PHYSICAL REVIEW A VOLUME 20, NUMBER 5 NOVEMBER 1979

Collision-induced three-photon ionization

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(Received 7 November 1978)

A semiclassical treatment of collision-induced three-photon ionization of atoms with a near two-photon resonance is presented. The system is described by an effective two-level system. The wavelength dependence of the ionization yield does not obey a power law. When the first excited state is far from resonance, and with a C_6/R^6 interatomic potential, a first-order correction to the expected $-3/2$ power law obeys a $-1/2$ power law. This three-photon process promises to be an extremely sensitive method for the study of collisional effects in the far wing of two-photon S-S and S-D transitions, and without the requirement of high densities.

Recently, I suggested collision-induced photoionization (or laser-induced collisional ionization) as a means for studying the collisional parameters of the colliding system.[1] Because detection of charge is much more sensitive than detection of photons in absorption or fluorescence, this method allows considerable reduction of the required absorption tubes temperature and the pressure of the buffer gases as was shown in the first experimental demonstration of the process.[2,3] The reduction of the pressure reduces such effects as self-broadening, dimer absorption, and three-body processes, thus providing better resolution of the two-body collision parameters.[3] In my earlier theoretical analysis of the process,[1] only dipole allowed transitions were considered with an overall two-photon ionization process of the colliding system. The reduction in the required densities would also allow studies of electric dipole forbidden states where the absorption is much weaker, such as electric quadrupole or two-photon allowed S-D transitions. Moreover, the increased sensitivity would allow studies of S-S transition excited by two-photon absorption. The study of two-photon S-S transition in alkali-metal atoms perturbed by rare gases has received more interest recently. The shift and broadening were shown to be readily calculable,[4] and some recent absorption data were taken.[5,6] The absorption at the line center of S-S transition in Na–rare-gas pairs was recorded near the line center.[5] At the wing, the absorption in the case of Rb–rare-gas pairs was taken[6]; however, in the case of Na–rare-gas pairs, attempts were unsuccessful because of large Na_2 absorption at high densities.[7]

Laser-induced collisional ionization has recently received more theoretical interest.[8-13] This interest is aimed at the understanding of its nature. Quantum-mechanical[8-11] calculations were performed as opposed to the semiclassical theories.[1,12,13] Investigation of the effect of the rising intensity of the field where the field can actually interact with the collision dynamics was carried out.[8] New effects arise because the absorption of photons makes deeper parts of the continuum accessible to the interaction. These overlapping electronic continua play important roles in treating the collision dynamics. As a result, the intense field is predicted to lead to interesting effects, which include emission of electrons having distributions in kinetic energies which are roughly shifted by $\hbar\omega$ on either side of the laser-field-free emitted electrons.[8]

Experimentally, laser-induced ionization has recently received more interest too. Laser-induced Penning and associative ionization in Li-Li collisions were observed.[14] Ionization of dense atomic samples by slow electrons in the presence of resonant intense laser fields was shown to occur. It is believed that the initial electrons gain the required energy for ionization through superelastic collisions with the excited atoms.[15]

In this paper, I extend the ionization method to the study of collisional effects of S-S and S-D transitions. This is done by analyzing three-photon ionization of the colliding system with near two-photon resonance. I treat two regimes of the interaction. The first regime is when the ionization rate is high enough so that appreciable ionization takes place in a single collision. The second regime is when the ionization rate is slow so that the ionization takes place between collisions. I derive the dependence of the ionization yield on the excitation power, the field detuning from the first excited state, and on the interatomic potentials. Saturation of the ionization in the second limit in which the rate equation formalism is applicable can be achieved at much reduced powers than what is needed in the limit of single collisions.

The wavelength dependence of the ionization yield from the wing of the two-photon resonance exhibits deviation from the power law. This deviation is caused by the presence of the first excited state. Corrections to the $-\frac{3}{2}$ power law which is expected

for a C/R^6 interaction are generated with the first-order contribution obeying a $-\frac{1}{2}$ power law.

