^{(k)}(\tau_2)\tau_3] . \end{aligned} \tag{E13a}$$

As $|j_e\rangle$ is nondegenerate, we also have

$$U^{(k)}(\tau_2,0)=1 . \tag{E13b}$$

Under these conditions, we find

$$\begin{aligned} \mathrm{Re}D_2(feeg,z=0)-\mathrm{Re}D_3(fege,z=0) = \frac{N}{V} 4\pi \int_0^\infty dv\, v^2 f(v) 2\pi \int_0^\infty db\, bv \int_{-\infty}^{\infty} dt_0 \\ \times 2\int_0^\infty d\tau_2 \langle\langle j_f,j_e | V_1^{(k)}(\tau_2)\pi\delta(\Delta_2 - iV_1^{(k)}(\tau_2)) | j_f,j_e \rangle\rangle \\ \times \langle\langle j_e,j_g | \pi\delta(\Delta_1 - iV_i^{(k)}(0)) V_1^{(k)}(0) | j_e,j_g \rangle\rangle . \end{aligned} \tag{E14}$$

Thereby, we used relation (E9) and the fact that the Cauchy principal part contributions cancel each other. From this expression we see that this collisional quantity describes a process, where the laser photon $(\omega_1,\mathbf{e}_1)$ is absorbed at the internuclear distance R_{S_1} and the excited radiator-perturber collision complex subsequently *evolves* to the internuclear distance R_{S_2}, where the second laser photon $(\omega_2,\mathbf{e}_2)$ is absorbed. In the case where the stationary phase points of the τ_2 integration are located well inside the integration interval, which is the case as long as R_{S_1} and R_{S_2} are not too close, we can evaluate Eq. (E14) easily and obtain

$$\frac{2\,\mathrm{Re}D_2 - 2\,\mathrm{Re}D_3}{\Delta_1\Delta_2} = -\frac{N}{V}\left[4\pi\int_0^\infty dv\, v^2 f(v)\frac{1}{v}\right](2\pi)^3 \frac{1}{\frac{1}{\hbar}\left|\frac{dV_{fe}(R)}{dR}\right|_{R=R_{S_2}} \frac{1}{\hbar}\left|\frac{dV_{eg}(R)}{dR}\right|_{R=R_{S_1}}} 2R_<^2 f(R_{S_2}/R_{S_1}) \tag{E15a}$$

with

$$\begin{aligned} &V_{fe}(R) = \langle f | V(R) | f\rangle - \langle e | V(R) | e\rangle , \\ &V_{eg}(R) = \langle e | V(R) | e\rangle - \langle g | V(R) | g\rangle , \\ &\hbar\Delta_1 = V_{eg}(R_{S_1}) , \\ &\hbar\Delta_2 = V_{fe}(R_{S_2}) , \\ &R_< = \min\{R_{S_1},R_{S_2}\} \end{aligned} \tag{E15b}$$

and

$$f(R_{S_1}/R_{S_2})=\frac{R_{S_1}R_{S_2}}{R_<^2}\ln\left[\frac{R_{S_1}+R_{S_2}}{(R_{S_1}^2-R_<^2)^{1/2}+(R_{S_2}^2-R_<^2)^{1/2}}\right]\rightarrow 1 \text{ as } R_{S_1}/R_{S_2}\rightarrow\infty \text{ or as } R_{S_1}/R_{S_2}\rightarrow 0 .$$

Thereby we have assumed that only one value of R_{S_1} and one value of R_{S_2} exist which fulfill Eq. (E15b). Numerically, it turns out that even if R_{S_2} and R_{S_1} are not much different from each other $f(R_{S_1}/R_{S_2})\rightarrow 1$ is a good approximation. Equation (E15a) explicitly shows how the derivatives of the difference potentials at the points of absorption R_{S_1} and R_{S_2} determine the second-order collisional quantity.[25]

In order to compare the contribution (E15a) to the redistributed intensity with contributions from lower-order collisional quantities, let us evaluate Eq. (15a) for the simple case of difference potentials of the form

$$V_{fe}(R)=\frac{C_2}{R^{n_2}}$$

and

$$V_{eg}(R)=\frac{C_1}{R^{n_1}}$$

and a well-defined velocity of perturbers v_0 [i.e., $f(v)=(1/4\pi v^2)\delta(v-v_0)$]. We define collision times $\tau_c^{(i)}=R_{W_i}/v_0$ and Weisskopf radii R_{W_i} by

