Two-photon laser-induced radiative collisions

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We present a semiclassical treatment of two-photon laser-induced radiative collisions. We treat the two-photon–one-collision and two-photon–two-collision cases. We find a new intensity-induced collisional shift which makes the two-photon line shape highly sensitive to the intensity, and may make the line shape symmetric.

During the last few years considerable theoretical and experimental efforts have been devoted to describing absorption or stimulated emission resonances that are only present during collisions of excited atoms with ground-state atoms of another element (radiative collision). In a radiative collision the initially excited atom, having excitation energy ϵ, returns to its ground state and leaves the second atom in an excited state of excitation energy nearly equal to $\epsilon \pm \hbar\omega$. Large cross sections (i.e., several Å^2) are predicted[1] and were measured at power levels $\sim 10^7$ W/cm^2 in cases where no excitation transfer occurs in the absence of the laser field. Although the possibility of laser-induced multiphoton radiative collisions has been previously suggested,[2] it is only recently that an experimental effort has dealt with it.[3] During the collision of Ba and Tl ground-state atoms, two photons are absorbed which result in the simultaneous excitation of both atoms.

In this paper we examine the theoretical aspect of two-photon induced radiative collisions using a semiclassical approach. We find that when all the radiative interactions take place with only one of the atoms, the process can be transformed to an equivalent form of a single-photon radiative process except for an ac Stark shift and the introduction of an effective two-photon coupling in place of the single-photon coupling. The line shape has an extended red wing as is encountered in a single-photon radiative collision.[4,5] However, in the case where both atoms couple to the electromagnetic field, we find that the process proceeds via a two-collision process and hence, the above simple substitution does not hold. The overall radiative collision coupling is proportional to the product of an effective two-photon coupling and an effective two-collision coupling. In addition to ac Stark shifts, we find that a new intensity-induced collisional shift is introduced. This induced shift is interesting since it makes the line shape highly sensitive to the laser intensity. Moreover, it may cancel a major part of the collisional shifts and hence, cause the two-photon line shape to exhibit symmetry for a certain intensity while the absence of this shift will in general result in an extended tail.

We consider the collision of atoms A and B in their ground states in the presence of the radiation field $\epsilon = E_0 \cos\omega t$ which does not resonate with any of the transitions in either atom. We are interested in the process where both atoms emerge from the interaction excited. In describing the process, we treat the motion of the nuclei classically; moreover, we assume that the dominant contribution comes from large internuclear separation where electronic overlap is negligible. Hence, we represent the system with a product of atomic states, and write

$$\hat{H} = \hat{H}_A + \hat{H}_B + \hat{V}_{AB} - \vec{\mu}_A \cdot \vec{\epsilon} - \vec{\mu}_B \cdot \vec{\epsilon}\,, \qquad (1)$$

where $\hat{H}_A$ and $\hat{H}_B$ are the electronic Hamiltonians of isolated atoms A and B, $\hat{V}_{AB}(t)$ is the atom-atom interaction, and the other terms are the laser field-atom interaction terms in the dipole-classical field approximation. We will treat the magnetic number degeneracy by treating the atom-atom interaction in the rotating atom approximation where $\hat{V}_{AB}$ matrix elements are evaluated by assuming the transition moments are always aligned along the line joining the nuclei.

Consider the first case where only one atom interacts with the field. The state vector of the system is taken to be of the form (see Fig. 1)

$$|\psi(t)\rangle = a_0(t)\,|0a\rangle\,|0b\rangle + a_1(t)\,|1a\rangle\,|0b\rangle \exp(i\omega_1 t) + a_2(t)\,|2a\rangle\,|0b\rangle \exp[i(\omega_1+\omega_2)t] + a_3(t)\,|1a\rangle\,|1b\rangle \exp[i(\omega_1+\omega_3)t]\,. \qquad (2)$$

In the process the initial state $|0a\rangle|0b\rangle$ is virtually excited by the electromagnetic field to the state $|1a\rangle|0b\rangle$, which in turn is virtually excited by the electromagnetic field to the state $|2a\rangle|0b\rangle$. Finally, a collisional transfer from $|2a\rangle|0b\rangle$ to $|1a\rangle|1b\rangle$ nearly converses the overall energy for