An impact-parameter method will be used where the internuclear coordinates are treated classically and without acceleration in the motion. I represent the system by field-free adiabatic electronic states $\phi_i(\vec{x},\vec{R})$ and only consider three discrete states and a continuum (Fig. 1). For simplicity the magnetic sublevels will not be included in this treatment,[1,16] and thus,

$$\psi(\vec{x},\vec{R}) = a_1(t)\phi_1(\vec{x},\vec{R})\exp\left(-\frac{i}{\hbar}\int_{t_1}^{t} w_1(\vec{R})dt\right) + a_2(t)\phi_2(\vec{x},\vec{R})\exp\left(-\frac{i}{\hbar}\int_{t_1}^{t} w_2(\vec{R})dt\right) + a_3(t)\phi_3(\vec{x},\vec{R})\exp\left(-\frac{i}{\hbar}\int_{t_1}^{t} w_3(\vec{R})dt\right) + \int a_c(w_c,t)\phi_c(\vec{x},\vec{R})\exp\left(-\frac{i}{\hbar}\int_{t_1}^{t} w_c(\vec{R})dt\right)dw_c , \tag{1}$$

where w_i are the field-free adiabatic potential energy surfaces, t_1 is some initial time, and a_i are time-dependent amplitudes. Explicit forms for a_i are found by solving the Schrödinger equation, given the initial conditions $a_1(-\infty)=1$ and $a_2(-\infty)=a_3(-\infty)=a_c(-\infty)=0$.

In the case where the system is electronically adiabatic in the absence of the field, I drop terms containing nonadiabatic couplings, and in the rotating wave approximation, a_i satisfy the following equations:

$$\frac{da_1}{dt} = i\mu_{12}E\exp\left(-i\int_{t_1}^{t}\delta_1(t')dt'\right)a_2 , \tag{2}$$

$$\frac{da_2}{dt} = i\mu_{21}E\exp\left(i\int_{t_1}^{t}\delta_1(t')dt'\right)a_1 + i\mu_{23}E\exp\left(-i\int_{t_1}^{t}\delta_2(t')dt'\right)a_3 , \tag{3}$$

$$\frac{da_3}{dt} + \gamma_1 a_3 = i\mu_{32}E\exp\left(i\int_{t_1}^{t}\delta_2(t')dt'\right)a_2 + iE\int \mu_{3c}\exp\left(-i\int_{t_1}^{t}\delta_c(t')dt'\right)a_c dw_c' , \tag{4}$$

$$\frac{da_c}{dt} = i\mu_{c3}E\exp\left(i\int_{t_1}^{t}\delta_c(t')dt'\right)a_3 , \tag{5}$$

where

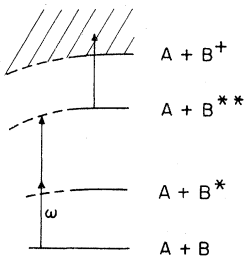

FIG. 1. Energy-level diagram of the colliding system.

$$\delta_1(t) = \frac{1}{\hbar}(w_2 - w_1 - \hbar\omega) ,$$

$$\delta_2(t) = \frac{1}{\hbar}(w_3 - w_2 - \hbar\omega) ,$$

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

μ_{ij} are the matrix elements of the dipole operator in units of $\hbar$, and γ_1 is introduced phenomenologically to describe the decay of the second excited state. Note that in writing Eqs. (2)–(5) I have neglected scattering between the continuum states by neglecting the coupling between them in Eq. (5).

