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Radiative collision-induced photoionization

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Semiclassical expressions of two-photon ionization of atoms induced by radiative collisions are derived. The dependence of the ionization yield on the atomic forces, field intensity, and energy gap is derived. Although absorption tends to decrease as the field intensity rises due to stimulated emission at the second crossing, the two-photon ionization yield can be nearly saturated at the first crossing, thus enhancing the absorption. Both regions, ionization in single collisions and ionization between collisions, are treated. In the latter we find that saturation of the ionization can be achieved at much reduced intensities. This process promises an extremely sensitive method for studying radiative collisions, especially when absorption or fluorescence becomes extremely weak.

I. INTRODUCTION

Atomic collisions in the presence of electromagnetic fields are continuing to receive attention theoretically and experimentally[1-24] because of their relevance to laser fusion and isotope separation and to numerous other interesting applications which include development of radiative-collision lasers,[11] up conversion of long-wavelength radiation, increasing the reaction rates of selected gas-phase chemical reactions,[18] extracting potential curves of the interacting system,[16] and studying spin and charge exchange.[15,18] Recently we extended the optical-collision studies by studying two-photon ionization of the colliding atoms.[19] Because complete conversion of every absorption event to an ion pair is possible,[23] the ionization channel promises extreme sensitivity since it is easier to detect a small number of electrons than a small number of photons. This allows measurement at the extreme wing where absorption or fluorescence becomes vanishingly small.[24] Even single absorption events can be detected with ease by gas proportional counters which are sensitive to single electrons.[23]

In this work, we study some aspects of atom-atom (-ion) collisions in the presence of electromagnetic fields by studying two-photon ionization of atoms assisted by radiative collision. The process involves an atom in an excited state colliding with another atom (ion). We assume that, in absence of the collision, the two-photon ionization has a vanishingly small cross section because of the absence of resonant intermediate states or because of a high ionization potential. In the presence of the collision and when the photon energy plus the energy of the excited state of the atom matches an energy level of the atom, resonant collisional transfer takes place, thus providing a real resonant intermediate level for the laser field interaction with the system. These systems can be chosen such that one more photon absorbed by the system can further ionize it. Ionizing the atom-atom system, therefore, can be sensitive in monitoring near resonant collisional transfer, especially when the yield becomes vanishingly small.

We derive the ionization-yield dependence on the interaction forces between the atoms, as well as on the excitation intensity and the energy gap. Although the absorption of the system might normally decrease as the intensity of excitation increases due to stimulated emission at the second crossing, the two-photon ionization yield can be nearly saturated at the first crossing, thus enhancing the absorption. When the absorption is weak and the ionization takes place between collisions, saturation of the ionization can be achieved at moderate excitation intensities. The far-wing wavelength dependence of the ionization yield induced by collisional transfer falls off with the square root of the detuning, while the corresponding effect in charge exchange drops faster and is more complicated since it is due to overlap.

This paper consists of four sections. In Sec. II, we give the formulation and the solution for the absorption probabilities. Section III treats the ionization yield, and, in Sec. IV, we give some concluding remarks.

II. ABSORPTION PROBABILITY

We consider an atom-atom (-ion) collision in the presence of an electromagnetic field. One atom A is assumed to be in an excited state, while the other atom (ion) B is in its ground state. In the case where the process can occur at long range with no overlap taking place, an atomic basis of the process can be used. However, in the case where overlap is an integral part of the interaction, the process should be treated from the viewpoint of quasimolecular absorption. In any case, when radiative collisions are considered, where one of the colliding partners is in an excited state, the effective interaction Hamiltonian depends on both the collisional coupling and the electromagnetic field coupling. This effective Hamiltonian can be best derived taking an atomic viewpoint of the interaction. Therefore, we will consider the atomic viewpoint first.

To solve for the two-photon ionization of the system, we start with the Schrödinger equation in the dipole classical-field approximation:

$$i\hbar \frac{\partial}{\partial t}\psi = H\psi, \tag{1}$$

$$H = H_A + H_B + H_{AB} - \vec{\mu}_A \cdot \vec{\epsilon}, \tag{2}$$

where H_A and H_B are the electronic Hamiltonians of the isolated atoms; H_{AB} is the atom-atom interaction; $\vec{\mu}_A$ and $\vec{\mu}_B$ are the dipole moments of atoms A and B, respectively; and $\vec{\epsilon}$ is the classical electromagnetic field $\vec{E}\cos\omega t$ with frequency ω. In writing H_{AB}, the impact-parameter method will be used where the internuclear coordinates are treated classically and without acceleration in the motion. That is, $\vec{R} = \vec{b} + \vec{V}_t$ and $\vec{b}\cdot\vec{V} = 0$, where $\vec{b}$ is the impact parameter and $\vec{V}$ the relative velocity of the nuclei. However, deviation from straight-line trajectories will be considered in the case of charge transfer at slow velocities.

We assume that the dipole-moment matrix elements between $|2a\rangle$ and $|0a\rangle$ and between $|1b\rangle$ and $|0b\rangle$ are oriented along the lines joining the two atoms (rotating-atom approximation). The motive for using the rotating-atom approximation is that it eliminates the magnetic sublevels and thus simplifies the calculation. However, it is only good to a factor of 2. This approximation has been previously used in dealing with collisions in line broadening[25] (50% error), in Penning ionization by atoms in resonance states[26] (30% error), and in several other types of collisions.[27] Therefore, the system is represented by field-free electronic states, and we consider only three product discrete states and an infinite set of continuum states (Fig. 1). The wave function of the system can then be written as follows:

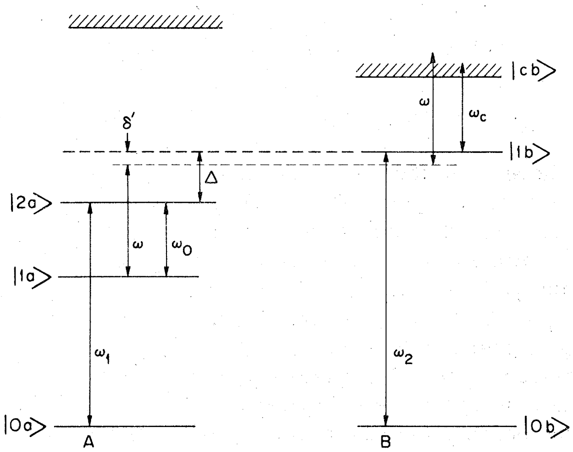

FIG. 1. Energy level diagram of the colliding system.

$$\psi = a_0 \exp[-i(\omega_{A1}+\omega_{B0})t]\,|1a\rangle\,|0b\rangle + a_1 \exp[-i(\omega_{A2}+\omega_{B0})t]\,|2a\rangle\,|0b\rangle + a_2 \exp[-i(\omega_{A0}+\omega_{B1})t]\,|0a\rangle\,|1b\rangle + \int a_c \exp[-i(\omega_{A0}+\omega_{Bc})t]\,|0a\rangle\,|cb\rangle\, d\hbar\omega_{Bc}, \tag{3}$$

where ω_{xi} is the absolute frequency of level $|ix\rangle$ with $i = 0, 1, 2$, or c; and $x = A$ or B. The product state $|1a\rangle|0b\rangle$ is the ground state of the system where atom A is an initial excited state $|1a\rangle$ while the atom B is in its ground state $|0b\rangle$. State $|2a\rangle|0b\rangle$ is reached after the system absorbs one photon, and thus atom A is excited to $|2a\rangle$ state while atom B is still in its ground state $|0b\rangle$. After the collision takes place and the transfer occurs, the system evolves to the product state $|0a\rangle|1b\rangle$ where atom A is in the ground state and atom B is in an excited state $|1b\rangle$. The product $|0a\rangle|cb\rangle$ describes the photoionization of the system after the transfer process has occurred. State $|cb\rangle$ is a continuum state of the atom B. An infinite set of continuum states has been included by performing the integration over the energy of the photoelectron. Time-dependent amplitudes of the discrete states and continuum states are represented by a_m and a_c, respectively.

