Resonance fluorescence in radiative collisions

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A theoretical study of the resonance fluorescence emitted in a radiative collision is presented. A treatment of the spontaneous emission based on the short-pulse approximation is shown to be suitable for an analysis of the spectral distribution of the scattered radiation. Following an adiabatic dressed-state picture, a seven-peak spectral structure is predicted, in agreement with the three-level nature of the problem. Some of the spectral lines are found to be due to emission processes taking place only during the collision, allowing a characterization of the process as resonance fluorescence of a transient molecule.

I. INTRODUCTION

Since the first discussion by Gudzenko and Yakovlenko in 1972[1] a great deal of effort has been devoted to the study of atomic radiative collisions, described by the general reaction

$$A_i + B_i + n\hbar\Omega \rightarrow A_f + B_f + (n \pm 1)\hbar\Omega \ , \qquad (1)$$

where $A_{i,f}$ and $B_{i,f}$ denote initial and final states of the atomic species A and B, colliding in the presence of a laser field with n photons of frequency Ω. Depending on the initial states, the processes represented by (1) can take place in absorption or in stimulated emission.

Among radiative collisions, laser-induced collisional energy transfer[2-12] (LICET) and pair absorption[13-15] and emission[16] have been extensively studied both experimentally and theoretically. Up to now these processes have been mainly studied from the viewpoint of evaluating excitation rates, which are of great importance for the achievement of collision-induced population inversion.[17,18]

The processes represented by reaction (1) are induced by the combined action of the collisional and radiative interactions, which are required to be present simultaneously for the reaction to proceed. The problem is conveniently described in terms of adiabatic quasimolecular states, considering the interatomic transitions taking place in (1) as due to the radiative transitions of the transient molecule (quasimolecule) which is formed during the collision.

The quasimolecular approach, besides providing a deeper understanding of the physical principles underlying the processes, allows a straightforward extension of the class of radiative collisions. A significant example, supporting the utility of this approach, can be found in the study of multiphoton radiative collisions.[19-23]

Among the radiative processes of a transient molecule interacting with a laser field, near-resonant scattering appears of great interest. Resonance fluorescence of two- or three-level atoms as a probe of the collisional dynamics has been extensively studied in the framework of the collisional redistribution of radiation.[24-27] However, to our knowledge, there is no published study describing the spectrum of the resonance fluorescence in radiative collisions.

We present here a theoretical study of the resonance fluorescence spectrum emitted by a collision pair during a LICET reaction, with the aim of stimulating an experimental investigation which, in our opinion, can be of interest in several respects.

In the product-state basis of uncoupled (infinite-distance) atoms, the LICET process is described, under proper assumptions, by a three-level model, with radiative and collisional couplings. However, in a dressed-state picture, it has been shown that, for a wide range of field intensities, the transition probability to the final state can be accurately evaluated by solving a two-level problem.[8,12] One might therefore draw the conclusion that the excitation spectrum is not closely related to a three-level dynamics, being mainly determined by the collisional interaction. The main point of interest for the study of near-resonant scattering is that the spectral structure of the emitted fluorescence strongly reflects the three-level nature of the problem, with line shapes affected by the collisional interaction. Moreover, observation of the resonance-fluorescence spectrum would allow the study of the combined radiative-collisional interaction (peculiar to a LICET process) even in the absence of a significant transfer of population to the final state (adiabatic interaction). This condition seems suitable, for instance, to the study of collisional dynamics in the presence of a strong laser field, since it avoids the contribution of concomitant processes which are extraneous to the one under study.

Following a description of the physical system (Sec. II), we present in Sec. III an extension to the present problem of the short-pulse approximation, introduced by Robin-

son and Berman for the study of the resonance fluorescence of a two-level atom.[28] Although this method is suitable to a numerical analysis of the full spectral distribution of the emitted fluorescence (including line shapes), the main features of the spectrum can be easily predicted in the framework of a dressed-state picture (Sec. IV). Finally, in Sec. V, a perturbative approach in the laser-atom interaction, based on the introduction of adiabatic collisional dressed states, is described, with the aim of gaining more insight into the physical process.