The same procedure used in earlier works will be used to deal with the continuum states.[1,13] The procedure results in replacing the continuum states by a power-dependent frequency shift and a photoionization rate of the second excited state. The system (2)–(5) becomes

$$\frac{da_1}{dt} = L_1 a_2 , \tag{6}$$

$$\frac{da_2}{dt} = L_2 a_1 + L_4 a_3 , \tag{7}$$

$$\frac{da_3}{dt} + (\gamma + is_c)a_3 = L_3 a_2 , \tag{8}$$

where

$$\gamma(t) = \gamma_1 + \gamma_e, \quad s_c = -E^2 P\int \frac{\mu_{c3}^2}{\delta_c}dw_c, \qquad \gamma_e = \pi\hbar E^2\mu_{c3}^2 , \tag{9}$$

$$L_1 = i\mu_{12}E\exp\left(-i\int \delta_1(t')dt'\right), \quad L_2 = i\mu_{21}E\exp\left(i\int \delta_1(t')dt'\right), \quad L_3 = i\mu_{32}E\exp\left(i\int_{t_1}^{t}\delta_2(t')dt'\right), \quad L_4 = i\mu_{23}E\exp\left(-i\int_{t_1}^{t}\delta_2(t')dt'\right), \tag{10}$$

and P in Eq. (9) stands for the principal value.

Because the field is far away from resonance with the intermediate state when the atoms at infinite internuclear separation, the colliding system will exhibit a two-photon resonance at an internuclear separation which is drastically different from the internuclear separation which brings the field in resonance with the intermediate state. Therefore, at internuclear separation where two-photon resonance occurs, δ_1 and δ_2 are large. When the rate of change of a_1, da_1/dt, is much less than δ_1 and the rate of change of a_3, da_3/dt, is much less than δ_2, then the integral for a_2,

$$a_2 = i\mu_{21}\int E\exp\left(i\int_{t_1}^{t}\delta_1(t')dt'\right)a_1 dt + i\mu_{23}\int E\exp\left(-i\int_{t_1}^{t}\delta_2(t')dt'\right)a_3 dt\,, \tag{11}$$

can be evaluated by parts and we retain only the first terms in the asymptotic series. This results in an expression for a_2 which is a linear combination of a_1 and a_3:

$$a_2 = \mu_{21}E\frac{a_1}{\delta_1}\exp\left(i\int\delta_1(t')dt'\right) - \mu_{23}E\frac{a_3}{\delta_2}\exp\left(-i\int\delta_2(t')dt'\right). \tag{12}$$

Equation (12) is then used to eliminate a_2 from Eqs. (6) and (8), yielding an effective two-state problem with a_1 and a_3 connected directly by an effective interaction. With

$$a_1 = \exp\left(i\int S_1 dt\right)\bar{A}_1$$

and

$$a_3 = \exp\left(i\int(S_2+S_c)dt\right)\bar{A}_3\,,$$

where

$$S_1 = -\frac{\mu_{12}^2E^2}{\delta_1} \quad\text{and}\quad S_2 = \frac{\mu_{23}^2E^2}{\delta_2}\,, \tag{13}$$

I get

$$\frac{d\bar{A}_1}{dt} = \alpha_1\bar{A}_3\,, \tag{14}$$

$$\frac{d\bar{A}_3}{dt} + \gamma\bar{A}_3 = \alpha_3\bar{A}_1\,, \tag{15}$$

where

$$\alpha_1 = -\frac{i\mu_{12}\mu_{23}}{\delta_2}E^2\exp\left(-i\int\delta(t)dt\right), \tag{16}$$

$$\alpha_3 = -\frac{i\mu_{21}\mu_{32}}{\delta_1}E^2\exp\left(i\int\delta(t)dt\right), \tag{17}$$

$$\delta = \delta_0 + S,\quad \delta_0 = \delta_1+\delta_2 = \frac{1}{\hbar}(W_3 - W_1 - 2\hbar\omega)\,,$$

