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Laser-induced autoionization of transient molecules

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Laser-induced autoionization of transient molecules is investigated. The peculiarity of the process is that three different kinds of interaction (collisional, radiative, and Coulombic) are simultaneously present. The results show that laser-induced quantum interferences occurring in the continuum of the ionization of atoms can play an important role also in processes dominated by strong collisions.

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Quantum interferences occurring in the continuum of ionization of atoms have received a revival of interest since the recent proposal by Harris of radiation amplification without population inversion [1]. Laser-induced autoionization of atoms is characterized by two interfering ionization channels (photoionization and autoionization) leading, in the weak-field limit, to the Fano absorption profile [2] and, in the strong-field regime, to other coherent phenomena such as the trapping of atomic population [3], the confluence of coherences in the electron spectrum [4], and the enhancement of the photon yield [5]. The possibility of inducing structures in the continuum of ionization using an intense radiation field has also attracted theoretical [6] and experimental [7] attention.

In this paper a theoretical study of laser-induced quantum interferences occurring in the continuum of ionization of transient molecules is presented. Transient molecules are formed during collisions between different atoms with quasiresonant excited states whose energy difference is much larger than the inverse of the collisional time. Significant examples of radiative transitions involving transient molecules, usually called radiative collisions, are provided by laser-induced collisional energy transfer (LICET) [8–10], pair absorption and emission [11], multiphoton transitions [12], and resonance fluorescence [13] in radiative collisions.

The LICET process is described by the reaction

$$A^* + B + \hbar\Omega \rightarrow A + B^* , \qquad (1)$$

where the asterisks denote electronic excited states of atoms A and B colliding in the presence of a monochromatic laser field of frequency Ω near resonant with the A^*-B^* interatomic transition. The process is conveniently described in terms of quasimolecular states, considering the interatomic transition taking place in (1) as due to a transfer of energy among adiabatic states of a transient molecule formed during the collision. The extension of the LICET reaction to the case that the final state of atom B is a discrete level imbedded in a continuum of free states (autoionizing level) provides the scheme for laser-induced autoionization of a transient molecule. The peculiarity of the process is that three different kinds of interaction (collisional, radiative, and Coulombic) are simultaneously present. A major motivation for this work is to point out whether quantum interference effects in the continuum of ionization of atoms can play an important role also in processes dominated by strong collisions.

Figure 1 shows a schematic energy-level diagram of the model. It is assumed that atom A can be described by two discrete states $|\alpha_j\rangle$ ($j=1,2$) and atom B by three discrete states $|\beta_j\rangle$ ($j=1,2,3$) and a flat continuum of free states $|\beta_\omega\rangle$. State $|\beta_3\rangle$ overlaps the continuum $|\beta_\omega\rangle$ and the Coulombic interaction mixes these states [2]. The first ionization limit of atom A lies in energy well above state $|\beta_3\rangle$ and no excited state of atom A is near resonant with $|\beta_3\rangle$. States $|\alpha_1\rangle$ and $|\alpha_2\rangle$ are coupled by a one-electron, dipole-allowed transition, as well as states $|\beta_1\rangle$ and $|\beta_2\rangle$, $|\beta_2\rangle$ and $|\beta_3\rangle$, and $|\beta_2\rangle$ and $|\beta_\omega\rangle$.

In the following, while keeping the formulation general, I have in mind the case of collisions between two dissimilar atoms with two valence electrons each. For such a system the energy-level scheme can be similar to that shown in Fig. 1, where $|\alpha_1\rangle$ and $|\beta_1\rangle$ are the $(n_A s^2)S$ and $(n_B s^2)S$ ground states, $|\alpha_2\rangle$ and $|\beta_2\rangle$ are $(n_A s, n'_A p)P$ and $(n_B s, n'_B p)P$ excited states, $|\beta_3\rangle$ is a $(n'_B p, n''_B p)S$ autoionizing state, and $|\beta_\omega\rangle$ denotes the $[B^+(n_B s)+e(l=0)]S$ continuum states of atom B.