To calculate the two-photon ionization amplitude, one has to solve the equations of motion (1)–(3) with the initial condition $a_0(-\infty) = 1$, $a_1(-\infty) = a_2(-\infty) = a_c(-\infty) = 0$. Substituting Eq. (3) in Eq. (1) and using the rotating-wave approximation, one gets the following set of equations for the amplitudes a_m and a_c when the field is linearly polarized:

$$\frac{d}{dt}a_0 = i\mu_A E e^{-i\Delta_1 t} a_1, \tag{4}$$

$$\frac{d}{dt}a_1 = i\mu_A^* E e^{i\Delta_1 t} a_0 + i v e^{i\Delta_2 t} a_2, \tag{5}$$

$$\frac{d}{dt}a_2 = iv^* e^{-i\Delta_2 t}a_1 + i\int \mu_B E e^{-\Delta_c t} a_c \, d\hbar\omega_{Bc}, \tag{6}$$

$$\frac{d}{dt}a_c = i\mu_B^* E e^{i\Delta_c t} a_2, \tag{7}$$

where μ_A is the matrix element in units of $\hbar$, of the atomic dipole operator between states $|1a\rangle$ and $|2a\rangle$; v is the matrix element, in units of $\hbar$, of the interaction Hamiltonian H_{AB} between states $|2a\rangle$ and $|1b\rangle$; $\Delta_c = \omega_c - \omega$; $\Delta_1 = \omega_0 - \omega$; $\Delta_2 = \omega_1 - \omega_2$; μ_B is the matrix element, in units of $\hbar$, of the dipole operator between the $|1b\rangle$ state and the continuum state $|cb\rangle$, where ω_i are given in Fig. 1. In writing Eqs. (4)–(7), we have neglected scattering between the continuum states by neglecting the coupling between them in Eq. (7).

In order to simplify the calculation, we separate the continuum states into two sets; the first set is close to the resonance condition $|\Delta_c| \leq |\Delta_c^0|$, where $|\Delta_c^0|$ is a small quantity, and the second set is that which is sufficiently far away from resonance $|\Delta_c| \geq |\Delta_c^0|$. When Δ_c is large, energy is not conserved as a result of nonresonant continuum states; consequently, intensity-dependent frequency shifts are introduced in level $|1b\rangle$. The near-resonant continuum states, however, result in intensity-dependent sink, or decay to level $|1b\rangle$. When Δ_c is large, the right side of Eq. (7) oscillates swiftly; and if the field is a slowly varying function of time, one can solve Eq. (7) for a_c by integrating over time by parts:

$$a_c = (\mu_B^* E/\Delta_c) e^{i\Delta_c t} a_2. \tag{8}$$

However, when near-resonant states are considered, i.e., Δ_c is small, a_c can only be represented as a full integral:

$$a_c = i\mu_B^* \int E e^{i\Delta_c t} a_2(t)\, dt. \tag{9}$$

Substituting expression (8), which is valid for $|\Delta_c| \geq |\Delta_c^0|$, in Eq. (6) results in an expression for the shift as an integral over Δ_c. Substituting expression (9), which is valid for $|\Delta_c| \leq |\Delta_c^0|$, in Eq. (6) and carrying out the integration over Δ_c first with the assumption that μ_B is fairly constant for $|\Delta_c| \leq |\Delta_c^0|$ enables one to easily carry out the integration over time:

$$\frac{da_0}{dt} = i\mu_A E e^{-i\Delta_1 t} a_1, \tag{10}$$

$$\frac{da_1}{dt} = i\mu_A^* E e^{i\Delta_1 t} a_0 + ive^{i\Delta_2 t} a_2, \tag{11}$$

$$\frac{da_2}{dt} + (\Gamma + is)a_2 = iv^* e^{-i\Delta_2 t} a_1, \tag{12}$$

where

$$\Gamma = \gamma_1(t) + \gamma_0, \tag{13}$$

γ_0 is a spontaneous-emission decay rate included phenomenologically,

$$s = -E^2 P \int \frac{\mu_B^2}{\Delta_c}\, dh\omega_{Bc}, \tag{14}$$

$$\gamma_1 = h\pi E^2 \mu_B^2, \tag{15}$$

and P stands for principal value. The above scheme of eliminating the continuum states was also used in photoionization of isolated[28] and colliding atoms.[19] We consider cases where the laser is tuned to near resonance, i.e., $\Delta_1 \sim \Delta_2$, and write this as $\Delta_1 = \Delta_2 + \delta'$, $\Delta_2 = \Delta$, where $\delta' \ll \Delta_2$. Also, let us define $a_0 = \bar{A}_0$, $a_1 = \bar{A}_1 \exp[i(\Delta_2 + \delta')t]$, and $a_2 = \bar{A}_2 e^{i\delta' t}$. Equations (10)–(12) reduce to

$$\frac{d\bar{A}_0}{dt} = i\mu_A E \bar{A}_1, \tag{16}$$

$$\frac{d\bar{A}_1}{dt} + i(\Delta + \delta')\bar{A}_1 = i\mu_A^* E \bar{A}_0 + iv\bar{A}_2, \tag{17}$$

$$\frac{d\bar{A}_2}{dt} + i(\delta' + s - i\Gamma)\bar{A}_2 = iv^* \bar{A}_1. \tag{18}$$

The interesting situation is when $\hbar\Delta \gg kT$ so that thermal collisional transfer does not take place. Also, to prevent thermal transfer, $\mu_A E$ has to be much smaller than $\hbar\Delta$ so that power broadening will not bridge the gap. Therefore, in this situation $\bar{A}_1$ is sufficiently far from resonance that $d\bar{A}_1/dt$ can be neglected relative to $\Delta\bar{A}_1$ in Eq. (17); thus, one can solve for $\bar{A}_1$ in terms of $\bar{A}_0$ and $\bar{A}_2$. This procedure of eliminating a nonresonant intermediate state results in frequency shift of the effective collisionally induced photoabsorption process

$$\bar{A}_1 = \frac{\mu_A^* E}{\Delta + \delta'}\bar{A}_0 + \frac{v}{\Delta + \delta'}\bar{A}_2. \tag{19}$$

