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Two-photon ionization of colliding atoms*

Munir H. Nayfeh†
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

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Semiclassical expressions of two-photon ionization of two colliding atoms are derived for a wide range of electromagnetic field intensity and detunings from the isolated atom line. The dependence of the ionization yield on the details of the interaction potential of the system is derived. This process promises an extremely sensitive method for studying line broadening on the far wing, especially when absorption or fluorescence becomes very weak.

In the last few years there has been a growing interest in photon absorption by atoms colliding in an external electromagnetic field. This includes processes where the frequency of the field is close to the characteristic frequency of one of the atoms (optical collision)[1-10] and to the frequency difference between transitions in both atoms (radiative collision).[4,11-14] Experimental evidence for laser-induced collisional transfer has been established recently in a number of experiments.[15] Optical collisions have been used extensively in line-broadening studies from which potential curves of the colliding atoms can be extracted, since the amount of absorption or fluorescence can be related to the detail of the interaction. In this work we extend the optical-collision studies by studying two-photon ionization of the colliding atoms. Because complete conversion of every absorption event to an ion pair is possible,[16] the ionization channel promises extreme sensitivity since it is easier to detect a small number of electrons than a small number of photons. This will allow measurements at the extreme wing where absorption or fluorescence becomes vanishingly small. Even single absorption events can be detected with ease by gas proportional counters which are sensitive to single electrons.[16]

The theoretical aspects of line broadening of many systems have been studied by many researchers. Here we give a semiclassical derivation of the two-photon ionization of a gas mixture. The system is approximated by two field-free adiabatic electronic states and an infinite set of continuum states. The ionization yield is derived for an arbitrary field strength and for a wide range of detunings from the isolated atom line. The dependence of the ionization yield on the details of the interaction is derived; therefore, the ionization channel can be used as a monitor of the details of the interaction.

Now we develop a theoretical picture of the two-photon ionization of the mixture. An 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 b is the impact parameter and v is the relative velocity of the nuclei. Let us consider the time-dependent electronic-field Schrödinger equation:

$$i\frac{\partial}{\partial t}\psi(\vec{x},\vec{R})=(H_{\mathrm{el}}+H_{\mathrm{In}})\psi(\vec{x},\vec{R})\,, \tag{1}$$

$$H_{\mathrm{el}}=T_x+V(\vec{x},\vec{R})\,, \tag{2}$$

where $\vec{x}$ and $\vec{R}$ stand for electronic and nuclear coordinates, respectively; T_x is the electronic kinetic energy operator; $V(x,R)$ is the electrostatic interaction among electrons and nuclei; and H_{In} is the classical interaction potential between the molecular system and the laser field. In the dipole approximation and with a linearly polarized field amplitude $\epsilon=\epsilon_0\cos\omega t$, H_{In} is written $-\mu\epsilon_0\cos\omega t$, where μ is the dipole operator and ω is the frequency of the exciting field. We represent the system by two field-free adiabatic discrete electronic states $\phi_i(\vec{x},\vec{R})$ and a continuum ϕ_c (Fig. 1). We assume $\langle\phi_i|\phi_j\rangle=\delta_{ij}$, where i, $j=1$, 2, and 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.[17] Therefore,

$$\begin{aligned}\psi(\vec{x},\vec{R})={}&a_1(t)\phi_1(\vec{x},\vec{R})\exp\left(-\frac{i}{\hbar}\int_{t_1}^{t}w_1(\vec{R})\,dt\right)\\&+a_2(t)\phi_2(\vec{x},\vec{R})\exp\left(-\frac{i}{\hbar}\int_{t_1}^{t}w_2(\vec{R})\,dt\right)\\&+\int a_c(w_c\,,t)\phi_c(\vec{x},\vec{R})\\&\qquad\times\exp\left(-\frac{i}{\hbar}\int_{t_1}^{t}w_c(\vec{R})\,dt\right)dw_c\,,\end{aligned} \tag{3}$$

where ϕ_i are the field-free adiabatic discrete electronic states, w_i are the corresponding field-free

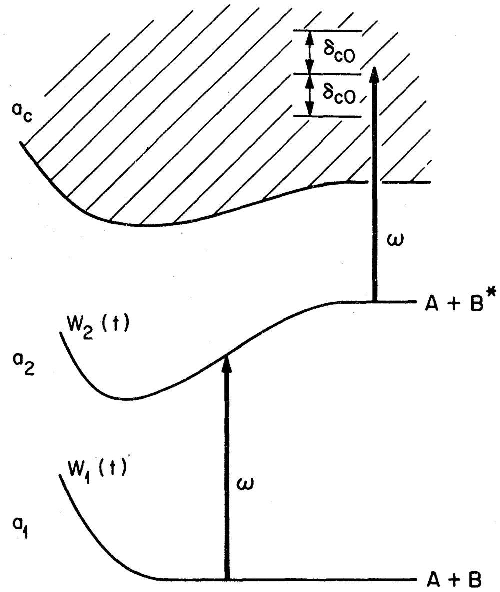

FIG. 1. Energy-level diagram showing a restricted basis of two discrete states and the continuum states.