and

$$S = S_2 - S_1 + S_c\,.$$

The coupling between $\bar{A}_1$ and $\bar{A}_3$ is an effective two-photon coupling which is scaled down by the detunings δ_1 and δ_2 and oscillates at the two-photon detuning frequency δ. In the absence of damping, the above elimination of the intermediate state is equivalent to a unitary transformation of the original Hamiltonian.[17] The transformation is valid up to second order of the parameter $\vec{\mu}\cdot\vec{E}/\hbar\bar{\Delta}$, where $1/\bar{\Delta} = \frac{1}{2}(1/\delta_1 - 1/\delta_2)$ is the inverse of the frequency offset of the intermediate state; this requires the magnitude of δ_1 and δ_2 to be large. This condition, however, does not require the two-photon resonance offset frequency $\delta_1+\delta_2$ to be small in general as one can easily show from Eqs. (14) and (15). Because the wavelength dependence of the process is sought, namely the variation with $\sim\delta_1+\delta_2$, care must be taken to ensure the validity of the unitarity condition. In some cases excitations with a two-mode field may give a wider range of applicability. The present treatment can be easily generalized to the two-mode case provided the two frequencies are very different.

The fact that the coupling is scaled down by either δ_1 or δ_2 indicates that it is dependent on the internuclear separation through its dependence on the adiabatic potentials of the intermediate and final state. This is in contrast to the single-photon absorption between discrete states where the coupling between the initial and final state depends only on the electromagnetic field amplitude. The elimination of the nonresonant intermediate state resulted also in the introduction of intensity-dependent frequency shifts in the two-photon resonance. These shifts are also inversely proportional to either δ_1 and δ_2 and therefore depend on the internuclear separation where the two-photon absorption takes place.

I now solve Eqs. (14) and (15) for $\bar{A}_3$ from which expressions for the photoionization yield can be derived. Since changes in the two-photon amplitude can occur only at the resonance condition $\delta(t_0)=0$, we consider times near t_0. Let

$$A_3 = \exp\left(\int_0^\tau\frac{\gamma(t)}{2}dt\right)\exp\left(-\frac{1}{2}\int_0^\tau\frac{d}{dt}\ln\alpha_3\,dt\right)\bar{A}_3\,, \tag{18}$$

where $\tau = t - t_0$. Substituting Eq. (18) in Eqs. (14) and (15) gives

$$\left(\frac{d^2}{d\tau^2} + f(\tau)\right)A_3 = 0\,, \tag{19}$$

where

$$f(\tau) = -\alpha_1\alpha_3 - \frac{1}{4}\left(\gamma + \frac{d}{d\tau}\ln\alpha_3\right)^2 + \frac{1}{2}\frac{d\gamma}{d\tau} + \frac{1}{2}\frac{d^2}{d\tau^2}\ln\alpha_3 . \tag{20}$$

On the far wing, the laser radiation brings the system to a sharp crossing, and therefore changes in the amplitudes can only occur at the instantaneous resonance $\delta(t_0) = 0$. We solve Eq. (19) by the Landau-Zener method near the resonance time $t = t_0$, and consider cases where the time $\Delta\tau$ over which the solution of the transition probability reaches its asymptotic values satisfies the following condition:

$$\left(\frac{d}{d\tau}\ln F\right)^2\Big|_{t=t_0} (\Delta\tau)^2 \ll 1 ,$$

where F is the coupling between the initial and final state A_1 and A_3 and is defined below in Eq. (25). This condition implies that $d\ln F/d\tau$ varies by a small fraction over the entire time interval of transition. Thus we expand the function F around $\tau = t - t_0 = t_0 = 0$ and keep only terms of the order $d/dt \ln F(0)\tau$. Also close to $\tau = 0$, we expand δ as $\tau d\delta/d\tau(0)$ and γ as $\gamma(0) + [d\gamma(0)/d\tau]\tau$. This gives

$$f(\tau) = g_0 + \frac{i}{2}g_1 + \frac{g_1^2}{4}\left(\tau - \frac{i\beta_1}{g_1} - \frac{i\gamma(0)}{g_1} + 2\frac{F^2(0)\beta}{g_1^2}\right)^2 , \tag{21}$$