Substituting Eq. (19) in Eqs. (16) and (18), we get

$$\left[\frac{d}{dt} - \frac{i\mu_A^2 E^2}{\Delta + \delta'}\right]\bar{A}_0 = \frac{i\mu_A E v_2}{\Delta + \delta'}\bar{A}_2, \tag{20}$$

$$\left[\frac{d}{dt} + i\left(\delta' + s - i\Gamma - \frac{v_1^2}{\Delta + \delta'}\right)\right]\bar{A}_2 = \frac{i\mu_A^* E v_2}{\Delta + \delta'}\bar{A}_0. \tag{21}$$

Note that we labeled the matrix elements v by v_1 and v_2 in order to allow for the possibility of overlap in the interaction, as we will explain in more detail below. Equations (4)–(7), which describe the two-photon ionization process assisted by collisional transfer, are reduced to two-state problems with frequency shifts caused by both the electric field and by the collisional coupling. The intermediate nonresonant state $|2a\rangle|0b\rangle$ causes a shift in the ground state $|1a\rangle|0b\rangle$. The continuum state causes a complex shift $\gamma_1 + is$ in the collisionally populated state $|0a\rangle|1b\rangle$. The real part γ_1 is an intensity-induced decay due to photoionization, and the imaginary part s is an intensity-induced frequency shift due to the virtual transitions with the continuum states. The two-state system is coupled by an effective interaction potential which is the product of the laser field and the collision interaction potential, and scaled down by the frequency gap Δ. With a phase transformation

$$\bar{A}_0 = \exp\left[\frac{i\mu_A^2}{\Delta+\delta'}\int E^2\,dt\right]A_0,$$
$$\bar{A}_2 = \exp\left[\frac{i\mu_A^2}{\Delta+\delta'}\int E^2\,dt\right]A_2, \tag{22}$$

Eqs. (20) and (21) become

$$\frac{d}{dt}A_0 = i\alpha A_2, \tag{23}$$

$$\frac{d}{dt}A_2 + (i\delta+\Gamma)A_2 = i\alpha^* A_0, \tag{24}$$

where

$$\delta(t) = \left(\delta' + s + \frac{\mu_A^2 E^2}{\Delta+\delta'} - \frac{v_1^2}{\Delta+\delta'}\right), \tag{25}$$

$$\alpha = \frac{\mu_A E v_2}{\Delta+\delta'}. \tag{26}$$

Note that when the process occurs at long range, where there is no overlap, $v_1 = v_2$. This arises in atom-atom collisions. However, when overlap is an integral part of the interaction, as is the case in charge-exchange collisions between an ion and an atom, $v_1 \neq v_2$. Below we discuss both cases. The classical Hamiltonian for the interaction of a singly charged ion and a neutral atom is given by $H' = e^2 r/R^2$, where r is the local coordinate of the electron and R is the internuclear separation. To calculate the energy shift, one uses an atomic basis set which for a two-level atom and to second order gives an interaction shift $v_1^2 = -c_4/R^4$. The classical interaction Hamiltonian between two neutral atoms when dipole-dipole or Van der Waals interaction is dominant is $e^2 x_1 x_2/R^3$, where x_1 and x_2 are the local coordinates of the electrons of each atom and R is the internuclear separation. To second order, this Hamiltonian yields a shift $v_1^2 = -c_6/R^6$, if the two atoms are different, as here, where c_6 is the Van der Waals interaction constant.

Let us consider the form of the interaction coupling v_2. For the case of the interaction of a hydrogen atom and a proton, the interaction potential can be explicitly evaluated. The long-range interaction takes the form

$$v_2 = -\frac{e^2}{\hbar a_0}\frac{R}{a_0}e^{-R/a_0}, \tag{27}$$

where e is the electronic charge, a_0 is the Bohr radius, and R is the internuclear separation. For a single electron charge-exchange collision between different partners, Olson *et al.*[29] showed that the interaction potential can be approximated by a similar formula with an effective internuclear separation R_0 and strength

$$v_2 = -\frac{G}{\hbar}\frac{R_0}{a_0}\exp\left(\frac{-0.86R_0}{a_0}\right). \tag{28}$$

The above form is expected to hold when the colliding particles are sufficiently far apart and when the wave functions are nearly hydrogenic. The strength G depends on the ionization potential of the respective atoms:

$$G = I_H (I_1 I_2/I_H^2)^{1/2}\left[(I_1/I_H)^{1/2} + (I_2/I_H)^{1/2}\right], \tag{29}$$

where $I_H = e^2/2a_0$ is the ionization potential of hydrogen and I_1 and I_2 are the ionization potentials of the colliding atoms.

When the charge transfer takes place in an intense field, the form of the interaction Hamiltonian can be derived as discussed above, using atomic basis. The result is the product $\mu_A E v_2/(\Delta+\delta')$; therefore, this product, when v_2 is substituted, becomes

$$H_{\text{in}} = \left(\frac{\mu_A E}{\Delta+\delta'}\right)\frac{G}{\hbar}\frac{R_0}{a_0}\exp\left(\frac{-0.86R_0}{a_0}\right), \tag{30}$$

where R_0 is the internuclear separation where absorption takes place.

Equations (20) and (21) with $v_1 \neq v_2$ describe many physical problems. These include dipole-dipole, dipole-quadrupole, quadrupole-quadrupole, charge transfer, S-S transition, and spin change. In the case where overlap is important (as, for example, charge exchange), one can use the quasimolecular absorption viewpoint, as discussed above. For completeness, we describe briefly the two-photoionization process induced by the charge-transfer analog of radiative collision, using the quasimolecular picture.

Let us consider the time-dependent, electronic-field Schrödinger equation:

$$i\frac{\hbar\partial}{\partial t}\psi(\vec{x},\vec{R}) = (H_{\text{el}} + H_{\text{in}})\psi(\vec{x},\vec{R}), \tag{31}$$

$$H_{\text{el}} = T_x + V_e(\vec{x},\vec{R}), \tag{32}$$

where $\vec{x}$ and $\vec{R}$ stand for electronic and nuclear coordinates, respectively; T_x is the electronic kinetic energy operator; $v_e(\vec{x},\vec{R})$ is the electrostatic interaction among electrons and nuclei; and H_{in} is the classical interaction potential between the molecular system and the laser field.