$$\frac{|C_i/\hbar|}{R_{W_i}^{n_i}}\frac{R_{W_i}}{v_0}=1\ ,\quad i=1,2\ .$$

In terms of these parameters, we find in the quasistatic limit with $f(R_{S_1}/R_{S_2})=1$ the relations

$$-\frac{2\,\mathrm{Re}D_2-2\,\mathrm{Re}D_3}{\Delta_1\Delta_2}=\begin{cases}\left|\dfrac{\gamma_{eg}(\Delta_1)}{\Delta_1^2\Delta_2(\Delta_1+\Delta_2)}\right|\left[\dfrac{12\pi}{n_2}\left|1+\dfrac{\Delta_1}{\Delta_2}\right|(|\Delta_2|\tau_c^{(2)})^{(n_2-1)/n_2}\right] & \text{if } R_{S_1}\ll R_{S_2}\\[2ex] \left|\dfrac{\gamma_{fe}(\Delta_2)}{\Delta_1\Delta_2^2(\Delta_1+\Delta_2)}\right|\left[\dfrac{12\pi}{n_1}\left|1+\dfrac{\Delta_2}{\Delta_1}\right|(|\Delta_1|\tau_c^{(1)})^{(n_1-1)/n_1}\right] & \text{if } R_{S_1}\gg R_{S_2}\ .\end{cases} \tag{E16}$$

The first factor is the contribution of a zero-order collisional quantity to the redistributed intensity. Equation (E16) and estimate (D9) together with the discussion at the end of Appendix G show that for an antistatic detuning of $\Delta_1+\Delta_2$ with $|\Delta_1+\Delta_2|\tau_c\gg 1$ the molecular "two-step" process represented by the expression of Eqs. (27) and (E15a) gives the dominant contribution to the redistributed intensity provided all detunings are large, i.e., $|\Delta\tau_c|^{-5/6}\ll 1$ for a van der Waals potential.

APPENDIX F: ANTISTATIC BEHAVIOR OF COLLISIONAL QUANTITIES

In the antistatic limit the detunings of the laser frequencies from their atomic transition frequencies Δ are such that $|\Delta|\tau_c\gg 1$ and *no* stationary phase point exists at any internuclear separation. In the zero-order collisional quantities, which depend only one particular detuning Δ, the situation is quite simple. As soon as this detuning becomes antistatic, the corresponding collisional quantity goes to zero as may be seen from the discussion of $\gamma_{eg}(\Delta_1)$ in Appendix E. The determination of the antistatic behavior of the first- and second-order collisional quantities, which depend on more than one detuning, is not so straightforward in general, as mixed cases may exist with one detuning antistatic and the others not. In the following, we shall restrict our discussion only to the cases where all detunings determining a collisional quantity are antistatic.

Let us first of all consider the collisional quantity $C(K,feee,z=0)$ of Eq. (D5). If the detuning Δ_2 is antistatic and large ($|\Delta_2|\tau_c\gg 1$) we can approximately write

$$V_1^I(\tau_1,0)\rightarrow V_1^I(0,0)\ , \tag{F1a}$$

$$U_1(\tau_1,0)\rightarrow U_I(0,0)=1\ . \tag{F1b}$$

The first approximation is due to the fact that the time of interest in the τ_1 integral $\tau_I=1/|\Delta_2|$ is much smaller than the collision time τ_c. The second simplification assumes that only weak collisions with $|V_1^I(\tau_1,0)|<1/\tau_c\ll 1/|\Delta_2|$ significantly contribute to $C(K,feee,z=0)$. As no strong collision can match the detuning Δ_2, because we are antistatically detuned, the contributions of strong collisions should average to zero (due to the integration over impact parameters in a classical path approximation and noting that the phase is a strong function of impact parameter. Using the approximations of Eqs. (F1a) and (F1b) we find

$$2i\,\mathrm{Im}C(K,feee,z=0)$$

$$=\sum_{\substack{\mu_1,\mu_2,\ldots,\mu_5,\\ Q}}(-1)^{\mu_1+\mu_3}\begin{bmatrix}1 & 1 & K\\ \mu_3 & -\mu_4 & Q\end{bmatrix}\begin{bmatrix}1 & 1 & K\\ \mu_1 & -\mu_2 & Q\end{bmatrix}N$$

$$\times\int d^3p_1d^3p_2d^3p_3d^3p_4\rho(p_4)$$

$$\times\left[\frac{i}{\Delta_2}\frac{1}{i\hbar}[\langle j_f0\mathbf{p}_1\,|\,V^I(0,0)\,|\,j_f0\mathbf{p}_2\rangle\langle j_e\mu_2\mathbf{p}_1\,|\,j_e\mu_5\mathbf{p}_3\rangle-\langle\mathbf{p}_1\,|\,\mathbf{p}_2\rangle\langle j_e\mu_2\mathbf{p}_1\,|\,V^I(0,0)\,|\,j_e\mu_5\mathbf{p}_3\rangle^*]\right.$$