Atom A, prepared in the excited state $|\alpha_2\rangle$, undergoes a collision with atom B, in the ground state, in the presence of a monochromatic laser field, of frequency Ω, near resonant with the $|\alpha_2\rangle$-$|\beta_3\rangle$ interatomic transition. If $|\beta_2\rangle$ is nearly resonant with $|\alpha_2\rangle$, the process is characterized by the formation, during the collision, of a transient molecule that can follow two different pathways to ionize. An appropriate basis to study the problem is then provided by

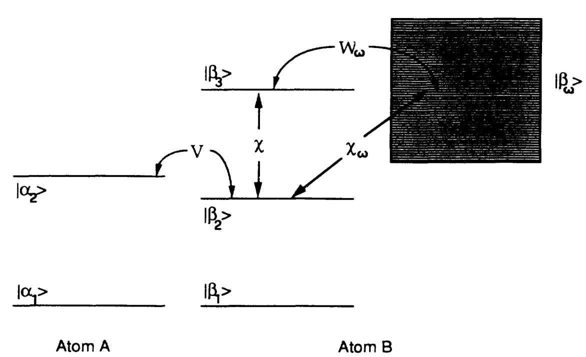

FIG. 1. Schematic energy-level diagram of the model.

the following product states:

$$|1\rangle=|\alpha_2\rangle|\beta_1\rangle\,,\quad |2\rangle=|\alpha_1\rangle|\beta_2\rangle\,,$$
$$|3\rangle=|\alpha_1\rangle|\beta_3\rangle,\quad |\omega\rangle=|\alpha_1\rangle|\beta_\omega\rangle\,, \tag{2}$$

which are of energy $\hbar\omega_j$ $(j=1,2,3)$ and $\hbar\omega$, respectively. In the following I assume $\omega_1>\omega_2$. The process is governed by three different kinds of interaction characterized by the following matrix elements:

$$V=\langle 2|\hat{V}|1\rangle,\quad \chi=\langle 3|\hat{\chi}|2\rangle\,,$$
$$\chi_\omega=\langle\omega|\hat{\chi}|2\rangle,\quad W_\omega=\langle\omega|\hat{W}|3\rangle\,, \tag{3}$$

where $\hat{V}$, $\hat{\chi}$, and $\hat{W}$ denote the operators describing the collisional, radiative, and Coulombic interactions, respectively.

The equations of motion for the probability amplitudes of states (2) are written, in the rotating-wave approximation, as follows:

$$i\dot{a}_1=\omega_1 a_1+Va_2\,,$$
$$i\dot{a}_2=\omega_2 a_2+Va_1-\left[\chi a_3-\sum\!\!\!\!\!\!\int_\omega \chi_\omega a_\omega\right]\exp[i\Omega t]\,,$$
$$i\dot{a}_3=\omega_3 a_3-\chi a_2\exp[-i\Omega t]+\sum\!\!\!\!\!\!\int_\omega W_\omega a_\omega\,,$$
$$i\dot{a}_\omega=\omega a_\omega-\chi_\omega a_2\exp[-i\Omega t]+W_\omega a_\omega\,, \tag{4}$$

with initial conditions $a_1(-\infty)=1$, $a_2(-\infty)=a_3(-\infty)=a_\omega(-\infty)=0$.

In writing (4) the same basic assumptions of existing LICET theoretical models have been made [8,9]: (i) The atoms are assumed to follow classical and rectilinear trajectories with interatomic separation $R=(b^2+v^2t^2)^{1/2}$ (b is the impact parameter and v the relative velocity); (ii) the laser field, assumed constant during the collision, is described classically; (iii) the magnetic degeneracy of the states involved in the transitions is neglected and the collisional interaction is described by a scalar potential.

The photoelectron spectrum $P_e(\Omega,\omega)$ and the cross section $P(\Omega)$ of the process (ion yield versus laser frequency) are then given, after averaging over the impact parameters b, respectively, by

$$P_e(\Omega,\omega)=2\pi\int_0^{+\infty} b(|a_\omega(+\infty)|^2)db\,, \tag{5}$$

$$P(\Omega)=2\pi\int_0^{+\infty} b\left(\sum\!\!\!\!\!\!\int_\omega |a_\omega(+\infty)|^2\right)db\,. \tag{6}$$

The solution of the problem is not trivial. However, in the weak-field limit, it is possible to uncouple the time evolution of states $|1\rangle$ and $|2\rangle$ from that of states $|3\rangle$ and $|\omega\rangle$ diagonalizing separately the collisional interaction between states $|1\rangle$ and $|2\rangle$ and the Coulombic interaction among states $|3\rangle$ and $|\omega\rangle$.