II. THEORETICAL FRAMEWORK

In our model an atom A prepared in an excited state $|\alpha_2\rangle$ undergoes a collision with an atom B in its ground state $|\beta_1\rangle$ in the presence of a monochromatic laser field nearly resonant with an interatomic transition. Due to the simultaneous absorption of a photon of energy $\hbar\Omega$ from the laser field, the excitation energy of atom A is transferred during the collision to atom B, which is then left in its excited state $|\beta_3\rangle$. If an excited level $|\beta_2\rangle$ of atom B is nearly resonant with $|\alpha_2\rangle$, one channel of excitation dominates the process. The energy-level scheme of the atoms can then be depicted as in Fig. 1, and the process is conveniently studied in the following product-state basis:

$$\begin{aligned} |i\rangle &= |\alpha_2\rangle|\beta_1\rangle \ , \\ |x\rangle &= |\alpha_1\rangle|\beta_1\rangle \ , \\ |f\rangle &= |\alpha_1\rangle|\beta_3\rangle \ . \end{aligned} \tag{2}$$

After several assumptions,[8] the equations of motion for the probability amplitudes of states (2) are written as follows:

$$\begin{aligned} i\dot{a}_i(t) &= V(t)a_x(t)\exp(i\Delta t) \ , \\ i\dot{a}_x(t) &= V(t)a_i(t)\exp(-i\Delta t) - \chi a_f(t)\exp(i\delta t) \ , \\ i\dot{a}_f(t) &= -\chi a_x(t)\exp(-i\delta t) \ , \end{aligned} \tag{3}$$

with $\Delta=(E_i-E_x)/\hbar$ and $\delta=\Omega-(E_f-E_x)/\hbar$, and where $V(t)$ and χ describe, respectively, the collisional and the atom-field interactions. As a result of the short time scale of the collision, χ is usually assumed constant, while the explicit form of $V(t)$ depends on the particular interatomic potential. For a dipole-dipole interaction, assuming classical and rectilinear trajectories for the atoms during the collision, $V(t)$ is given by

$$V(t)=d_A d_B/\hbar(b^2+v^2t^2)^{3/2} \ , \tag{4}$$

where d_A and d_B are the dipole moments of the $|\alpha_1\rangle$-$|\alpha_2\rangle$ and $|\beta_1\rangle$-$|\beta_2\rangle$ transition, b is the impact parameter and v is the relative speed of the atoms. The validity of the approximations used to obtain (3) has been confirmed both theoretically[12] and experimentally.[9,10]

In the following, while keeping the formulation general, we will have in mind the specific case of collisions between europium and strontium atoms for which numerical calculations are in progress. For this system, the energy-level scheme is similar to that shown in Fig. 1, where $|\alpha_2\rangle$ is the $(6s6p)^8P_{9/2}$ excited state of Eu and $|\beta_2\rangle$ and $|\beta_3$ are respectively the $(5s5p)^1P_1$ and $(5p^2)^1D_2$ excited states of Sr. The frequency difference between the product states $|i\rangle$ and $|x\rangle$ is $\Delta=63\ \mathrm{cm}^{-1}$ and the collisional interaction is well described by (4) with a dipole-dipole interaction energy given by $d_A d_B=2.17\times10^{-35}$ erg cm^3.[12]

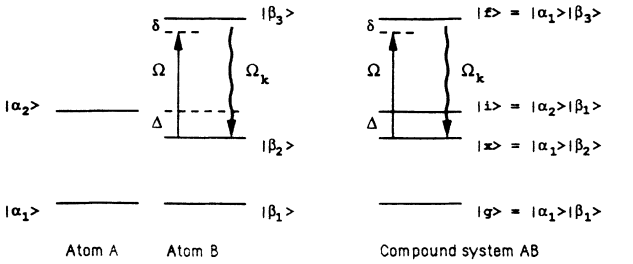

FIG. 1. Schematic energy-level diagram of a LICET process. Energy levels of the relevant product states are shown on the right.

III. FLUORESCENCE SPECTRUM

If levels $|\beta_2\rangle$ and $|\beta_3\rangle$ are strongly coupled by a dipole transition, then level $|\beta_3\rangle$ can radiate to level $|\beta_2\rangle$ during the collision, emitting a photon of energy $\hbar\Omega_k$. We follow the approach introduced by Robinson and Berman for the study of the resonance fluorescence of a two-level atom in interaction with a short laser pulse.[28] Since the collision takes place on a time scale of the order of 1–10 ps, much shorter than the typical radiative lifetime of level $|\beta_3\rangle$, at most one fluorescence photon per atom is emitted during the collision. An appropriate basis to describe the process is therefore provided by the states

$$\begin{aligned} |1\rangle &= |i\rangle|n,0\rangle \ , \\ |2\rangle &= |x\rangle|n,0\rangle \ , \\ |3\rangle &= |f\rangle|n-1,0\rangle \ , \end{aligned} \tag{5a}$$

$$\begin{aligned} |1,\mathbf{k}_\sigma\rangle &= |i\rangle|n-1,\mathbf{k}_\sigma\rangle \ , \\ |2,\mathbf{k}_\sigma\rangle &= |x\rangle|n-1,\mathbf{k}_\sigma\rangle \ , \\ |3,\mathbf{k}_\sigma\rangle &= |f\rangle|n-2,\mathbf{k}_\sigma\rangle \ , \end{aligned} \tag{5b}$$

where $|j\rangle$ describes the atoms in the product states (2) with no emitted photons, and $|j,\mathbf{k}_\sigma\rangle$ describes the atoms in the product states (2) and the fluorescence field in the state defined by one photon with propagation vector $\mathbf{k}$ and polarization σ. The number of photons in the strong laser mode is n.