$$\times\int_0^\infty d\tau_2 e^{i[E(\mathbf{p}_3)-E(\mathbf{p}_2)+i\gamma_e]\tau_2}\langle\!\langle j_e\mu_1\mathbf{p}_2,j_e\mu_5\mathbf{p}_3\,|\,U_I(\tau_2,0)V_1^I(0,0)\,|\,j_e\mu_3\mathbf{p}_4,j_e\mu_4\mathbf{p}_4\rangle\!\rangle$$

$$-\frac{i}{\Delta_2}\frac{1}{i\hbar}[\langle j_f0\mathbf{p}_1\,|\,V^I(0,0)\,|\,j_f0\mathbf{p}_2\rangle^*\langle j_e\mu_2\mathbf{p}_1\,|\,j_e\mu_5\mathbf{p}_3\rangle-\langle\mathbf{p}_1\,|\,\mathbf{p}_2\rangle\langle j_e\mu_2\mathbf{p}_1\,|\,V^I(0,0)\,|\,j_e\mu_5\mathbf{p}_3\rangle]$$

$$\left.\times\int_0^\infty d\tau_2 e^{i[-E(\mathbf{p}_3)+E(\mathbf{p}_2)+i\gamma_e]\tau_2}\langle\!\langle j_e\mu_5\mathbf{p}_3,j_e\mu_1\mathbf{p}_2\,|\,U_I(\tau_2,0)V_1^I(0,0)\,|\,j_e\mu_4\mathbf{p}_4,j_e\mu_3\mathbf{p}_4\rangle\!\rangle\right]$$

$$=\sum_{\substack{\mu_1,\mu_2,\mu_3,\mu_4,\\ Q}}(-1)^{\mu_1+\mu_3}\begin{bmatrix}1 & 1 & K\\ \mu_3 & -\mu_4 & Q\end{bmatrix}\begin{bmatrix}1 & 1 & K\\ \mu_1 & -\mu_2 & Q\end{bmatrix}$$

$$\times N\int d^3p_1d^3p_2\rho(p_2)\frac{i}{\Delta_2}$$

$$\times\int_0^\infty d\tau_2 e^{-\gamma_e\tau_2}\langle\!\langle j_e\mu_1\mathbf{p}_1,j_e\mu_2\mathbf{p}_1\,|\,V_1^I(\tau_2,0)U_I(\tau_2,0)V_1^I(0,0)\,|\,j_e\mu_3\mathbf{p}_2,j_e\mu_4p_2\rangle\!\rangle$$

or

$$2\Delta_2\mathrm{Im}C(K,feee,z=0)\underset{\text{antistatic}}{\overset{\Delta_2}{\longrightarrow}}-\gamma^K\,. \tag{F2}$$

Thereby we used the relations

$$\langle\!\langle 1,2\,|\,U_I(\tau,0)V_1^I(0,0)\,|\,3,4\rangle\!\rangle^*=\langle\!\langle 2,1\,|\,U_I(\tau,0)V_1^I(0,0)\,|\,4,3\rangle\!\rangle\,,$$

$$\langle\!\langle 12\,|\,V_1^I(\tau,0)\,|\,34\rangle\!\rangle=\frac{1}{i\hbar}[\langle 1\,|\,V^I(\tau,0)\,|\,3\rangle\langle 2\,|\,4\rangle^*-\langle 1\,|\,3\rangle\langle 2\,|\,V^I(\tau,0)\,|\,4\rangle^*]\,,$$

and relabeled the summation and integration variables. Similarly we find

$$\mathrm{Im}C(fgeg,z=0)\underset{\text{antistatic}}{\overset{\Delta_1+\Delta_2,\Delta_1}{\longrightarrow}}0\,,$$

$$\mathrm{Im}C(fefg,z=0)\underset{\text{antistatic}}{\overset{\Delta_1+\Delta_2,\Delta_2}{\longrightarrow}}0\,,$$

$$2\Delta_1\mathrm{Im}C(K,eeeg,z=0)\underset{\text{antistatic}}{\overset{\Delta_1}{\longrightarrow}}-\gamma^K\,, \tag{F3}$$

$$\mathrm{Re}D_1(K,feeg,z=0)\underset{\text{antistatic}}{\overset{\Delta_2,\Delta_1+\Delta_2,\Delta_1}{\longrightarrow}}0\,,$$

$$2\,\mathrm{Re}D_2(K,feeg,z=0)$$

$$-2\mathrm{Re}D_3(K,fege,z=0)\underset{\text{antistatic}}{\overset{\Delta_1,\Delta_2}{\longrightarrow}}\frac{\gamma^K}{\Delta_1\Delta_2}\,.$$

Terms of higher order in the parameter (spontaneous decay rate)/(detuning) have thereby been neglected. Such terms have already been neglected in using the approximation of Eq. (20).