The first diagonalization is accomplished by introducing the collisional dressed states [9] defined by

$$|+\rangle=\cos\theta|1\rangle+\sin\theta|2\rangle,\quad |-\rangle=\cos\theta|2\rangle-\sin\theta|1\rangle \tag{7}$$

with $\tan(2\theta)=2V/(\omega_1-\omega_2)$. The collisional dressed states (7) are quasimolecular states with adiabatic time-dependent eigenvalues given by

$$\lambda_+=\{\omega_1+\omega_2+[(\omega_1-\omega_2)^2+4V^2]^{1/2}\}/2\,,$$
$$\lambda_-=\{\omega_1+\omega_2-[(\omega_1-\omega_2)^2+4V^2]^{1/2}\}/2\,. \tag{8}$$

The second diagonalization is accomplished by introducing the Fano states $|\varepsilon\rangle$ of energy $\hbar\varepsilon$ defined by [2]:

$$|\varepsilon\rangle=(\sin\Delta/\pi W_\omega)|3\rangle_d-\cos\Delta|\omega\rangle\,, \tag{9}$$

where

$$|3\rangle_d=|3\rangle+\mathrm{P}\sum\!\!\!\!\!\!\int_\omega [W_\omega/(\varepsilon-\omega)]|\omega\rangle \tag{10}$$

is the discrete state $|3\rangle$ dressed by the continuum (P indicates the principal part),

$$\tan\Delta=\pi|W_\omega|^2/[\omega_3+F(\varepsilon)-\varepsilon]\,, \tag{11}$$

and $F(\varepsilon)$ is a small energy shift that will be ignored hereafter.

The matrix elements of $\hat{\chi}$ between the discrete state $|2\rangle$ and the continuum of states in the new and old basis are related by

$$\chi_\varepsilon=\chi_\omega(q\sin\Delta-\cos\Delta)\,, \tag{12}$$

where q is the Fano parameter given by

$$q=\langle 2|\hat{\chi}|3\rangle_d/(\pi W_\omega\chi_\omega)\approx\chi/(\pi W_\omega\chi_\omega)\,. \tag{13}$$

When the condition

$$|\dot{V}/V|\ll(\omega_1-\omega_2) \tag{14}$$

is satisfied, the following solution to the first order in the laser field is easily obtained for the probability amplitudes a_ε of states $|\varepsilon\rangle$:

$$a_\varepsilon\approx i\chi_\varepsilon\exp(-i\varepsilon t)\int_{-\infty}^{t}\sin\theta\exp\left[-i\int_{-\infty}^{t'}(\Omega+\lambda_+-\varepsilon)dt''\right]dt'\,. \tag{15}$$

The photoelectron spectrum is then given by

$$P_e(\Omega,\varepsilon)=2\pi\int_0^{+\infty} b|a_\varepsilon(+\infty)|^2db=2\pi|\chi_\varepsilon|^2\int_0^{+\infty} b\left|\int_{-\infty}^{+\infty}\sin\theta\exp\left[-i\int_{-\infty}^{t}(\Omega+\lambda_+-\varepsilon)dt'\right]dt\right|^2$$
$$=|\chi_\varepsilon|^2\sigma(\Omega,\varepsilon)\,, \tag{16}$$

while the cross section $P(\Omega)$ assumes the expression of a convolution integral

$$P(\Omega)=2\pi\int_0^{+\infty} b\left(\sum\!\!\!\!\!\!\int_\varepsilon |a_\varepsilon(+\infty)|^2\right)db=\sum\!\!\!\!\!\!\int_\varepsilon |\chi_\varepsilon|^2\sigma(\Omega,\varepsilon)\,, \tag{17}$$

where $|\chi_\varepsilon|^2$ is the asymmetric Fano profile [2],

$$|\chi_\varepsilon|^2=|\chi_\omega|^2(q\gamma/2-\omega_3+\varepsilon)^2/[(\omega_3-\varepsilon)^2+(\gamma/2)^2]\,, \quad (18)$$

characterizing the $|\beta_2\rangle$-$|\beta_3\rangle$ transition ($\gamma=2\pi|W_\omega|^2$, autoionization decay rate), and

$$\sigma(\Omega,\omega_3)=2\pi\int_0^{+\infty} b\left|\int_{-\infty}^{+\infty}\sin\theta \times\exp\left[-i\int_{-\infty}^{t}(\Omega+\lambda_+-\omega_3)dt'\right]dt\right|^2 db \quad (19)$$

is the expression of the LICET excitation spectrum for a bound final state [9].

In the present model, level $|\beta_3\rangle$ can be removed by taking the limit $\gamma\rightarrow 0$ with $q\gamma\rightarrow 0$, while the continuum $|\beta_\omega\rangle$ can be removed by taking the limit $\gamma\rightarrow 0$ with $q\gamma\neq 0$. In the first case the photoelectron spectrum reproduces the LICET excitation spectrum, while $P(\Omega)$ becomes a flat function of Ω. In the second limit $|\chi_\varepsilon|^2$ reduces to a delta function centered at ω_3 and $P(\Omega)$ to the LICET excitation spectrum.