Starting with no photons in the scattered field modes at a time t^- just before the collision, the fluorescence spectrum emitted up to a time t^+ immediately following the collision can be written as

$$P(\Omega_k)\propto\sum_\sigma\int_0^\infty b\left[\sum_j|a_{j\mathbf{k}\sigma}(t^+)|^2\right]db \ , \tag{6}$$

where $a_{j\mathbf{k}\sigma}(t)$ is the probability amplitude for finding the system in state $|j,\mathbf{k}_\sigma\rangle$ at time t.

The equations of motion for the state amplitudes $a_{j\mathbf{k}\sigma}(t)$ follow from a perturbative treatment to first order in the vacuum radiation field of the time-dependent Schrödinger equation. The following differential equations are obtained in the interaction picture and rotating-wave approximation:

$$i\dot{\mathbf{a}}(t)=\underline{H}(t)\mathbf{a}(t)\ , \tag{7a}$$

$$i\dot{\mathbf{a}}_{\mathbf{k}\sigma}(t)=\underline{H}(t)\mathbf{a}_{\mathbf{k}\sigma}(t)+\mathbf{F}(t)\ , \tag{7b}$$

with

$$\mathbf{a}(t)=\begin{bmatrix}a_1(t)\\a_2(t)\\a_3(t)\end{bmatrix}=\begin{bmatrix}a_i(t)\\a_x(t)\\a_f(t)\end{bmatrix}\ . \tag{8}$$

$$\mathbf{a}_{\mathbf{k}\sigma}(t)=\begin{bmatrix}a_{1\mathbf{k}\sigma}(t)\\a_{2\mathbf{k}\sigma}(t)\\a_{3\mathbf{k}\sigma}(t)\end{bmatrix}\ , \tag{9}$$

$$\underline{H}(t)=\begin{bmatrix}0 & V(t)\exp(i\Delta t) & 0\\ V(t)\exp(-i\Delta t) & & -\chi\exp(i\delta t)\\ 0 & -\chi\exp(-i\delta t) & 0\end{bmatrix}\ , \tag{10}$$

$$\mathbf{F}(t)=V_k a_f(t)\exp(i\delta_k t)\begin{bmatrix}0\\1\\0\end{bmatrix}\ , \tag{11}$$

where $\delta_k=\Omega_k-(E_f-E_x)/\hbar$, and V_k is the matrix element of the atom-vacuum field interaction. The boundary conditions for (7) are

$$\mathbf{a}(t^-)=\begin{bmatrix}1\\0\\0\end{bmatrix}\quad a_{\mathbf{k}\sigma}(t^-)=\begin{bmatrix}0\\0\\0\end{bmatrix}\ .$$

The solution of (7b) can be written as

$$\mathbf{a}_{\mathbf{k}\sigma}(t)=-i\underline{U}(t)\int_{t^-}^{t}dt'\underline{U}^{-1}(t')\mathbf{F}(t')\ , \tag{12}$$

where $\underline{U}(t)$ is the time-evolution operator, solution of

$$i\dot{\underline{U}}(t)=\underline{H}(t)\underline{U}(t)\ . \tag{13}$$

Since $\underline{H}(t)$ is Hermitian, $\underline{U}(t)$ is unitary, i.e.,

$$\underline{U}^{\dagger}(t)=\underline{U}^{-1}(t)\ , \tag{14}$$

and the fluorescence spectrum (6) reduces to the compact expression

$$P(\Omega_k)\propto\sum_\sigma\int_0^\infty b\left|\int_{t^-}^{t^+}dt\underline{U}^{\dagger}(t)\mathbf{F}(t)\right|^2 db\ . \tag{15}$$

IV. ADIABATIC DRESSED-STATE APPROACH

Expression (15) provides the starting point for a numerical analysis of the collision-induced fluorescence spectrum. However, a sketch of the main spectral features can be easily given in the framework of a dressed-state picture. The introduction of time-dependent dressed states has already proved to be of great utility for the study of the resonance fluorescence emitted by two- or three-level atoms driven by near-resonant laser pulses.[25] In fact, in the case of adiabatic interaction (off-resonance smooth laser pulses) and well-separated spectral lines, this description can predict both the line positions and integrated intensities. The latter is accomplished via Fermi's golden rule applied to the evaluation of spontaneous-emission transition rates among dressed states.