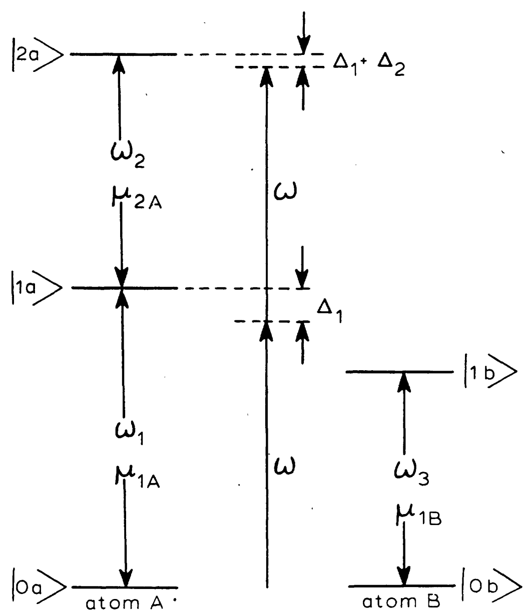

FIG. 1. A partial energy-level diagram of the two-photon–one-collision interaction.

the transition. Thus, substituting Eqs. (1) and (2) in the time-dependent Schrödinger equation gives the following equations for the time-dependent coefficients in the rotating-wave approximation:

$$\frac{da_0}{dt}=i\mu_{1A}E_0\exp(i\Delta_1 t)a_1\,,$$

$$\frac{da_1}{dt}=i\mu^*_{1A}E_0\exp(-i\Delta_1 t)a_0+i\mu_{2A}E_0\exp(i\Delta_2 t)a_2\,,$$

$$\frac{da_2}{dt}=i\mu^*_{2A}E_0\exp(-i\Delta_2 t)a_1+iV_2\exp(i\Delta'_0 t)a_3\,,$$

$$\frac{da_3}{dt}=iV^*_2\exp(-i\Delta'_0 t)a_2\,,$$

where $\Delta_1=\omega_1-\omega$, $\Delta_2=\omega_2-\omega$, $\Delta'_0=\omega_3-\omega_2$, μ_{iA} is the matrix element of the dipole moment μ_{iz} of atom A in units of $\hbar$, and V_2 is the matrix element $\langle|1a|\langle 1b|V_{ABz}|2a\rangle|0b\rangle/\hbar$.

We take $|\Delta_1|$, $|\Delta_2|$, and $|\Delta'_0|$ large enough such that $\Delta_1\gg\mu_{1A}E_0$, $\Delta_2\gg\mu_{2A}E_0$, $\Delta'_0\gg V_2$, and $|\Delta_1+\Delta_2|\geq\mu_{2A}E_0$. These conditions also imply that $da_0/dt\ll\Delta_1$, $da_2/dt\ll\Delta_2$, Δ_0; hence, we can integrate the equation for a_1 by parts and keep only the leading term. The resulting expression for a_1 is then substituted in the rest of the equations. Integrating the resulting equation for a_2 by parts, keeping the lowest-order term, and substituting back gives

$$\frac{da_0}{dt}+i(b'_1E_0^2+b'_2E_0^4)a_0=ic'_0E_0^2V_2\exp(i\delta t)$$

and

$$\frac{da_3}{dt}+ib_3V_2^2a_3=ic'_3E_0^2V_2\exp(-i\delta t)a_0\,,$$

where b'_i and c'_i are functions of the various detunings, and $\delta=\Delta_1+\Delta_2+\Delta_0$ is the detuning from exact resonance. These two equations are identical to those of single-photon radiative collisions,[1] except for the two-photon coupling $C'_0E_0^2$ and the Stark shifts. In the weak-field limit, these two equations reduce to $a_0=1$ and

$$\frac{da_3}{dt}-i\left(\frac{V_2^2}{\Delta_0}\right)a_3$$
$$=i\mu^*_{1A}\mu^*_{2A}E_0^2V^*_2[\Delta_1(\Delta_1+\Delta_2)]^{-1}\exp(-i\delta t)\,. \quad (3)$$

In the dipole-dipole interaction $V^*_2=\hbar\mu_{2A}\mu_{1B}/R^3$ where $R^2(t)=\rho^2+V^2t^2$, ρ is the impact parameter, and V is the relative speed of the atoms. When E_0 changes very little over the time of collision, Eq. (3) gives

$$|a_3(\infty)|^2=4\alpha^2E_0^4\left|\int_0^\infty R^{-3}(t)\cos\left(\int_0^t[CR^{-6}(t)+\delta]\,dt\right)dt\right|^2\,, \quad (4)$$

where $\alpha^2=\hbar^2\mu_{1A}^2\mu_{2A}^4\mu_{1B}^2[\Delta_1(\Delta_1+\Delta_2)]^{-2}$ and $C=\hbar^2\mu_{2A}^2\mu_{1B}^2/\Delta_0$.