Theoretical [9] and experimental [10] studies show that the LICET cross section $\sigma(\Omega,\omega_3)$, peaked at the interatomic transition frequency $\omega_3-\omega_1$, is characterized by a strongly asymmetric shape with an exponential falloff on one side, and an extended wing, following the double-slope law $\sigma(\Omega,\omega_3)\propto(\omega_3-\omega_1-\Omega)^{-0.5}(\omega_3-\omega_2-\Omega)^{-1.5}$, in the frequency region where the energy defect of the laser photon can be compensated by the collisional shift of atomic levels. A very good analytical expression for $\sigma(\Omega,\varepsilon)$ is then provided by

$$\sigma(\Omega,\varepsilon)=\begin{cases}\sigma_0\exp[(\varepsilon-\omega_1-\Omega)/\Delta_c], & (\varepsilon-\omega_1-\Omega)\le 0\\ \sigma_0\omega_{12}^{1.5}\Delta_c^{0.5}\{(\varepsilon-\omega_1-\Omega)+\Delta_c\exp[(\Omega+\omega_1-\varepsilon)/\Delta_c]\}^{-0.5}(\varepsilon-\omega_2-\Omega)^{-1.5}, & (\varepsilon-\omega_1-\Omega)\ge 0\,,\end{cases} \quad (20)$$

where $\omega_{ij}=\omega_i-\omega_j$, $\Delta_c=2\pi/t_c$ (t_c, typical collisional time $\approx$1–10 ps) and $\omega_{12}/\Delta_c\gg 1$ satisfying the adiabaticity condition (14). The exponential factor appearing in the lower part of Eq. (20) has been introduced in a phenomenological way to describe the experimental behavior of the LICET cross section at the line center. Expressions (16) and (17) have been calculated for different values of q and γ/Δ_c using (18) and (20).

For $\gamma/\Delta_c\ll 1$ the autoionization lifetime is much longer than the collisional time and autoionization of level $|\beta_3\rangle$ follows in time the transfer of population from state $|\alpha_2\rangle$ to state $|\beta_3\rangle$ due to the combined action of collisional and radiative interactions. For $q\rightarrow 0$ (predominant photoionization) the electron spectrum, peaked at $\varepsilon=\Omega+\omega_1$, reproduces the LICET cross section and $P(\Omega)$ becomes a

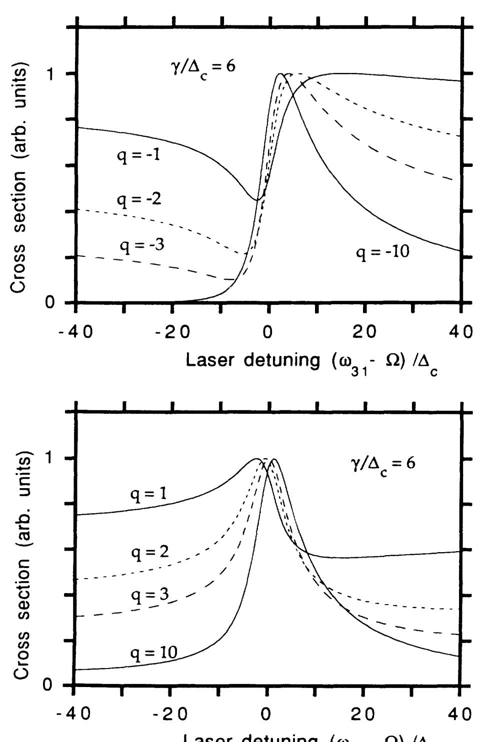

FIG. 2. Normalized ion yield vs adimensional laser detuning $(\omega_{31}-\Omega)/\Delta_c$ for $\omega_{12}/\Delta_c=40$, $\gamma/\Delta_c=6$, and different values of Fano q parameter.