In our case, the condition of adiabaticity can certainly be fulfilled for a laser detuning in the antistatic region of the excitation spectrum ($\Delta+\delta>0$), where no transfer of population between states $|i\rangle$ and $|f\rangle$ occurs. As the laser detuning approaches the peak of the excitation spectrum ($\Delta+\delta\to0$), the adiabatic character of the combined collisional-radiative interaction is progressively lost, since the population transfer among dressed states will tend to become significant, affecting the relative integrated intensities of the spectral lines. However, even in this case, the position of the spectral lines can be immediately found.

First we use the unitary transformation

$$\mathbf{c}(t)=\underline{T}(t)\mathbf{a}(t) \tag{16}$$

with

$$\underline{T}(t)=\begin{bmatrix}\exp(-i\Delta t) & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & \exp(i\delta t)\end{bmatrix} \tag{17}$$

to write

$$i\dot{\mathbf{c}}(t)=\underline{H}'(t)\mathbf{c}(t)\ , \tag{18}$$

where

$$\underline{H}'(t)=\begin{bmatrix}\Delta & V(t) & 0\\ V(t) & 0 & -\chi\\ 0 & -\chi & -\delta\end{bmatrix}\ . \tag{19}$$

Then we introduce the time-dependent adiabatic eigenstates of $\underline{H}'$ defined by

$$|D_i,n\rangle=\sum_{j=1}^{3}D_{ij}(t)|j\rangle \tag{20}$$

with

$$\begin{aligned}D_{i1}(t)&=V(t)[\mu_i(t)+\delta]/S_i(t)\ ,\\ D_{i2}(t)&=[\mu_i(t)-\Delta][\mu_i(t)+\delta]/S_i(t)\ ,\\ D_{i3}(t)&=\chi[\Delta-\mu_i(t)]/S_i(t)\ ,\end{aligned} \tag{21}$$

and

$$\begin{aligned}S_i^2(t)=&V^2(t)[\mu_i(t)+\delta]^2\\ &+[\mu_i(t)-\Delta]^2[\mu_i(t)+\delta]^2+\chi^2[\Delta-\mu_i(t)]^2\ .\end{aligned} \tag{22}$$

The time-dependent adiabatic eigenvalues $\mu_i(t)$ are given by the solutions of the third-order secular equation

$$|\underline{H}'(t)-\mu(t)\underline{I}|=0\ . \tag{23}$$

For $t \rightarrow \pm\infty$, $V(t) \rightarrow 0$, and (23) reduces to

$$(\mu-\Delta)(\mu^2+\delta\mu-\chi^2)=0 , \tag{24}$$

whose roots are given by

$$\begin{aligned} \mu_1&=\Delta , \\ \mu_2&=-[\delta+(\delta^2+4\chi^2)^{1/2}]/2 , \\ \mu_3&=-[\delta-(\delta^2+4\chi^2)^{1/2}]/2 . \end{aligned} \tag{25}$$

The energy levels of the dressed states (20) appear as an infinite ladder of equally spaced triplets whose temporal evolution during the collision is shown in Fig. (2a).

Due to the vacuum-field radiative coupling between $|\beta_3\rangle$ and $|\beta_2\rangle$, the adiabatic dressed states of two adjacent multiplets are radiatively coupled with time-dependent matrix elements given by

$$W_{ij}(t)=V_k D_{i3}(t) D_{j2}(t) . \tag{26}$$

Since the resonance fluorescence emitted during the collision can be viewed as arising from transitions among the adiabatic eigenstates (20), the fluorescence spectrum is expected to exhibit a seven-peak structure with lines centered at the frequencies

$$\begin{aligned} \Omega_k&=\Omega , \\ \Omega_k&=\Omega\pm\{\Delta+[\delta-(\delta^2+4\chi^2)^{1/2}]/2\} , \\ \Omega_k&=\Omega\pm\{\Delta+[\delta+(\delta^2+4\chi^2)^{1/2}]/2\} , \\ \Omega_k&=\Omega\pm(\delta^2+4\chi^2)^{1/2} . \end{aligned} \tag{27}$$