Since the effective interaction potential H_{in} is derived, one can proceed to treat the two-photon process from the quasimolecular viewpoint. We represent the system by two field-free adiabatic discrete electronic states $\phi_i(\vec{x},\vec{R})$ and a continuum ϕ_c. We assume $\langle\phi_i|\phi_j\rangle=\delta_{ij}$, where $i,j=1,\ 2$, or c. We will not attempt to include the magnetic sublevels in this study in order to simplify the derivation. Calculations of line broadening where anisotropy of the system was included indicated that the two-level calculation is only 50% off from the complete calculation.[22-24] Therefore,

$$\psi(\vec{x},\vec{R})=a_1(t)\phi_1(\vec{x},\vec{R})\exp\left(-\frac{i}{\hbar}\int_{t_1}^{t}w_1(\vec{R})\,dt\right)+a_2(t)\phi_2(\vec{x},\vec{R})\exp\left(-\frac{i}{\hbar}\int_{t_1}^{t}w_2(\vec{R})\,dt\right)$$
$$+\int a_c(w_c,t)\phi_c(\vec{x},\vec{R})\exp\left(-\frac{i}{\hbar}\int_{t_1}^{t}w_c(\vec{R})\,dt\right)dw_c, \tag{33}$$

where ϕ_i are the field-free adiabatic discrete electronic states, w_i are the corresponding field-free adiabatic potential energy surfaces, ϕ_c are continuum states with corresponding w_c energies, t_1 is some initial time, and a_i and a_c are time-dependent amplitudes. Explicit forms for a_1, a_2, and a_c are found by solving the equation of motion (26) given the initial conditions $a_1(-\infty)=1$ and $a_2(-\infty)=a_c(-\infty)=0$.

In the case where the system is electronically adiabatic in the absence of the field, we drop terms containing the nonadiabatic coupling $\langle\phi_1|\dot{\phi}_2\rangle$, $\langle\phi_2|\dot{\phi}_1\rangle$, $\langle\phi_2|\dot{\phi}_c\rangle$, and $\langle\phi_c|\dot{\phi}_2\rangle$; and in the rotating-wave approximation Eqs. (31)–(33) reduce to the following set of equations:

$$\frac{da_1}{dt}=i\alpha\exp\left(-i\int_{t_1}^{t}\tilde{\delta}(t')\,dt'\right)a_2, \tag{34}$$

$$\frac{da_2}{dt}+\gamma_0 a_2=i\alpha^*\exp\left(i\int_{t_1}^{t}\tilde{\delta}(t')\,dt'\right)a_1$$
$$+iE\int\mu_B\exp\left(-i\int_{t_1}^{t}\delta_c(t')\,dt'\right)a_c\,dw_{Bc}, \tag{35}$$

$$\frac{da_c}{dt}=i\mu_B^*E\exp\left(i\int_{t_1}^{t}\delta_c(t')\,dt'\right)a_2\ , \tag{36}$$

where

$$\tilde{\delta}(t)=(1/\hbar)(w_2-w_1-\hbar\omega), \tag{37}$$

$$\delta_c(t)=(1/\hbar)(w_c-w_2-\hbar\omega), \tag{38}$$

$$\alpha=\langle 1|H_{\text{in}}|2\rangle=\frac{\mu_A E}{(\Delta+\delta')}\,\frac{G}{\hbar}\,\frac{R^*}{a_0}e^{-0.86R^*/a_0}. \tag{39}$$

Note that we used the matrix elements μ_A and μ_B which we used in the atomic viewpoint.

We eliminate the continuum states using the procedure described above in the atom-atom collision case. Equations (34)–(36) reduce to

$$\frac{da_1}{dt}=L_1 a_2, \tag{40}$$

$$\frac{da_2}{dt}+\tilde{\Gamma}(t)a_2=L_2 a_1, \tag{41}$$

where

$$\tilde{\Gamma}(t)=\gamma_0+is+\gamma_1, \tag{42}$$

$$\Gamma(t)=\gamma_0+\gamma_1,$$

$$L_1=i\alpha\exp\left(-i\int\tilde{\delta}(t')\,dt'\right), \tag{43}$$

$$L_2=i\alpha^*\exp\left(i\int\tilde{\delta}(t')\,dt'\right), \tag{44}$$

$$s=-E^2\mathrm{P}\int\frac{\mu_B^2}{\delta_c}\,dw_c \tag{45}$$

$$\gamma_1=\hbar\pi\mu_B^2E^2, \tag{46}$$

and P stands for principal value.

Note that with a phase transformation of the amplitude $a_2=A_2\exp(i\int\delta dt)$, Eqs. (40) and (41) become identical in form to Eqs. (23) and (24) derived using the atomic viewpoint. The two sets become identical if $\tilde{\delta}+s$ in Eqs. (40) and (41) is the same as δ in Eq. (25). This implies that the difference frequency with all the interactions taken into account is

$$s+\mu_A^2E^2/(\Delta+\delta')-v^2/(\Delta+\delta').$$

This includes Stark shifts due to nonresonant continuum and discrete states.

The above system of two coupled equations with time-varying amplitudes arises in many physical situations such as collision phenomena, laser interactions with isolated systems, and collisions in the presence of laser fields.

We now proceed to solve Eqs. (40) and (41) for a_2, from which expressions for the photoionization can be calculated. Since changes in the amplitudes can only occur at the resonance condition

$\delta(t_0)=0$, we consider times near t_0 and define the quantity A_2:

$$A_2=\exp\left(\int_0^\tau \frac{\tilde{\Gamma}(t)}{2}dt\right)\times\exp\left(-\frac{1}{2}\int_0^\tau \frac{d}{dt}\ln L_2\,dt\right)a_2, \tag{47}$$

where $\tau=t-t_0$ and t_0 is the time where resonance occurs, $\delta(t_0)=0$. Substituting Eq. (47) in Eqs. (40) and (41), we obtain

$$\left(\frac{d^2}{d\tau^2}+f(\tau)\right)A_2=0, \tag{48}$$

where

$$f(t)=-L_1L_2-\frac{1}{4}\left(\tilde{\Gamma}+\frac{d}{dt}\ln L_2\right)^2+\frac{1}{2}\frac{d}{dt}\tilde{\Gamma}+\frac{1}{2}\frac{d^2}{dt^2}\ln L_2\,. \tag{49}$$

We proceed to solve Eq. (48) by the Landau-Zener method near the resonance time t_0. We first write $f(\tau)$ explicitly in terms of the field intensity, detuning, and decay:

$$f(t)=\alpha^2+\frac{1}{4}\left(\delta-i\frac{d}{d\tau}\ln\alpha-i\Gamma\right)^2+\frac{1}{2}\frac{d\Gamma}{d\tau}+\frac{1}{2}\left(\frac{d^2}{d\tau^2}\ln\alpha+i\frac{d\delta}{d\tau}\right), \tag{50}$$

where we have defined $\delta=\tilde{\delta}+s$. Close to $t=t_0$ or $\tau=0$, one can expand $\delta(\tau)$ as $\tau d\delta(0)/d\tau$ and write

$$f(t)=g_0+\frac{1}{2}ig_1+\frac{g_1^2}{4}\left(\tau-\frac{i}{g_1}\frac{d}{d\tau}\ln\alpha-\frac{i\Gamma}{g_1}\right)^2, \tag{51}$$

$$g_0=\alpha^2+\frac{1}{2}\frac{d}{d\tau}\Gamma+\tfrac{1}{2}\frac{d^2}{d\tau^2}\ln\alpha, \tag{52}$$

$$g_1=\frac{d\delta(0)}{d\tau}. \tag{53}$$

Substituting Eqs. (51)–(53) in Eq. (48), and with the definitions of z and n,

$$z=\left(\tau-\frac{i}{g_1}\frac{d}{d\tau}\ln\alpha-\frac{i\Gamma}{g_1}\right)g_1^{1/2}e^{-i\pi/4}, \tag{54}$$