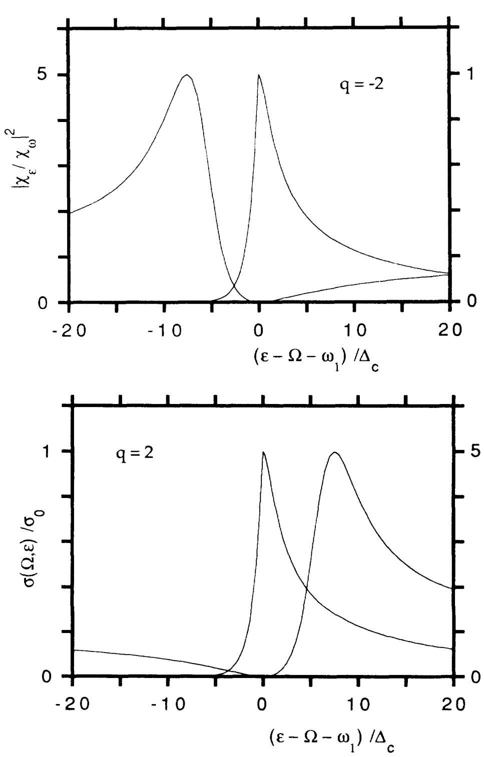

FIG. 3. Spectral behavior of $|\chi_\varepsilon|^2$ and $\sigma(\Omega,\varepsilon)$ for $q=\pm 2$, $\omega_{12}/\Delta_c=40$, $\gamma/\Delta_c=6$, and laser detuning $\omega_{31}-\Omega=q\gamma/2$.

flat function of Ω, while for $q \gg 1$ (negligible photoionization) $P_e(\Omega,\varepsilon)$ becomes a Lorentzian function of width γ centered at $\varepsilon=\omega_3$ and $P(\Omega)$ reduced to the LICET cross section.

For $\gamma/\Delta_c \gtrsim 1$ autoionization of level $|\beta_3\rangle$ occurs during the collisional interaction. For a strongly asymmetric Fano profile ($|q| \approx 1$–3), the electron spectrum shows the effect of quantum interferences in the range $|q|\gamma/2 \lesssim (\omega_{31}-\Omega) \lesssim \omega_{12}$ for both positive and negative values of q. However, as shown in Fig. 2, destructive interferences lead to a deep minimum in the cross section $P(\Omega)$ only for $q<0$. Figure 3, showing the spectrum behavior of $|\chi_\varepsilon|^2$ and $\sigma(\Omega,\varepsilon)$, explains this result. When the laser is tuned at the minimum of the Fano profile ($\Omega+\omega_1=\omega_3-q\gamma/2$) the peak of $\sigma(\Omega,\varepsilon)$ overlaps the minimum of $|\chi_\varepsilon|^2$, leading to a strong destructive interference in the electron spectrum at $\varepsilon=\omega_3-q\gamma/2$ for both positive and negative values of q. However, while for $q<0$ the peak of $|\chi_\varepsilon|^2$ is in the frequency range where $\sigma(\Omega,\varepsilon)$ vanishes exponentially, for $q>0$ the peak of $|\chi_\varepsilon|^2$ overlaps the static wing of $\sigma(\Omega,\varepsilon)$, leading to an enhancement in the electron spectrum at $\varepsilon=\omega_3+\gamma/2q$ which widely compensates for the minimum at $\varepsilon=\omega_3-q\gamma/2$. When $|q|\gamma$ is of the order of the collisional shift of level $|\alpha_2\rangle$ ($\gamma/\omega_{12} \gtrsim 1$), the minimum of $P(\Omega)$ tends to zero and $P(\Omega)$ reproduces essentially the Fano profile $|\chi_\varepsilon|^2$ (Fig. 4).

In summary, laser-induced autoionization of transient molecules has been investigated. The presence of deep minima in the cross section of the process shows that destructive interferences between the two ionization pathways of the transient molecule formed during the collision can partially inhibit the ionization of the colliding atoms. This suggests that laser-induced quantum-interference effects in the continuum of ionization of atoms can play an important role also in processes dominated by strong collisions.

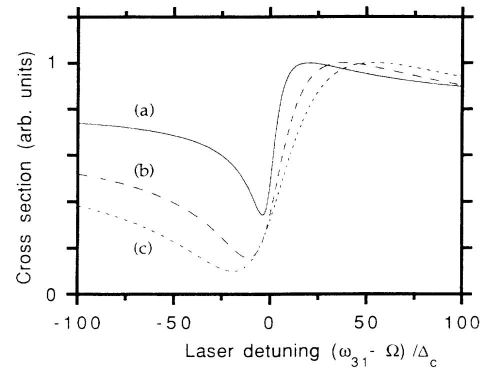

FIG. 4. Normalized ion yield vs adimensional laser detuning $(\omega_{31}-\Omega)/\Delta_c$ for $\omega_{12}/\Delta_c=40$, $q=-1$, and different values of γ/Δ_c [(a) 10, (b) 30, and (c) 50].

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