This spectral structure, typical of the resonance fluorescence of a three-level system,[29] is shown in Fig. 2(b), where the relative intensities of the lines are not significant. For a weak laser field, the separation between the outer doublets and the central line is $\approx\Delta$ while the line separation within each multiplet is $\approx|\Delta+\delta|$, that is the laser detuning from the interatomic transition $|i\rangle$-$|f\rangle$. For a strong laser field, the actual positions of the spectral lines are determined by the dynamic Stark shift of the energy levels of the compound system while the line shapes are affected by the collisional van der Waals shift. The collisional shift gives rise to wings in the anelastic scattering lines of the fluorescence spectrum, whose origin is closely related to the far wing of the excitation spectrum. The collision-induced elastic component of the fluorescence spectrum is expected to be symmetric with a width related to the inverse of the average collision time, instead of the laser bandwidth as in usual near-resonant Rayleigh scattering.

While the line shapes of all the components of the spectrum are at least somewhat affected by the collisional interaction, some of them can be actually considered totally collision induced, in the sense that they are due to emission processes occurring only during the collisional interaction. In Fig. 3 we have reported the time evolution of the dimensionless radiative decay rates

$$\Gamma_{ij}(t)=|W_{ij}(t)|^2/|V_k|^2 ,$$

calculated for the specific case of a collision between Eu and Sr atoms with an impact parameter $b=18$ Å, a laser detuning of 6 cm^{-1} in the antistatic region of the excitation spectrum ($\Delta+\delta=6$ cm^{-1}) and an atom-field interaction $\chi=6$ cm^{-1}. We note that outside the collision ($t \rightarrow \pm\infty$) some of the $\Gamma_{ij}(t)$ vanish while others remain different from zero. In fact, as shown by (26), the temporal behavior of the $\Gamma_{ij}(t)$ reflects the time dependence of the components $D_{ij}(t)$ of states $|j\rangle$ in the dressed states $|D_i,n\rangle$. In the absence of collisional interaction, state $|D_1,n\rangle$ has no $|2\rangle$ and $|3\rangle$ components, while states $|D_2,n\rangle$ and $|D_3,n\rangle$ are linear combinations of states $|2\rangle$ and $|3\rangle$. As a result, while lines originating from transitions between dressed states $|D_2,n\rangle$ and $|D_3,n\rangle$ [1, 4, and 5 in Fig. 2(b)] can also be emitted in the absence of collisions, all the other lines characterize the resonance fluorescence of a transient molecule.

In the case of a well-resolved spectrum, the frequency-integrated line intensity I_{ij} emitted in the transition

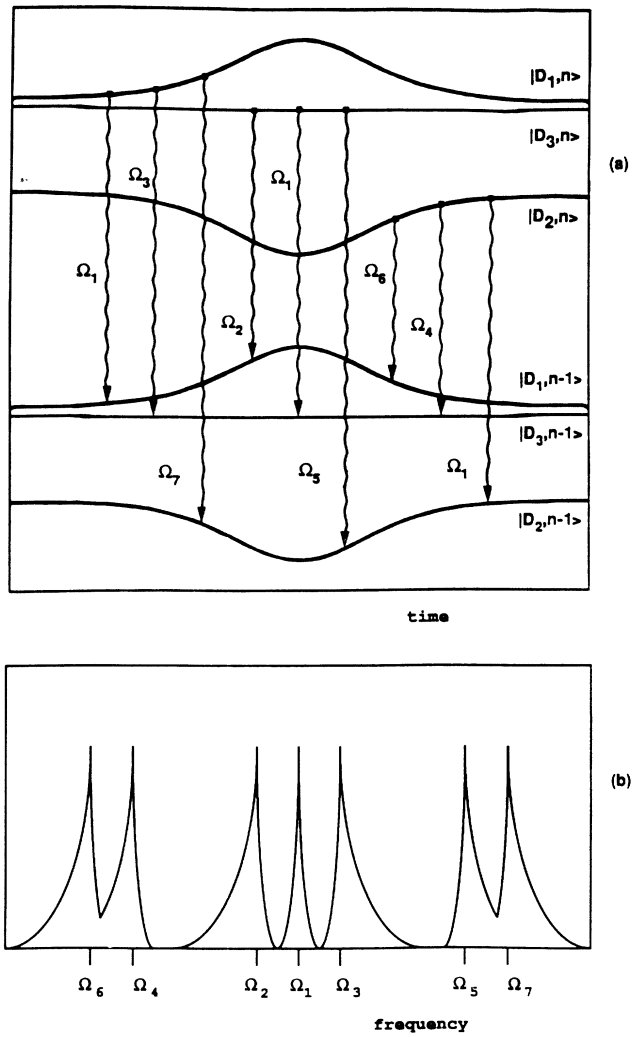

FIG. 2. Structure of the resonance-fluorescence spectrum: (a) spontaneous-emission transitions among time-dependent adiabatic dressed states; (b) corresponding spectrum, showing the collision-induced spectral wings.