$$n=\frac{ig_0}{g_1}=g+ip, \tag{55}$$

where q and p are real, Eq. (48) reduces to the following equation:

$$\left(\frac{d^2}{dz^2}+n+\frac{1}{2}-\frac{z^2}{4}\right)A_2=0. \tag{56}$$

Equation (56) reduces to Weber equation if n is time independent. For constant pulse amplitude and slowly moving particles, this condition can be assumed; therefore, one can easily show that the asymptotic probability

$$|a_2|^2=(1-e^{-2\pi p})e^{-\Gamma\tau}, \tag{57}$$

where

$$p=\frac{\alpha^2}{d\delta(0)/d\tau}. \tag{58}$$

Note that the absorption probability $1-e^{-2\pi p}$ depends exponentially on the function p. Since $p=\alpha^2(d\delta(0)/d\tau)$, the absorption depends on the square of the coupling α and on the time rate of change of the detuning from the isolated atom level evaluated at the point of crossing. In radiative-type collisions, as the processes we are discussing, the coupling α of the reduced two-level system depends on the product of the collisional and electromagnetic field couplings. This results in the dependence of p on the parameters of the collisional interaction through α^2 and $d\delta/d\tau$. This is in contrast to optical-type collisions where the electromagnetic field is tuned near the resonance in one atom. In these collisions, the only dependence on the collisional parameters enter through δ.

The absorption probability decays exponentially due to spontaneous decay rate γ_0 and the induced ionization rate γ_1, which depends on the intensity of the field and on the oscillator strength of the transition between the excited state and the continuum state.

III. IONIZATION YIELD

Equation (57) describes the absorption at one crossing point where the system is initially in the ground state. In a single collision, there are two times where the system comes into resonance with the photon field: when the two atoms, separated by a distance R, are approaching to, and departing from each other. Since, during collision, not much decay or ionization takes place unless those rates are of order 10^{12} sec^{-1}, one can show that after two symmetric resonance times $|a_2|^2$ is

$$|a_2|^2=2(1-e^{-2\pi p})e^{-2\pi p}, \tag{59}$$

where we have taken the probabilities induced at the first crossing as initial conditions at the second crossing.

We discuss now some limiting cases of Eq. (59). The above calculated probability is valid for both the weak- and strong-field cases. For strong fields where $2\pi p\gg 1$, $|a_2|^2$ goes to zero. Note that after one crossing [Eq. (57)] $|a_2|^2$ reduces to 1 for strong fields, which indicates that the first crossing induces complete inversion, while the second crossing induces complete stimulated emission which leaves a_2 unpopulated. Since in the limit of very weak field $|a_2|^2$ goes to zero, there exists an intermediate field where $|a_2|^2$ reaches a maximum. However, when $2\pi p \ll 1$, then $|a_2|^2$ becomes linear in the field intensity:

$$|a_2|^2 = 4\pi p. \tag{60}$$

Far away in the wing—e.g., when the atoms get closer to each other, resulting in more distortion of the resonance lines—we expect the slope of δ to be large. Therefore, in this regime the condition $2\pi p \ll 1$ holds; and the population of the excited state is linear in the field intensity. This picture is consistent with the fact that the inverse of the slope of the potential-curve difference is a measure of the time the system stays in resonance.

We consider now the ionization yield. We first consider the case where the ionization rate is of the order 10^{12}; there, appreciable ionization is achieved before other collisions take place and before the second crossing. This condition requires power densities of the order 10^{11} W/cm^2 for a photoionization cross section of the order 10^{-17} cm^2. Such high power will induce power broadening of the order of 5×10^{13} sec^{-1} which will tend to wash out the crossing. However, very far away on the wing, i.e., when the atoms get very close to each other, the potential curves become very steep and a slight change in R will induce a detuning effect larger than the power broadening. Therefore, on the extreme far wing and for nearly complete ionization and inversion during the collision, one needs to consider only one crossing as given in Eq. (57).

We next calculate the ionization yield. Since the continuum states were eliminated from the coupled equations by introducing a shift and a decay to the excited state, one can use this scheme to calculate the total ionization probability. From Eq. (41) and from the result that the decay of the excited state into the continuum is given by γ_1 [Eq. (46)], one writes the total probability of ionization r as

$$r = \int_{-\infty}^{\infty} \gamma_1 |a_2|^2\, dt. \tag{61}$$

Using the asymptotic expressions calculated for $|a_2|^2$, one finds that

$$r = \frac{\gamma_1(1-e^{-2\pi p})}{\gamma_0+\gamma_1}\left\{1-\exp[-(\gamma_0+\gamma_1)T]\right\}, \tag{62}$$

where T is the pulse width. Saturation of the ionization can be achieved if $\gamma_1 \gg \gamma_0$ and $(\gamma_0+\gamma_1)T \gg 1$. In this case r reduces to

$$r = 1 - e^{-2\pi p}. \tag{63}$$

When $2\pi p \gg 1$, $\gamma_1 \gg \gamma_0$, and $\gamma_1 T \gg 1$, both states are saturated and the ionization probability becomes 1.

If the absorption is weak while the ionization is nearly saturated, one has to consider both crossings; and the ionization yield will be twice the yield in Eq. (63) in the limit of $2\pi p \ll 1$.

Let us consider a situation where the ionization rate is much smaller than the reciprocal of the time of resonance. This case typically arises with power densities of the order 10^8 W/cm^2 and ionization rates of the order 10^{10} sec^{-1}. After the absorption in a single collision takes place, the system evolves according to the slower processes between collisions. For a typical coupling and a distance of 10 Å, the frequency detunings can reach 10^{12} sec^{-1} which results in complete dephasing of the interaction. Therefore, the rate equation treatment is adequate for the processes between collisions. In the rate equation treatment, one calculates an absorption cross section first by integrating over the impact parameters. Far on the wing where $2\pi p \ll 1$, $|a_2|^2$ reduces to $4\pi p$, as given in Eq. (60); therefore, the cross section σ is

$$\sigma = 4\pi \int_0^{R_0} 2\pi b\, db\, p, \tag{64}$$

where R_0 is the internuclear separation where absorption takes place.

Substituting for p in Eq. (64) from (58) and carrying out the integration, we get

$$\sigma = \frac{4\pi^2}{3}\,\frac{\alpha_0^2}{V}\,\frac{dR_0^3}{d\delta}, \tag{65}$$

where α_0 is α evaluated at the crossing, and V is the relative speed.