APPENDIX G: REDISTRIBUTED INTENSITY AND CARE CROSS SECTIONS

In this appendix, we briefly outline the connection between the total redistributed intensity as defined in Eq. (16a) and dressed-state CARE cross sections.[10] We give the perturbative expression for the dressed-state CARE cross section in a nondegenerate three-level system, which describes the single-collision contribution. Similar expressions are possible in the degenerate case, but (see below) the modulus squared of *sums* of m-state matrix elements contribute.

In the weak-field limit, when the dressed states are well separated, i.e.,

$$|\Delta| \gg \gamma_c, \gamma_e, \gamma_f \tag{G1}$$

the total redistributed intensity is proportional to the stationary dressed-state population[15]

$$I_{\text{red}} \propto \sigma_{\text{III,III}}(t \to \infty) \tag{G2}$$

as may be seen from Eq. (11a). For the radiator considered in this paper, the energies of the dressed states are shown in Fig. 6. Determining the dressed-state stationary population from our density matrix Eq. (A2), we find in lowest order in $\gamma_c/|\Delta|$ and in the weak-field limit

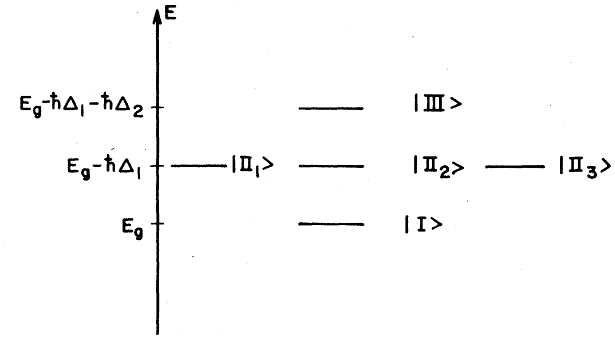

FIG. 6. Energies of the dressed states of the radiator studied in this paper in the weak-field limit neglecting the quadratic Stark shifts.

$$\gamma_f \sigma_{\text{III,III}}(t \to \infty) = \sum_{|i\rangle = \{|\text{I}\rangle, |\text{II}_1\rangle, |\text{II}_2\rangle, |\text{II}_3\rangle\}} N\,\text{Tr}_P\{\rho_P \langle\langle \text{III}\,\text{III} \,|\, U_I(\infty,0) V_1^I(0,0) \,|\, ii \rangle\rangle\} \sigma_{ii}(t \to \infty) \,. \tag{G3a}$$

Thereby we have used the fact that whenever condition (G1) is fulfilled, i.e., dressed states are well separated, the secular approximation indicates that nondiagonal dressed-state density-matrix elements are negligible.[15] In addition, we have performed a partial integration under the assumption that all collisions are completed (i.e., $\gamma_e \tau_c, \gamma_f \tau_c \ll 1$, see Ref. 13) and defined the interaction picture in a similar manner to in Eqs. (D1a) and (D1b) but with

$$U_0(t_1,t_2) = e^{(L_P + L_{\text{eff}})(t_1 - t_2)} \,. \tag{G3b}$$

In the classical path straight-line trajectory approximation we further get

$$\gamma_f \sigma_{\text{III,III}}(t \to \infty) = \sum_i \frac{N}{V} 4\pi \int_0^\infty dv\, v^2 f(v) v \int \frac{d\Omega_v}{4\pi} 2\pi \int_0^\infty db\, b \,|\langle \text{III} \,|\, X\rangle_{t\to\infty}^{(i)}|^2 \sigma_{ii}(t \to \infty) \,,$$

where we have integrated over t_0. The time evolution of the electronic radiator-perturber state is determined by

$$i\hbar \frac{d}{dt} |X\rangle_t^{(i)} = [H_{\text{eff}} + V^{(b,v)}(t)] \,|X_t^{(i)}\rangle \tag{G5a}$$

with

$$V^{(b,v)}(t) = V(R(t))$$

and

$$R^2(t) = b^2 + v^2 t^2 \,.$$

This equation has to be solved with the initial condition

$$|X\rangle_{t\to-\infty}^{(i)} = |i\rangle \,. \tag{G5b}$$

$\langle j \,|\, X\rangle_{t\to\infty}^{(i)}$ is therefore an S-matrix element between the dressed states $|j\rangle$ and $|i\rangle$.