where

$$g_0 = F^2(0) - \beta_1^2 - \beta^2\frac{F^4(0)}{g_1^2} + i\frac{\beta}{g_1}F^2(0)[\beta_1 + \gamma(0)] , \tag{22}$$

$$g_1 = \left(1 - i\frac{d\gamma(0)}{d\tau}\Big/\frac{d\delta(0)}{d\tau}\right)\frac{d\delta(0)}{d\tau} , \tag{23}$$

$$F_1 = -\frac{i\mu_{21}\mu_{32}E^2}{\delta_1} , \quad \beta_1 = \frac{d}{d\tau}\ln F_1(0) , \tag{24}$$

$$F^2 = \frac{\mu_{12}^2\mu_{23}^2E^4}{\delta_1\delta_2} , \quad \beta = \frac{d}{d\tau}\ln F^2(0) . \tag{25}$$

Equation (19) can now be rewritten in the form of a Weber equation by defining the following quantities z and n:

$$z = \left(\tau - \frac{i\beta_1}{g_1} - \frac{i\gamma(0)}{g_1} + 2\frac{F^2(0)\beta}{g_1^2}\right)g_1^{1/2}e^{-i\pi/4} , \tag{26}$$

$$n = \frac{ig_0}{g_1} = q + ip , \tag{27}$$

where q and p are real. The result is

$$\left(\frac{d^2}{dz^2} + n - \frac{z^2}{4}\right)A_3 = 0 . \tag{28}$$

When n is an integer, Eq. (28) has bounded solutions at infinity which are represented in parabolic cylinder functions $D_n(\pm z)$ and $D_{-1-n}(\pm iz)$. The positive time asymptotic solution is given by[18]

$$A_3 = \frac{\sqrt{2\pi}}{\Gamma(n+1)}\left(\frac{F(0)F(\tau)}{g_1}\right)^{1/2}[X(0)X(\tau)]^q \times \exp[-\tfrac{1}{2}\pi p - m(0) - m(\tau) + i\theta] , \tag{29}$$

where Γ is the Γ function,

$$m(\tau) = p\phi + \tfrac{1}{4}X^2\sin 2\phi , \tag{30}$$

$$\theta = P\ln X + q(\phi + \tfrac{1}{4}\pi) + \tfrac{1}{2}X^2\cos 2\phi , \tag{31}$$

and X and ϕ are the magnitude and angle of the complex vector z defined for positive τ:

$$z = X(\tau)e^{i\phi - i\pi/4} . \tag{32}$$

The frequency shift caused by the nonresonant intermediate state, $S_2 - S_1$, and the frequency shift caused by the nonresonant continuum states S_c, affect the absorption line shape in two ways. First, the position of the resonance is measured from the shifted second excited level, $\delta = \delta_1 + \delta_2 + S_2 - S_1 + S_c$. Secondly, because of the nature of the crossing at $\delta = 0$, the rate of change of δ at $\delta = 0$ enters in the absorption amplitude. Equations (21)–(25) show that $f(\tau)$ depends on the rate of change of the frequency shifts through β_1 and β explicitly and on $d\delta(0)/d\tau$. Small rates of change of the frequency shifts arise in the case of long, smooth, or square laser pulses, although their respective frequency shifts might be large.[18]

Let us consider the case where the collision is slow enough and the light pulse smooth enough so that β, β_1, and $d\gamma(0)/d\tau$ are very small. In this case q vanishes, and $F(0)$ may be taken equal to $F(\tau)$. Many collisions lie in this category; these involve heavy atoms and lower temperature conditions. Most pulses of the order of a few nanosecond durations fall into this category, because of the shortness of the resonant interaction times at the wing. In these limits, the asymptotic probability $|A_3|^2$ reduces at large τ to[18]

$$|a_3|^2 = (1 - e^{-2\pi p})e^{-\gamma\tau} , \tag{33}$$

$$|a_1|^2 = e^{-2\pi p - \gamma\tau} , \tag{34}$$

$$p = \frac{F^2(0)}{d\delta/d\tau(0)} = \frac{\mu_{12}^2\mu_{23}^2E^4}{\delta_1(0)\delta_2(0)d\delta(0)/d\tau} . \tag{35}$$