The velocity average can now be carried out. The result is a thermal rate constant k:

$$k = N(8KT/\pi M)^{1/2}\bar{\sigma}, \tag{66}$$

where

$$\bar{\sigma} = 2\int_0^{\infty} x^3 e^{-x^2}\sigma(x)\, dx, \tag{67}$$

k is the rate of absorption, M is the reduced mass of the system, T is the temperature, K is Boltzmann's constant, $x=(M/2KT)^{1/2}V$, and N is the foreign-gas density. This results in

$$k = \frac{8N\pi^2}{3}\,\alpha_0^2\,\frac{dR_0^3}{d\delta}. \tag{68}$$

When the collision between atoms is considered, $v_1 = v_2 = c_6^{1/2}/R^3$ and $\alpha_0^2 = \mu_A^2 E^2 v^2/(\Delta+\delta')^2$. Therefore, k becomes

$$k = \frac{4N\pi^2}{3}(\hbar c_6^{1/2})\,\frac{\mu^2{}_A E^2}{(\Delta+\delta')^2}\,\frac{1}{\delta^{1/2}} \tag{69}$$

which predicts that the absorption rate on the far wing goes like $\delta^{-1/2}$. This drop-off is much slower than that of optical collisions where the excitation frequency is tuned close to a transition in one of the atoms.[19] In such line-broadening cases the far-wing absorption rate goes like $\delta^{-3/2}$.

In the case of charge exchange, the wavelength dependence is much more complicated due to the overlap interaction energies. Substituting for α_0^2 from Eq. (38) and for $\hbar\delta$ the quantity c_4/R_0^4, we get for k:

$$k = N\pi^2 \frac{\mu_A^2 E^2}{(\Delta+\delta')^2} \frac{G^2}{\hbar^2}\left(\frac{c_4}{\hbar}\right)^{5/4} \frac{1}{a_0\delta^{9/4}} \times \exp\left[-\frac{1.72}{a_0\delta^{1/4}}\left(\frac{c_4}{\hbar}\right)^{1/4}\right]. \tag{70}$$

Note that for large $\delta^{1/4}$ the exponential becomes negligible and the rate of absorption becomes proportional to $\delta^{-2.25}$. The reason for this fast decay, as compared to (69), is that the distortion in the energy levels is less steep than that in atom-atom collision and the interaction energies at the crossing go like $1/R^4$ for small R compared to $1/R^6$ in the atom-atom collision.

Note that k can be written as $I\bar{\sigma}$, where I is the fluence of the light source and $\bar{\sigma}$ is an average cross section. Note also that the temperature dependence of the rate is absent. This result agrees with results that are derived from statistical theories. In these theories, the statistical distribution of frequencies is defined by regarding the intensity at frequency ν as proportional to the time interval during which ν is irradiated. This time interval in turn is proportional to the relative volume of configuration space in which the frequency perturbation is ν. Since our results [Eqs. (69) and (70)] were derived on the assumption that $2\pi p \ll 1$ in Eq. (60), we predict the statistical arguments will fail as the intensity of light increases. This can be reached at frequencies close to the line center. However, one has to be careful since our calculation requires sharp crossing, as was discussed after Eq. (60). This, in turn, requires somewhat steep potential curves. Therefore, higher powers of $2\pi p$ will be important; therefore, higher powers of the configuration space become important, resulting in temperature-dependent rate constants.

The assumption of straight-line trajectories in the case of interaction between an ion and a neutral is not valid at slow velocities. The attractive force resulting from the polarization of the neutral by the incident ion leads to curved or spiraling orbits. In the classical model, all particles incident at an impact parameter less than a certain value will, in fact, get trapped and spiral inward to the origin. Although some particles might approach at an impact parameter greater than that of the curve crossing, they may still make it to the crossing, but with a velocity that differs from that of the initial approach. Due to this orbiting effect, we consider a modification to the Landau-Zener result [Eq. (70)].

The total energy of the reduced system E is

$$E = \frac{1}{2}M\left(\frac{dR}{dt}\right)^2 + \frac{L^2}{2MR^2} - \frac{c_4}{R^4}, \tag{71}$$

where L is the angular momentum of the system and R and M are the internuclear separation and the reduced mass, respectively. Due to conservation of energy and angular momentum, the total energy and angular momentum can be written in terms of the initial velocity V_0 and impact parameter ρ_0 as $E = \frac{1}{2}MV_0^2$ and $L = MV_0\rho_0$. The classical capture radius ρ_c is defined as that at which E is equal to the maximum of the effective potential V_e:

$$v_e = \frac{MV_0^2\rho_0^2}{2R^2} - \frac{c_4}{R^4}. \tag{72}$$

This results in

$$\rho_c = (4c_4/E_0)^{1/4}. \tag{73}$$

For ρ greater than ρ_c, the maximum impact parameter $\rho_{\max}$ such that a curve crossing at $R = R_0$ can be reached can be calculated from Eq. (71) by putting $dR_0/dt = 0$. This results in

$$\rho_{\max} = R_0(1 + \rho_c^4/4R_0^4)^{1/2}. \tag{74}$$

Also, from Eq. (71) one can find the minimum curve crossing $R_{0_{\min}}$ which may be reached for a given impact parameter:

$$R_{0_{\min}} = \{\tfrac{1}{2}[\rho^2 - (\rho^4 - \rho_c^4)^{1/2}]\}^{1/2}. \tag{75}$$

The velocity at the curve crossing can also be derived from Eq. (71):

$$\frac{d}{dt}R_0 = v_0\left(1 - \frac{\rho^2}{R_0^2} + \frac{\rho_c^4}{4R_0^4}\right)^{1/2}. \tag{76}$$

Due to the orbiting phenomena which result in the above equations (73)–(76), the absorption cross section

$$\sigma = 4\pi\int_0^{\rho_{\max}} e^{-2\pi p}(1 - e^{-2\pi p})b\, db \tag{77}$$

gets modified. Note that the above equations imply that for a crossing radius R_0 in the range $0 < R_0 \leq \rho_c/\sqrt{2}$, $\rho_{\max}$ is equal to ρ_c; while for the range $\rho_c/\sqrt{2} < R_0 < \infty$, $\rho_{\max}$ is given by Eq. (74).

Using the above equations and with x and the dimensionless quantities λ and η defined below, one can show that Eq. (77) becomes

$$\sigma = 4\pi R_0^2 (1+\rho_c^4/4R_0^4) \int_0^{x_m} e^{-\eta x}(1-e^{-\eta x}) x^{-3}\, dx\,, \tag{78}$$

$$x_m = \frac{(1+\rho_c^4/4R_0^4)^{1/2}}{(\rho_c^2/2R_0^2)-1} \quad \text{for } 0 \leqslant R_0 \leqslant \rho_c/\sqrt{2}, \tag{79}$$

$$x_m = \infty \text{ for } \rho_c/\sqrt{2} \leqslant R_0 \leqslant \infty, \tag{80}$$

where

$$\lambda = \rho_c^4/4R_0^4, \tag{81}$$

$$\eta = \frac{2\pi\alpha^2}{(dR/d\delta)V_0(1+\lambda)^{1/2}}\,, \tag{82}$$

$$x = (1+\lambda)^{1/2}(1+\lambda-\rho^2/R_0^2)^{-1/2}, \tag{83}$$

and

$$2\pi p = \eta x\,. \tag{84}$$

Let us consider the case of weak fields such that $2\pi p \ll 1$ or η is very small, and the capture radius ρ_c is much larger than the crossing radius R_0. Then Eq. (78) gives

$$\sigma = 4\pi\rho_c^2 \frac{2\pi p}{V_0} \frac{\partial R_0}{\partial \tau}. \tag{85}$$