Using the procedure of Yeh and Berman[10] we find in the case of a nondegenerate three-level system for the S-matrix element between the dressed states $|\text{I}\rangle$ and $|\text{III}\rangle$ in the weak-field limit the expression[26]

$$\begin{aligned}
|\langle \text{III} \,|\, X\rangle_{t\to\infty}^{(I)}|^2 = {} & |\langle j_f \,|\, \boldsymbol{\mu}\cdot\mathbf{e}_2 \,|\, j_e\rangle \mathscr{E}_2|^2 \,|\langle j_e \,|\, \boldsymbol{\mu}\cdot\mathbf{e}_1 \,|\, j_g\rangle \mathscr{E}_1|^2 \frac{1}{\hbar^4} \\
& \times \left| \int_{-\infty}^{\infty} dt_1 \frac{1}{\Delta_1+\Delta_2} \left[\frac{V_{fe}(t_1)}{\hbar\Delta_1} - \frac{V_{eg}(t_1)}{\hbar\Delta_2} \right] \exp\left[-i \int_0^{t_1} dt_2 [\Delta_1 + \Delta_2 - V_{fe}(t_2)/\hbar - V_{eg}(t_2)/\hbar] \right] \right. \\
& \quad - i \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{t_1} dt_2 \frac{1}{\Delta_1\Delta_2} \frac{V_{fe}(t_1)}{\hbar} \frac{V_{eg}(t_2)}{\hbar} \exp\left[-i \int_0^{t_1} dt_3 [\Delta_2 - V_{fe}(t_3)/\hbar] \right] \\
& \quad \left. \times \exp\left[-i \int_0^{t_2} dt_4 [\Delta_1 - V_{eg}(t_4)/\hbar] \right] \right|^2 \,.
\end{aligned} \tag{G6}$$

Whereas Yeh and Berman's formula (6.1) (Ref. 10) is proportional to the total scattered intensity including both the collisional-induced Rayleigh and the Raman peak in the zero-density limit of perturbers, Eq. (G6) characterizes the single-collision contribution to the total redistributed intensity. Using the asymptotic formula of Berry and Tabor[27] for the integrals in (G6), which is valid as long as stationary phase points are well separated, we can easily discuss some limiting cases in the regime where $|\Delta_1|\tau_c \gg 1$, $|\Delta_2|\tau_c \gg 1$, and $|\Delta_1+\Delta_2|\tau_c \gg 1$. In particular, we see that $|\langle \text{III} \,|\, X\rangle_{t\to\infty}^{(\text{I})}|^2$ will be zero, whenever $\Delta_1+\Delta_2$ and Δ_1 or $\Delta_1+\Delta_2$ and Δ_2 are antistatically detuned. For an antistatic detuning of $\Delta_1+\Delta_2$ the first term in the modulus of Eq. (G6) vanishes and we are left with the two-step contribution (i.e., the square of the second term in the modulus), which is equivalent to Eq. (E15a). As soon as there is also a stationary phase point in $\Delta_1+\Delta_2$ we also have a direct contribution to the redistributed intensity [i.e., from the first term in the modulus of Eq. (G6)] as well as an additional endpoint contribution from the t_2 integral in the second term of Eq. (G6), and an interference term. Using the asymptotic formula of Berry and Tabor we see that the ratio between the direct contribution (which is of the order of a typical zero-order collision contribution) and the two-step contribution roughly varies like $|\Delta\tau_c|^{-5/6}$ for a van der Waals potential whereas the ratio between the interference and the two-step term decreases only as $|\Delta\tau_c|^{-5/12}$ [see Eq. (E16) and subsequent discussion]. This implies that even in the case of a stationary phase point associated with $\Delta_1+\Delta_2$ the two-step process dominates the redistributed intensity for sufficiently large detunings (at least as long as stationary phase points are well separated). However, due to the slow decrease of $|\Delta\tau_c|^{-5/12}$ there is a considerable range of detunings, where the interference term of Eq. (G6) is not negligible and $|\langle \mathrm{III}|X\rangle^{(\mathrm{I})}_{t\to\infty}|^2$ has to be investigated more carefully. In particular the endpoint contributions of the asymptotic formula of Berry and Tabor must be properly taken into account.

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