$|D_i,n\rangle \rightarrow |D_j,n^{-1}\rangle$ can be expressed as

$$I_{ij} \propto \sum_{\sigma} \int_0^{\infty} b \left[\int_{t^-}^{t^+} \Pi_i(t)\Gamma_{ij}(t)dt \right] db \ , \tag{28}$$

where

$$\Pi_i(t) = \left| \sum_{j=1}^{3} D_{ij}(t)c_j(t) \right|^2 \tag{29}$$

is the time-dependent population of the dressed state $|D_i,n\rangle$. Expression (28) can be easily computed for an adiabatic interaction ($\Delta+\delta>0$), being $\Pi_1(t)=1$ and $\Pi_2(t)=\Pi_3(t)=0$. In this case only the lines originating from transitions starting from state $|D_1,n\rangle$, denoted as 1, 3, and 7 in Fig. 2(b), will be present in the emission spectrum. A numerical calculation of (28) has been performed for the Eu-Sr pair with $\Delta+\delta=6$ cm^{-1} and the results are shown in Fig. 4 as a function of the laser intensity.

V. WEAK-FIELD REGIME: COLLISIONAL DRESSED-STATE PICTURE

In order to obtain more insight into the origin of the spectral lines it is convenient to make use of a diagrammatic representation, based on a perturbative treatment of the radiative interaction, involving adiabatic collisional dressed states (quasimolecular states).

In the absence of the laser field, the Hamiltonian (19) describes the collisional interaction between atoms A and B. It is shown in Ref. 8 that, when the condition

$$|\dot{V}(t)/V(t)| \ll \Delta \tag{30}$$

is satisfied, the time evolution of the colliding atoms is well described by adiabatic collisional dressed states defined as

$$\begin{aligned} |+\rangle &= (\cos\theta)|i\rangle + (\sin\theta)|x\rangle \ , \\ |-\rangle &= (\cos\theta)|x\rangle - (\sin\theta)|i\rangle \ , \end{aligned} \tag{31}$$