Result (85) shows that the effect of orbiting is to replace the crossing distance R_0 by the classical capture radius ρ_c. Note that ρ_c depends on the energy of the system as given in Eq. (73); therefore, the velocity dependence of the cross section becomes $1/v^2$ rather than $1/v$ as in the case of no orbiting. Substituting Eq. (73) in Eq. (85), we get

$$\sigma = 16\pi^2 \left(\frac{2c_4}{M}\right)^{1/2} p \frac{\partial R_0}{\partial t} \frac{1}{V_0^2}\,. \tag{86}$$

Note that the product $p(\partial R_0/\partial t)$ is a velocity-independent quantity. The thermal energy of the cross section yields an absorption rate k as given in Eqs. (66) and (67). The result is

$$\bar{\sigma} = \frac{8\pi^2}{KT}(2c_4 M)^{1/2} p \frac{\partial R_0}{\partial t}\,. \tag{87}$$

The absorption-rate k dependence on the detuning $\delta = c_4/\hbar R^4$ can now be written easily. Using Eqs. (39), (58), (66), and (87), we get

$$k = 32 N\pi^{3/2} \left(\frac{c_4}{KT}\right)^{1/2} \alpha_0^2 \frac{\partial R_0}{\partial \delta}\,. \tag{88}$$

Comparing Eq. (88) with Eq. (68) shows the reduced sensitivity to the crossing radius when orbiting effects are taken into consideration. Substituting c_4/R^4 for $\hbar\delta$ reduces Eq. (88) to

$$k = 8N\pi^{3/2}\left(\frac{c_4^2}{\hbar KT}\right)^{1/2} \frac{\mu_A^2 E^2}{(\Delta+\delta')^2} \frac{G^2}{a_0\hbar^2} \frac{1}{\delta^{3/2}} \times \exp\left[-\frac{1.72}{a_0\delta^{1/4}}\left(\frac{c_4}{\hbar}\right)^{1/4}\right]. \tag{89}$$

This absorption rate falls more slowly with δ than that of the case of straight trajectory.

With the absorption rates derived, one can write the rate equations describing the two-photon ionization.[19] Let n_0, n_1, and n_e be the populations of the ground state, excited state, and the number of atoms ionized, respectively, and N_0 be the initial population of the ground state. Then one writes

$$\frac{dn_0}{dt} = -\sigma_a I n_0 + \sigma_a I \frac{g_1}{g_0} n_1 + \gamma_0 n_1\,, \tag{90}$$

$$\frac{dn_1}{dt} + \gamma_0 n_1 = \sigma_a I n_0 - \sigma_a I \frac{g_1}{g_0} n_1 - \sigma_i I n_1\,, \tag{91}$$

$$\frac{dn_e}{dt} = \sigma_i I n_1\,, \tag{92}$$

where σ_a and σ_i are the absorption and ionization cross sections, respectively; I is the photon fluence; g_0 and g_1 are the g factors of the ground and excited states, respectively; and γ_0 is a spontaneous decay of the excited state. Or one may write

$$\left[\frac{d^2}{dt^2} + \left(\sigma_a I + \sigma_a I \frac{g_1}{g_0} + \sigma_i I + \gamma_0\right)\frac{d}{dt} + \sigma_a I\left(\gamma_0 + \sigma_a I \frac{g_1}{g_2} + \sigma_i I\right) - \sigma_a^2 I^2 \frac{g_1}{g_0} - \sigma_a I \gamma_0\right] n_1 = 0\,. \tag{93}$$

Note that $\sigma_i I$ is not equal to the isolated-pair ionization rate γ_1 [Eq. (46)] because here ionization takes place during collisions. During collision, quantum substates are mixed. The cross section σ_i includes the degeneracy of the excited state. Equation (93) can easily be shown to have the following solution:

$$n_1 = \frac{N_0 \sigma_a I}{f_2 - f_1}(e^{-f_1 t} - e^{-f_2 t})\,. \tag{94}$$

where

$$f_1 = \alpha - \beta\,,\quad f_2 = \alpha + \beta\,, \tag{95}$$

and

$$\alpha = \frac{1}{2}\left[\sigma_a I\left(1 + \frac{g_1}{g_0}\right) + \sigma_i I + \gamma_0\right], \tag{96}$$

$$\beta = \left[\frac{1}{4}\left(\gamma_0 + \sigma_a I \frac{g_1}{g_2} + \sigma_i I - \sigma_a I\right)^2 + \sigma_a^2 I^2 \frac{g_1}{g_0} + \sigma_a I \gamma_0\right]^{1/2}. \tag{97}$$

Therefore, the ionization yield can be derived from Eq. (92):

$$N_e = \sigma_i I \int_0^{\tau} n_1\, dt\,, \tag{98}$$

where τ is the pulse length. Substituting Eq. (94) in Eq. (98), we get

$$N_e = \frac{N_0\sigma_a I}{f_2-f_1}\sigma_i I\left(\frac{1-e^{-f_1\tau}}{f_1} - \frac{1-e^{-f_2\tau}}{f_2}\right). \tag{99}$$

Let us again consider the case where the ionization is saturated while the laser is tuned on the far wing. This case is of interest because the ionization line shape reduces to the absorption line shape; therefore, the analysis becomes simpler. When $\gamma_0 \ll \sigma_i I \gg \sigma_a I$, one can show that f_1 reduces to $\sigma_a I$ and f_2 reduces to $\sigma_i I$. Thus

$$N_e = N_0\left(1 - \frac{\sigma_i e^{-\sigma_a I\tau} - \sigma_a e^{-\sigma_i I\tau}}{\sigma_i - \sigma_a}\right), \tag{100}$$

which reduces when $\sigma_i \gg \sigma_a$ and $\sigma_i I\tau \gg 1$ to

$$N_e = N_0\left(1 - e^{-\sigma_a I\tau}\right). \tag{101}$$

Expressions (99) and (101) describe the ionization yield of the gas mixture for arbitrary degree of saturation of the ionization and for complete ionization, respectively. The latter expression is the absorption of the system since saturation of the ionization is achieved. On the far wing and when $\sigma_a I\tau \ll 1$, the absorption yield is

$$N_e/N_0 = \sigma_a I\tau. \tag{102}$$

Equation (102) shows linear dependence on buffer-gas pressure and on the light intensity. The dependence on the detuning enters in σ_a. Substituting the velocity-averaged cross section in the case of atom-atom scattering for σ_a, we get

$$\frac{N_e}{N_0} = \frac{4N\pi^2}{3}(c_6)^{1/2}\frac{\mu_A^2 E^2}{(\Delta+\delta')^2}\delta^{-1/2}. \tag{103}$$

At a particular intensity, $\ln N_e/N_0$ vs $\ln\delta$ is a straight line with slope $-\frac{1}{2}$ and intercept that depends on c_6 and the other parameters; therefore, an accurate measurement of the slope and intercept determines the interaction force. Similarly, substituting the velocity-averaged cross section for the case of charge-transfer collision for σ_a in the case of straight-line trajectory, we get

$$\frac{N_e}{N_0} = N\pi^2\frac{\mu_A^2 E^2}{(\Delta+\delta')^2}\frac{G^2}{\hbar^2 a_0}\left(\frac{c_4}{\hbar}\right)^{5/4}\delta^{-9/4} \times \exp\left[-\frac{1.72}{a_0}\left(\frac{c_4}{\hbar\delta}\right)^{1/4}\right]. \tag{104}$$