Equation (33) describes the two-photon absorption at one crossing point and a subsequent decay of the absorption after the system goes through the crossing. In a single collision, however, there are two times where the system comes into the two-photon resonance. At a particular internuclear separation, the system absorbs when the atoms are approaching and departing each other. In the case where no appreciable decay takes place between the two crossings, then one can show that after two crossings

$$|a_2|^2 = 2(1 - e^{-2\pi p})e^{-2\pi p}e^{-\gamma\tau} . \quad (36)$$

The dependence of the absorption on the parameters enters through the function p. From Eq. (35), p is proportional to the square of the field intensity, and inversely proportional to the time rate of change of the difference potential $W_3 - W_1$ at the internuclear separation R_0 where absorption takes place. Moreover, the absorption depends on the magnitude of the difference potentials $W_2 - W_1$ and $W_3 - W_2$ evaluated at R_0. This dependence on the magnitude of the difference potentials is absent in the case of single-photon absorption of collisionally broadened S-P transitions. The function p depends also on the detuning of the field from the first and second isolated atom transitions Δ_1 and Δ_2, respectively. Detailed analysis of these effects will be given below when we discuss the three-photon ionization line shape.

Equation (33) predicts that for $2\pi p > 0.7$, inversion can be achieved at the wing of the two-photon resonance. When the second crossing of the interaction is taken into account and with no appreciable photoionization between the crossings, then the absorption probability goes down as $2\pi p$ becomes large. This decrease is due to stimulated emission at the second crossing. When, on the other hand, appreciable ionization takes place between the crossings, then the photoionization yield will continue to rise. In this case stimulated emission is negligible at the second crossing.

In the case of weak excitation where $2\pi p \ll 1$, then $|a_3|^2$ becomes

$$|a_3|^2 = 4\pi p\ e^{-\gamma\tau} , \quad (37)$$

which is linear in p, and thus is proportional to the square of the intensity in lowest order, inversely proportional to the slope of the difference potential $W_3 - W_1$, and inversely proportional to the detunings product $\delta_1\delta_2$.

I now derive expressions for the ionization yield. First I consider a high ionization rate so that appreciable ionization is produced in a single collision. In this case one needs to consider one crossing, and the total ionization probability is

$$r = \int_{-\infty}^{\infty} \gamma_e |a_3|^2 dt , \quad (38)$$

which gives

$$r = \frac{\gamma_e(1 - e^{-2\pi p})}{\gamma}[(1 - e^{-\gamma\tau_0})] , \quad (39)$$

where τ_0 is the pulse width. Saturation of the ionization step where r becomes equal to $1 - e^{-2\pi p}$ is achieved if $\gamma_e \gg \gamma_0$ and $\gamma\tau_0 \gg 1$. When also $2\pi p \gg 1$, then near unity of the three-photon ionization is achieved. With collision times of the order 10^{-12} sec, $\gamma\tau_0 \gg 1$ requires ionization rates of the order of 10^{12}/sec.

Let us consider a situation where the ionization rate is much smaller than the reciprocal of the time of resonance, and thus most of the ionization takes place between collisions. For a typical C_6 coupling, 10^{-57} cm^6 erg, and at a distance of 10 Å, the frequency detunings can reach 10^{12} sec^{-1}, which results in complete dephasing of the interaction. Therefore, a rate equation treatment can be used to describe the process. In the rate equation treatment, one first derives a two-photon absorption cross section by integrating over the impact parameters. For $2\pi p \ll 1$, $|a_3|^2$ reduces to $4\pi p$. Since all impact parameters less than R_0 experience the curve crossing, the absorption cross section σ is given by

$$\sigma = 4\pi \int_0^{R_0} 2\pi b\, db p = 4\pi^2 R_0^2 p , \quad (40)$$

where b is the impact parameter and R_0 is the internuclear separation where the two-photon absorption takes place.