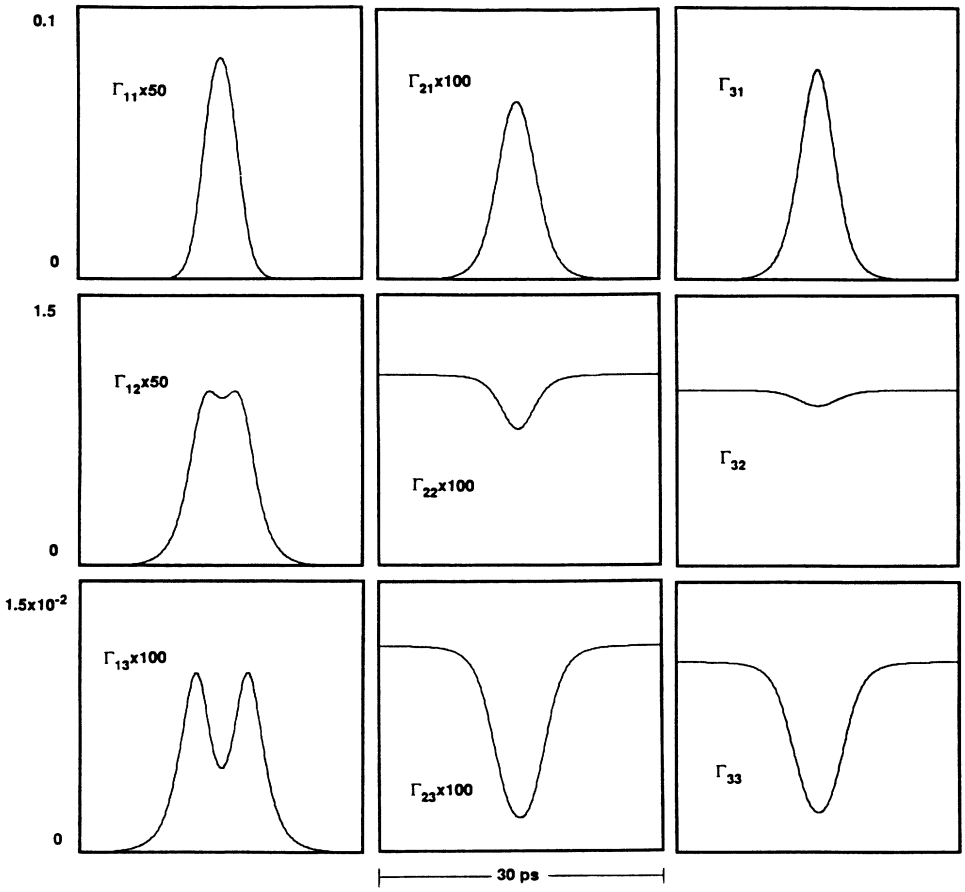

FIG. 3. Temporal evolution of the dimensionless radiative decay rates $\Gamma_{ij}(t)$ among adiabatic dressed states. The calculation refers to the specific case of a collision between Eu and Sr atoms with an impact parameter $b=18$ Å, a laser detuning of 6 cm^{-1} in the antistatic region of the excitation spectrum ($\Delta+\delta=6$ cm^{-1}), and an atom-field interaction $\chi=6$ cm^{-1}.

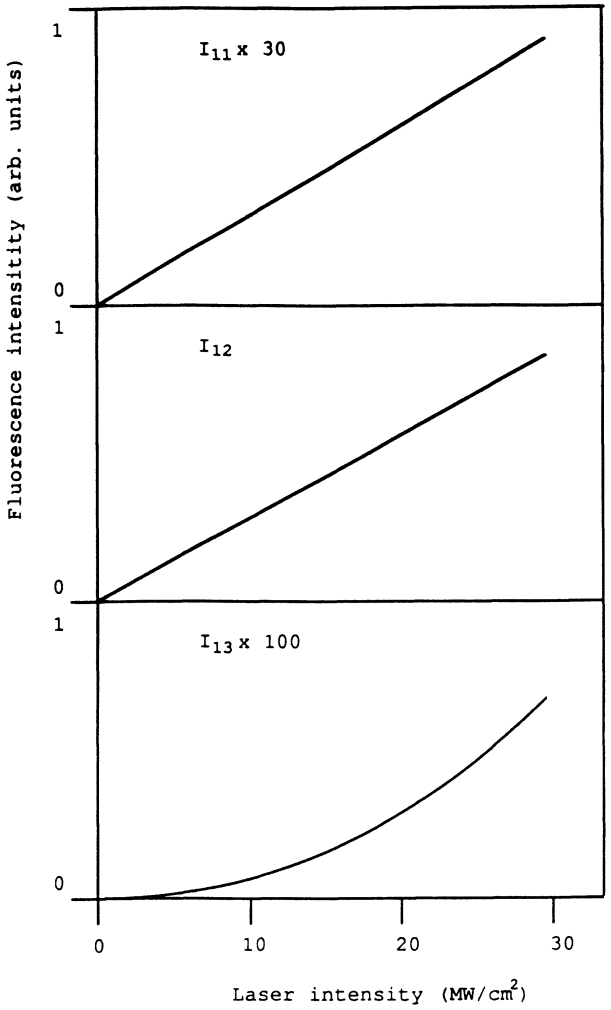

FIG. 4. Frequency-integrated line intensities I_{1j} as a function of the laser intensity. The calculation refers to the specific case of collisions between Eu and Sr atoms with a laser detuning of 6 cm^{-1} in the antistatic region of the excitation spectrum ($\Delta+\delta=6\ cm^{-1}$).