Consider now the second case where both atoms interact with the radiation field. The state vector of the system is taken to be of the form (see Fig. 2)

$$\psi(t)=|0a\rangle|0b\rangle a_0(t)+|0a\rangle|1b\rangle\exp(i\omega_3t)a_1(t)+|1a\rangle|0b\rangle\exp(i\omega_1t)a_2(t)$$
$$+|2a\rangle|0b\rangle\exp[i(\omega_1+\omega_2)t]a'_2(t)+|1a\rangle|1b\rangle\exp[i(\omega_1+\omega_3)t]a_3(t)\,. \quad (5)$$

In the process, the initial state $|0a\rangle|0b\rangle$ is virtually excited by the electromagnetic field to the state $|0a\rangle|1b\rangle$. A virtual collision then transfers the excitation from $|0a\rangle|1b\rangle$ to the state $|1a\rangle|0b\rangle$ which in turn gets virtually excited by the electromagnetic field to $|2a\rangle|0b\rangle$. Finally, a collisional transfer from $|2a\rangle|0b\rangle$ to $|1a\rangle|1b\rangle$ nearly conserves the overall energy for the transition. Thus the time-dependent Schrödinger equation gives in the rotating-wave approximation:

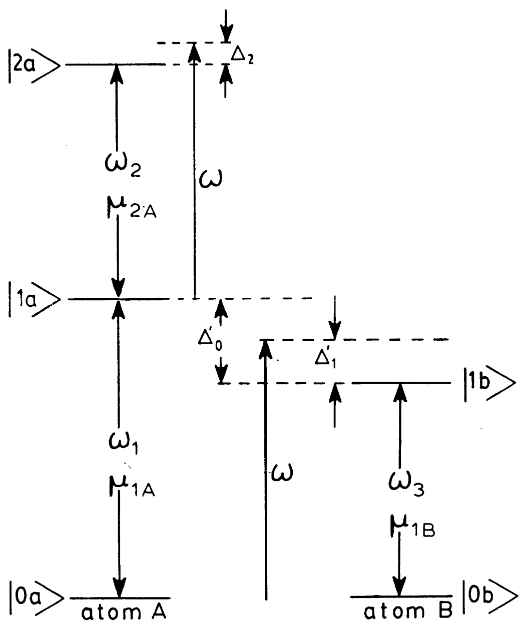

FIG. 2. A partial energy-level diagram of the two-photon–two-collision interaction.

$$\frac{da_0}{dt}=i\mu_{1B}E_0\exp(i\Delta_1't)a_1\,,$$

$$\frac{da_1}{dt}=i\mu_{1B}^*E_0\exp(-i\Delta_1't)a_0+iV_1\exp(-i\Delta_0't)a_2\,,$$

$$\frac{da_2}{dt}=iV_1^*\exp(i\Delta_0't)a_1+i\mu_{2A}E_0\exp(i\Delta_2t)a_2'\,,$$

$$\frac{da_2}{dt}=i\mu_{2A}^*E_0\exp(-i\Delta_2t)a_2+iV_2\exp(-i\Delta_0t)a_3\,,$$

$$\frac{da_3}{dt}=iV_2^*\exp(i\Delta_0t)a_2'\,,$$

where

$$\Delta_1'=\omega_3-\omega,\ \ \Delta_0'=\omega_3-\omega_1,$$

$$\Delta_2=\omega_2-\omega,\ \ \Delta_0=\omega_2-\omega_3\,,$$

$$\mu_{1B}=\langle 0b|\mu_{BZ}|1b\rangle/\hbar,\ \ \mu_{2A}=\langle 1a|\hat{\mu}_{AZ}|2a\rangle/\hbar\,,$$