I should mention that in carrying out the averaging over the impact parameters, care must be taken because of the presence of the intermediate state. The difficulty arises because encounters between atoms with impact parameters smaller than the internuclear distance at which 1-2 resonance occurs result in resonant absorption at 1-2 transition. This can cause an enhancement of the yield at the 1-3 transition. To isolate the 1-3 resonance yield, conditions can be chosen to minimize the yield from the resonance excitation of 1-2 transition. This can be achieved by choosing the laser wavelength such that the 1-2 resonance internuclear distance is extremely small. Also, this can be achieved by detuning to the blue side for an attractive 1-2 potential such that no collision-induced resonance occurs for all collisions. The velocity averaging gives a thermal rate constant K:

$$K = N(8kT/\pi\mu)^{1/2}\bar{\sigma} , \quad (41)$$

where

$$\bar{\sigma} = 2\int_0^{\infty} x^3 e^{-x^2}\sigma(x)\, dx . \quad (42)$$

K is the rate of absorption, μ is the reduced mass of the system, T is the temperature, k is Boltzmann's constant, $x = (\mu/2kT)^{1/2}v$, v is the relative speed, and N is the foreign gas density. With an effective two-photon absorption cross section and rate, one can describe the three-photon ionization by an effective two-level system and continuum states. I have previously solved this system in the case of two-photon ionization of colliding atoms.[1]

This gives

$$N_e = \frac{N_0 \sigma_a I}{f_2 - f_1} \sigma_i I \left(\frac{1 - e^{-f_1 \tau_0}}{f_1} - \frac{1 - e^{-f_2 \tau_0}}{f_2} \right), \tag{43}$$

where N_e is the number of photoelectrons, N_0 is the density of ground state, I is the laser intensity, σ_a and σ_i are the absorption and ionization cross sections, respectively, τ_0 is the pulse width, and

$$f_1 = \eta - \xi, \quad f_2 = \eta + \xi, \tag{44}$$

$$\eta = \tfrac{1}{2}(2\sigma_a I + \sigma_i I + \gamma_1), \tag{45}$$

$$\xi = [\tfrac{1}{4}(\gamma_1 + \sigma_i I)^2 + \sigma_a^2 I^2 + \sigma_a I \gamma_1]^{1/2}. \tag{46}$$

Let us consider the case where the ionization is saturated while the laser is tuned on the far wing. This situation makes the three-photon ionization line shape a direct monitor of the two-photon absorption line shape. With $\sigma_i I \tau \gg 1$ and $\sigma_i \gg \sigma_a$, the ionization yield is

$$\frac{N_e}{N_0} = (1 - e^{-\sigma_a I \tau}). \tag{47}$$

Near saturation of the three-photon process is achieved when $\sigma_a I \tau > 1$. Because, in the limit of ionization taking place between collisions, the two-photon absorption cross section is proportional to the density of foreign gas [Eqs. (41) and (42)], saturation of the process, $N_e = N_0$, can be achieved at much reduced powers than the case where ionization is achieved during the collision. With pulses of 1 μsec duration and absorption cross section equal to 10^{-19} cm^2, powers of the order 10 MW/cm^2 saturate the process. This is much less than what is needed in single collision processes.