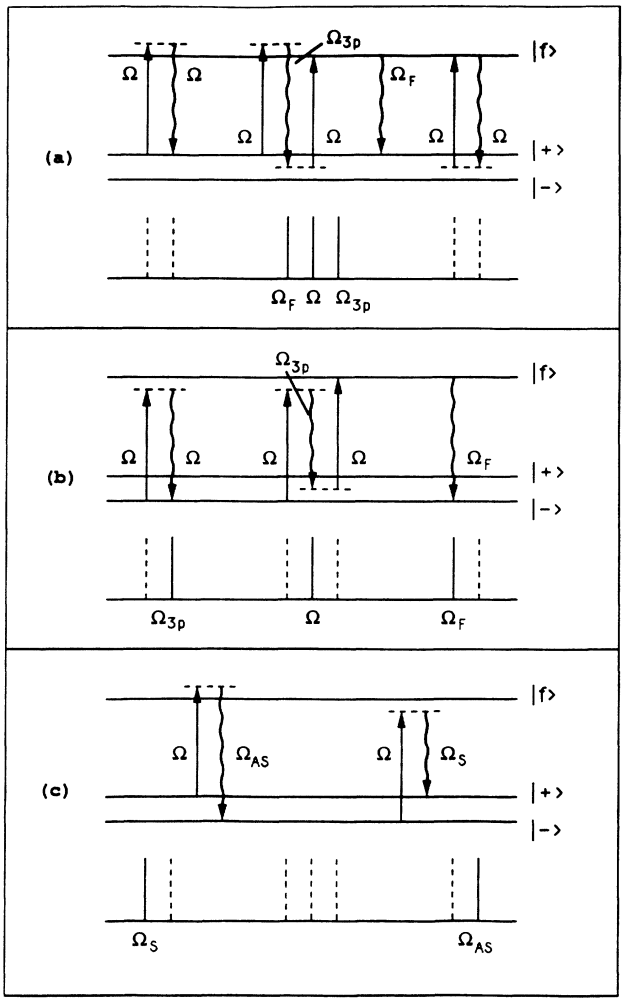

FIG. 5. Diagrammatic representation of the transitions contributing to the fluorescence spectrum: (a) near-resonant scattering between states $|+\rangle$ and $|f\rangle$; (b) near-resonant scattering between states $|-\rangle$ and $|f\rangle$; (c) Stokes and anti-Stokes Raman scattering between states $|+\rangle$ and $|-\rangle$.

with

$$\tan(2\theta)=2V(t)/\Delta\ .$$

The collisional dressed states (31) are quasimolecular states with adiabatic time-dependent eigenvalues given by

$$\begin{aligned}\mu_+(t)&=(\Delta/2)(1+\{1+[2V(t)/\Delta]^2\}^{1/2})\ ,\\ \mu_-(t)&=(\Delta/2)(1-\{1+[2V(t)/\Delta]^2\}^{1/2})\ .\end{aligned}\tag{32}$$

The effect of the laser field is to couple states $|+\rangle$ and $|-\rangle$ to the final state $|f\rangle$. In this picture, the spectral features shown in Fig. 2(b) can be viewed as resulting from the processes illustrated in Fig. 5, where the spontaneous emission transitions, occurring as a consequence of the absorption of one or two photons from the laser field, are represented. In Fig. 5, the Stark shift as well as the van der Waals shift of energy levels are neglected.

The transitions shown in Fig. 5(a), representing a near-resonant scattering involving states $|+\rangle$ and $|f\rangle$, and including Rayleigh scattering from state $|f\rangle$, give rise to a Mollow triplet [lines 1, 2, and 3 in Fig. 2(b)]. Since these emission processes require that both the collisional and the radiative interactions be present simultaneously, they can take place only during the collision. On the contrary, the transitions shown in Fig. 5 (b) [lines 1, 4, and 5 in Fig. 2(b)] represent a near-resonant scattering involving states $|-\rangle$ and $|f\rangle$, which are radiatively coupled even in the absence of the collision. Therefore, these lines contain a contribution due to resonance fluorescence emitted by atom B after the collision, as a result of the transfer of population from atom A to atom B due to the LICET reaction. Finally, the processes depicted in Fig. 5(c) represent Stokes and anti-Stokes near-resonant Raman scattering between states $|+\rangle$ and $|-\rangle$ of the transient molecule [lines 6 and 7 in Fig. 2(b)].

The diagrammatic representation of Fig. 5 allows us also to make some predictions on the frequency-integrated line intensities and on their dependence on

laser intensity. In fact, in the weak-field regime, most of the atomic population is in the $|+\rangle$ state.[8] Therefore, lines due to transitions starting from $|+\rangle$ state [1,3, and 7 in Fig. 2(b)] are expected to be more intense than lines resulting from transitions starting from $|-\rangle$ state. Furthermore, the three-photon emission process, originating lines 3 and 4 of the spectrum, requires the absorption of two laser photons. Therefore, these lines are expected to present a quadratic, rather than linear, dependence on laser intensity. This prediction is confirmed by the calculations reported in Fig. 4.

VI. CONCLUSIONS

We have presented a theoretical study of the resonance fluorescence emitted in a LICET reaction, providing an explicit expression for the spectrum. The spectral distribution of the radiation scattered by the collision pair driven by a laser field near resonant with an interatomic transition exhibits a seven-peak structure, strongly related to the collisional dynamics. In fact, some of the spectral lines are found to be due to transitions occurring only during the collision, characterizing the process as resonance fluorescence of a transient molecule. Following an adiabatic dressed-state picture, we have been able to provide quantitative predictions on the relative intensities of the spectral lines and their dependence on laser intensity for the specific case of the Eu-Sr pair. Further investigation, carried out by numerical calculations, is in progress for the evaluation of the spectral line shapes, which are closely related to the collisional interaction.

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