$$V_1=\langle 0b|\langle 1a|\hat{V}_{ABZ}|0a\rangle|1b\rangle/\hbar,$$

$$V_2=\langle 1a|\langle 1b|V_{ABZ}|0b\rangle|2a\rangle/\hbar\,.$$

We take $\mu_{1B}^*E_0 \ll |\Delta_1'|$, $V_1 = \ll |\Delta_0'|$, $\mu_{2A}E_0 \ll |\Delta_2|$, $V_2 \ll |\Delta_0|$, $|\Delta_1'-\Delta_0'| = |\Delta_1| \geq V_1$, and eliminate a_1, a_2, and a_2' sequentially by integrating their equations by parts. The resulting equations have the form

$$\frac{da_0}{dt}+iS_1a_0=C_0E_0^2V_1V_2\exp(i\delta t)\,a_3$$

and

$$\frac{da_3}{dt}+iS_2a_3=C_4E_0^2V_1^*V_2^*\exp(-i\delta t)\,a_0\,,$$

where $S_1=b_1E_0^2+b_2E_0^2V_1^2+b_3E_0^4V_1^2$, $S_2=b_4V_2^2$, $\delta=\Delta_1+\Delta_2-\Delta_0-\Delta_0'$ is the detuning from exact resonance, and the coefficients b_i and c_i depend on the various detunings and the dipole-moment matrix elements. This effective two-state system is similar to the single-photon process except that an effective two-photon coupling replaces the single-photon coupling, and an effective two-collision coupling replaces the single collision coupling, and except for some additional shifts. The additional shifts are the ordinary ac Stark shifts ($b_1E_0^2$) and new novel intensity-induced collisional shifts ($b_2E_0^2V_1^2+b_3E_0^4V_1^4$). These induced shifts can be used to control the overall shift between the initial and final states making the line shape highly dependent on the intensity. In fact, one can conceive of a situation where most of the shift cancels out. In this paper we will consider the weak-field case to explain the effects of these shifts, and leave the strong-field case for a later study. In the weak-field limit, the process is described by the following equations:

$$\frac{da_0}{dt}+i\alpha_0E_0^2(V_1^2/\Delta_0')a_0=0\,, \tag{6}$$

$$\frac{da_3}{dt}+i\left(\frac{V_2^2}{\Delta_0}\right)a_3=i\alpha_4E_0^2V_1^*V_2^*e^{-i\delta t}\,, \tag{7}$$

where

$$\alpha_0=\mu_{1B}^2[\Delta_1'(\Delta_0'-\Delta_1')]^{-1}\,,$$

$$\alpha_4=\mu_{1B}^*\mu_{2A}[\Delta_1'(\Delta_0'-\Delta_1')(\Delta_1'+\Delta_2-\Delta_0')]^{-1}\,,$$

$\Delta_0'-\Delta_1'=\omega-\omega_1$, and $\Delta_1'+\Delta_2-\Delta_0'=\omega_1+\omega_2-2\omega$. We keep the shift proportional to $E_0^2V_1^2$ in Eqs. (6) and (7) since even in the weak-field limit, this shift may be of the same order as V_2^2/Δ_0. When E_0 changes very little over the time of collision, Eqs. (6) and (7) give

$$|a_3(\infty)|^2=4\alpha_4^2E_0^4\left|\int_0^\infty V_1^*V_2^*\cos S\,dt\right|^2, \tag{8}$$

where

$$S=\int_0^t (C'R^{-6}-\delta)dt,$$

$$C'=\hbar^2\mu_{2A}^2\mu_{1B}^2\Delta_0^{-1}-\hbar^2\alpha_0E_0^2\mu_{1B}^2\mu_{1A}^2\Delta_0'^{-1}.$$

In the dipole-dipole interaction Eq. (8) becomes

$$|a_3(\infty)|^2=4|\alpha'|^2E_0^4\left|\int_0^\infty R^{-6}\cos S\,dt\right|^2, \tag{9}$$

where

$$\alpha' = \frac{\hbar^2 \mu_{1B}^3 \mu_{2A}^2 \mu_{1A}}{[\Delta_1'(\Delta_0' - \Delta_1')(\Delta_1' + \Delta_2 - \Delta_0')]} = \hbar(\mu_{1B}^2/\Delta_1')\alpha .$$