At a particular electromagnetic field intensity, $\ln N_e/N_0$ is

$$\ln(N_e/N_0) = -\tfrac{9}{4}\ln\delta - c_1\delta^{-1/4} + c_2, \tag{105}$$

which indicates that $\ln(N_e/N_0)$ vs $\ln\delta$ is not a straight line. The inclusion of orbiting in the analysis results in [Eqs. (89) and (102)]

$$\frac{N_e}{N_0} = 8N\pi^{3/2}\left(\frac{c_4^2}{\hbar KT}\right)^{1/2}\frac{\mu_A^2 E^2}{(\Delta+\delta')^2}\frac{G^2}{\hbar^2}\delta^{-3/2} \times \exp\left[-\frac{1.72}{\delta^{1/4}a_0}\left(\frac{c_4}{\hbar}\right)^{1/4}\right]. \tag{106}$$

which falls off as $\delta^{-3/2}$ for large δ.

In the wing, and although the absorption cross section falls off rapidly with detuning, $\sigma_a I\tau$ [Eq. (101)] can still be of the order of unity even for moderate electromagnetic fields. This can be achieved by increasing the buffer-gas pressure. With one atmosphere of buffer gas and with power densities of the order of MW/cm², nonlinear absorption takes place even as far out as 70 Å detunings. Saturation of the absorption with such power densities can be easily achieved at 10–15 Å detuning.

IV. CONCLUSION

We have derived expressions for two-photon ionization of atoms induced by radiative-type collisions or its charge-exchange analog. Both regimes where appreciable ionization takes place during single collisions and between collisions are treated. The dependence of the ionization yield on the interatomic forces at long range is derived, thus making these results of importance to experimental studies. This process promises an extremely sensitive method for studying radiative collisions, especially when absorption or fluorescence becomes extremely weak. This is made possible because of the ability with present lasers to ionize every absorption event.

Although absorption tends to decrease as the field intensity rises due to stimulated emission at the second crossing, the two-photon ionization yield can be nearly saturated at the first crossing, thus enhancing the absorption.

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[1] R. Karplus and J. Schwinger, Phys. Rev. 73, 1020 (1948).

[2] V. M. Fain, Kvantovayer radiofizike (Quantum Radiophysics), USSR radio, 1972 (unpublished).

[3] N. M. Kroll and K. M. Watson, Phys. Rev. A 8, 804 (1973).

[4] V. S. Lisitsa and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. 66, 1550 (1974) [Sov. Phys.-JETP 39, 759 (1974)].

[5] J. C. Y. Chen, T. Ishihari, and K. M. Watson, Phys. Rev. Lett. 35, 1574 (1975).

[6] V. S. Lisitsa and S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. 68, 479 (1975) [Sov. Phys.-JETP 41, 233 (1975)].

[7] A. M. Lau, Phys. Rev. A 13, 139 (1976).

[8] J. M. Yuan, T. F. George, and F. I. McLafferty, Chem. Phys. Lett. 40, 163 (1976).

[9] J. M. Yuan, J. R. Liang, and T. F. George, J. Chem. Phys. 66, 1107 (1977).

[10] H. Zimmerman, J. M. Yuan, and T. F. George, J. Chem. Phys. 66, 2638 (1977).

[11] S. I. Yakovlenko, Zh. Eksp. Teor. Fiz. 64, 2020 (1973) [Sov. Phys.-JETP 37, 1019 (1973)]; L. I. Gudzenko and S. I. Yakovlenko, *ibid.* 62, 1686 (1972) [Sov. Phys.-JETP 35, 877 (1972)].

[12] S. E. Harris and D. B. Lidow, Phys. Rev. Lett. 33, 674 (1975); Phys. Rev. Lett. 34, 172 (1975).

[13] M. G. Payne and M. H. Nayfeh, Bull. Am. Phys. Soc. 21, 156 (1976); M. G. Payne, C. W. Choi, and M. H. Nayfeh, Abstracts from International Conference on Multiphoton Processes, University of Rochester, 1977 (unpublished).

[14] S. Geltman, J. Phys. B 9, L569 (1976); J. Phys. B 10, 3057 (1977).

[15] D. A. Copeland and C. L. Tang, J. Chem. Phys. 65, 3161 (1976); R. Z. Vitlina, A. V. Chaplik, and M. V. Eutin, Sov. Phys.-JETP 40, 829 (1975).

[16] R. G. Breene, Jr., *The Shift and Shape of Spectral Lines* (Pergamon, London, 1961); I. I. Sobelman, *Introduction to the Theory of Atomic Spectra* (Pergamon, London, 1972); M. Baranger, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic, New York, 1962), p. 493.

[17] J. I. Gersten and M. H. Mittleman, J. Phys. B 9, 383 (1976).

[18] D. B. Lidow, R. W. Falcone, J. F. Young, and S. E. Harris, Phys. Rev. Lett. 36, 462 (1976); R. W. Falcone, W. R. Green, J. C. White, J. F. Young, and S. E. Harris, Phys. Rev. A 15, 1333 (1977); Phys. Today 29 (No. 10), 18 (1976).

[19] M. H. Nayfeh, Phys. Rev. A 16, 927 (1977).

[20] P. Milonni, J. Chem. Phys. 66, 3715 (1977).

[21] P. L. Knight, Phys. Lett. 61A, 22 (1977).

[22] J. C. Bellum and T. F. George, J. Chem. Phys. 68, (1978).

[23] G. S. Hurst, M. H. Nayfeh, and J. P. Young, Appl. Phys. Lett. 30, 229 (1977); Phys. Rev. A 15, 2283 (1977); G. S. Hurst, M. H. Nayfeh, J. P. Young, M. G. Payne, and L. W. Grossman, in *Laser Spectroscopy*, Vol. 7 of *Springer Series in Optical Sciences*, edited by J. L. Hall and J. L. Carlsten (Springer-Verlag, New York, 1977); Phys. Today 30 (No. 9), 17 (1977).

[24] M. H. Nayfeh, G. S. Hurst, M. G. Payne, and J. P. Young, Phys. Rev. Lett. 39, 604 (1977).

[25] T. Watanabe, Phys. Rev. 138, A1573 (1965); 140, A35 (1965).

[26] T. Watanabe and K. Katsuura, J. Chem. Phys. 47, 800 (1967).

[27] D. R. Bates, Proc. R. Soc. Lond. A 240, 437 (1957); 243, 15 (1957); 245, 299 (1958); M. G. Payne and M. H. Nayfeh, Phys. Rev. A 13, 595 (1976).

[28] M. G. Payne and C. W. Choi (unpublished); C. W. Choi and M. G. Payne (unpublished).

[29] R. E. Olson, F. T. Smith, and E. Bauer, Appl. Opt. 10, 1848 (1971).