On the far two-photon resonance wing where $\sigma_a I \tau \ll 1$, the ionization yield, with the ionization step being saturated, is

$$\frac{N_e}{N_0} = \sigma_a I \tau. \tag{48}$$

The function $d\delta/d\tau$, in Eq. (35), can be written as $(d\delta/dR)v$; thus the cross section σ goes like $1/v$, and thus, when the velocity average [Eqs. (41) and (42)] is carried out, Eq. (48) gives

$$\frac{N_e}{N_0} = \frac{8N\pi^2}{3} \frac{dR^3(0)}{d\delta} \frac{\mu_{12}^2 \mu_{23}^2 E^4}{\delta_1(0)\delta_2(0)}. \tag{49}$$

The saturated ionization when the laser is tuned to the far wing of the two-photon resonance depends quadratically on the pulse intensities as is expected for a two-photon process. The wavelength dependence of the absorption is governed by the derivative $dR^3/d\delta$ and by the dependence of δ_1 and δ_2 on the internuclear separation. Consider interaction potentials of the type c_1/R^6 for the difference potentials between the first excited and ground states, and c_2/R^6 for the difference potentials between the second and first excited states. The interaction potential between the second excited state and the ground state is then $(c_1 + c_2)/R^6$. The detunings δ_1, δ_2, and δ are then equal to

$$\Delta_1 - \frac{c_1}{R^6}, \quad \Delta_2 - \frac{c_2}{R^6}, \quad \text{and} \quad \Delta_1 + \Delta_2 + S - \frac{c_1 + c_2}{R^6},$$

respectively, where Δ_1 and Δ_2 are $\omega_2 - \omega$ and $\omega_3 - \omega_2 - \omega$, respectively. Here ω_i is the frequency of the isolated excited states with respect to the isolated ground state. Expression (49) is evaluated at resonance where $\delta = 0$, and thus we use

$$\Delta_1 + \Delta_2 + S = \Delta = \frac{c_1 + c_2}{R^6};$$

$\Delta_1 + \Delta_2$ is the detuning of the fields from the isolated two-photon resonance, while Δ takes into account the optical frequency shifts. Substituting for these detunings in (49), one gets

$$\frac{N_e}{N_0} = \frac{4N\pi^2}{3} \frac{(c_1 + c_2)^{1/2} \mu_{12}^2 \mu_{23}^2 E^4}{\Delta^{3/2} \{\Delta_1 - [c_1/(c_1 + c_2)]\Delta\}^2}. \tag{50}$$

The line shape in (50) does not follow a power law because of the effect of the nonresonant intermediate state. When Δ/Δ_1 is small so that one can neglect it, the line shape on the far wing goes like $\Delta^{-3/2}$. A first-order correction to the $\frac{3}{2}$ power law can be derived by expanding the denominator $\{\Delta_1 - [c_1/(c_1 + c_2)]\Delta\}^2$ in power series. Keeping the first-order contribution in Δ/Δ_1, we get

$$\frac{N_e}{N_0} = \frac{4N\pi^2}{3} \frac{(c_1 + c_2)^{1/2} \mu_{12}^2 \mu_{23}^2 E^4}{\Delta_1^2 \Delta^{3/2}} \left(1 + 2 \frac{c_1}{c_1 + c_2} \frac{\Delta}{\Delta_1} \right), \tag{51}$$

where the correction goes like $\Delta^{-1/2}$. This indicates that the correction falls off with Δ less rapidly than the main part.

In conclusion, I have derived expressions for the three-photon ionization with near two-photon resonance of colliding atoms. The effect of the intermediate state on the response is derived. The saturated ionization line shape as a function of the detuning from the two-photon resonance, and which is a monitor of the two-photon absorption, does not obey a power law. When the intermediate state is far away from resonance, and for c_6/R^6 coupling, the dominant power law is $-\frac{3}{2}$ and the first-order correction is a $-\frac{1}{2}$ power law. Because of the extra sensitivity achieved when the two-photon absorption is monitored by saturated ionization, this three-photon ionization process promises to be a very sensitive method for studying collisional effects of S-S and S-D transitions. Such experiments are being planned in our laboratory.

This work was supported by the University of Illinois Research Board.

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