We now discuss the line shape of the process. The absorption cross section σ is calculated from the integration of $|a_3(\infty)|^2$ over the impact parameters. A thermal average of the cross section $\bar{\sigma}$ then yields an absorption rate. For large C or C', all impact parameters can be integrated over because the frequency shift becomes large for R values $\lesssim 15$ Å, and there is no change in a_3 at R values where overlap is important and deviations from straight line trajectory occur. In fact, a universal line shape exists for the two-photon–one-collision case in analogy with the one-photon–one-collision case.[5] This line shape is given by the thermally average cross section, $\bar{\sigma} = \alpha^2 E_0^4 |C|^{-2/3}(2kT/\mu)^{-4/5} J(x)$ where T is the absolute temperature, μ is the reduced mass, $x = G|C|^{1/5}(2kT/\mu)^{-3/5}\delta$, G is the sign of C, and J is a function which essentially gives the line shape. The line shape is asymmetric with an extended red or blue tail corresponding to $G=+1$ and $G=-1$, respectively. A universal line shape also exists for the two-photon–two-collision case: It has a similar expression to the one-collision case except that J takes on a different function because the coupling involves R^{-6} rather than R^{-3}.

In the case where $C \simeq C'$ is large, the contribution from the two-collision case is smaller than the contribution from the one-collision case. This is because the radiative collision coupling in the latter is smaller than that of the former by V_1/Δ_0'. Although at small impact parameters this factor becomes larger, the dephasing factor cuts off contributions from this region more severely.

At some intensities, however, C' can become very small even in the weak-field limit. For example, taking $\mu_{2A}/\mu_{1A} = 0.1$ and $\Delta_0'/\Delta_0 = 0.1$, then $C' = 0$ for $\mu_{1B}^2 E_0^2/[\Delta_1'(\Delta_0' - \Delta_1')]^{-1} = 10^{-3}$. The situation where C' is very small suggests a large coupling coefficient in the absence of any dephasing effect for all internuclear separations $R \geq 4$ Å. This could lead to extremely large cross sections for the process. Moreover, because of the absence of the shift, the line shape is expected to be symmetric. However, because of the detuning at small R, orbiting phenomena play a significant role. An estimate of the magnitude of the cross section at the peak of the resonance can be determined from Eq. (9) by taking $C' = 0$ and $\delta = 0$. In this case $|a_3(\infty)|^2 = 1.5\pi\alpha'^2 E_0^4/(\rho^{10}V^2)$. A lower limit on the estimate can be found by calculating the contribution from impact parameters where orbiting is not important; that is,

$$\sigma_2 > \int_{\rho_c}^{\infty} 2\pi\rho\, d\rho |a_3(\infty)|^2 = 3\pi^2\alpha'^2 E_0^4 (V\rho_c^4)^{-2} .$$

Taking $\rho_c = 4$ Å, $V = 5\times10^4$ cm/sec., $\mu_{2A} = 0.4$ a.u., $\mu_{1A} = 4$ a.u., $\mu_{1B} = 4$ a.u., $\mu_{1B}^2 E_0^2/[\Delta_1'(\Delta_0' - \Delta_1')] = 10^{-3}$, $\Delta_1' - \Delta_2 - \Delta_0' = 2500$ cm^{-1}, and $\Delta_1 = 1000$ cm^{-1}, then $\sigma_2 > 0.6$ Å^2. The cross section at the peak of the two-photon–one-collision case is estimated to be $8\pi\alpha^2 E_0^4(V^2\rho_0^2)^{-1}$, where ρ_0 is the Weiskoff radius. The ratio of the cross section of the one-collision to the two-collision case is $\sim\hbar^2\mu_{1B}^4\rho_0^2(\Delta_1'^2\rho_c^8)^{-1}$. Taking $\Delta_0 = 5000$ cm^{-1}, then $\hbar^3\mu_{2A}^2\mu_{1B}^2/\Delta_0 = 1.2 \times 10^{-64}$ J cm^6, $\rho_0 = 13$ Å, and the ratio is 10^3. Therefore, the one-collision contribution is negligible compared to the two-collision contribution. The line shape in this case is symmetric.

The fact that the cross section of the two-collision case is larger than 0.6 Å^2 makes the process measurable. We will, however, analyze the strong-field case in a later work. The strong-field case allows more choices of a system for experimentation.

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