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 (1), 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 the equation of motion (1) becomes

$$\frac{da_1}{dt}=i\frac{\mu_{12}\epsilon_0}{2\hbar}\exp\left(-i\int_{t_1}^{t}\delta(t')\,dt'\right)a_2\,, \tag{4}$$

$$\frac{da_2}{dt}+\gamma_0 a_2=i\frac{\mu_{21}\epsilon_0}{2\hbar}\exp\left(i\int_{t_1}^{t}\delta(t')\,dt'\right)a_1 +\frac{i\epsilon_0}{2\hbar}\int\mu_{2c}\exp\left(-i\int_{t_1}^{t}\delta_c(t')\,dt'\right)a_c\,dw_{c'} \tag{5}$$

$$\frac{da_c}{dt}=\frac{i\mu_{c2}\epsilon_0}{2\hbar}\exp\left(i\int_{t_1}^{t}\delta_c(t')dt'\right)a_2\,, \tag{6}$$

where

$$\delta(t)=(1/\hbar)(w_2-w_1-\hbar w)\,, \tag{7a}$$

$$\delta_c(t)=(1/\hbar)(w_c-w_2-\hbar w)\,, \tag{7b}$$

μ_{ij} are the matrix elements of the dipole operator, and γ_0 is introduced phenomenologically to describe the decay of the intermediate state. Note that in writing Eqs. (4)–(6) we have neglected scattering between the continuum states by neglecting the coupling between them in Eq. (6).

Since transitions from ϕ_2 to the continuum obey the Franck-Condon principle, we separate the continuum states into two sets; the first set is close to the resonance condition ($|\delta_c|\leqslant|\delta_c^0|$), where $|\delta_c^0|$ is a small quantity, and the second set is that which is sufficiently far away from resonance ($|\delta_c|\geqslant|\delta_c^0|$). When δ_c is large, energy is not conserved as a result of nonresonant continuum states; consequently, intensity-dependent frequency shifts are introduced in the intermediate discrete level. The near-resonant continuum states, however, result in intensity-dependent sink source or decay of the intermediate discrete level. When δ_c is large, the right-hand side of Eq. (6) oscillates swiftly; and if the field is a slowly varying function of time, one can solve Eq. (6) for a_c by integrating over time by parts:

$$a_c=\frac{\mu_{c2}\epsilon_0(t)}{2\hbar\delta_c(t)}\exp\left(i\int\delta_c(t')\,dt'\right)a_2\,. \tag{8}$$

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

$$a_c=i\frac{\mu_{c2}}{2\hbar}\int\epsilon_0(t)\exp\left(i\int\delta_c(t')\,dt'\right)a_2(t)\,dt\,. \tag{9}$$

Substituting expression (8), which is valid for large $|\delta_c|$ ($|\delta_c|\geqslant|\delta_c^0|$), results in an expression for the shift as an integral over δ_c. Substituting expression (9), which is valid for $|\delta_c|\leqslant|\delta_c^0|$, in Eq. (5) and carrying out the integration over δ_c first with the assumption that μ_{c2} is fairly constant for $|\delta_c|\leqslant|\delta_c^0|$ enables one to easily carry out the integration over time. This procedure was also used in dealing with the continuum states in photoionization of isolated atoms.[18] The set of equations (4)–(6) reduces to

$$da_1/dt=L_1 a_2\,, \tag{10}$$

$$da_2/dt+\mathbf{\Gamma}(t)a_2=L_2 a_1\,, \tag{11}$$

where

$$\mathbf{\Gamma}(t)=\gamma_0+is_1(\epsilon_0^2)+\gamma_1(\epsilon_0^2)\,, \tag{12}$$

$$L_1=i\frac{\mu_{12}\epsilon_0}{2\hbar}\exp\left(-i\int\delta(t')\,dt'\right), \tag{13}$$

$$L_2=i\frac{\mu_{21}\epsilon_0}{2\hbar}\exp\left(i\int\delta(t')\,dt'\right), \tag{14}$$

$$s_1=-\frac{\epsilon_0^2}{4\hbar^2}\mathrm{P}\int\frac{\mu_{c2}^2}{\delta_c}dw_c\,, \tag{15}$$

$$\gamma_1=\hbar\pi[\epsilon_0^2(t)/4\hbar^2]\,\mu_{c2}^2\,, \tag{16}$$

where P in Eq. (15) stands for the principal value.

We would like to mention that the above handling of the continuum states results in shifts and decay which agree with the calculation carried out by Beers and Armstrong[19] when the effect of the foreign gas is eliminated. The above authors have treated the two-photon ionization of isolated atoms.

We now proceed to solve Eqs. (10)–(16) 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:

$$A_2=\exp\left(\int_0^t \frac{\Gamma(t)}{2}\,dt\right)\exp\left(-\frac{1}{2}\int_0^t \frac{d}{dt}\ln L_2\,dt\right)a_2\,, \tag{17}$$

where $\tau=t-t_0$ and t_0 is the time where resonance occurs, $\delta(t_0)=0$. Substituting Eq. (17) in Eqs. (10) and (11), we obtain

$$(d^2/d\tau^2+f(\tau))\,A_2=0\,, \tag{18}$$

where

$$f(t)=-L_1L_2-\frac{1}{4}\left(\Gamma+\frac{d}{dt}\ln L_2\right)^2+\frac{1}{2}\frac{d}{dt}\Gamma+\frac{1}{2}\frac{d^2}{dt^2}\ln L_2\,. \tag{19}$$

We proceed to solve **Eq.** (18) 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

$$f(t)=E^2+\frac{1}{4}\left(\delta-i\frac{d}{d\tau}\ln E-i\Gamma\right)^2+\frac{1}{2}\frac{d\Gamma}{d\tau}+\frac{1}{2}\left(\frac{d^2}{d\tau^2}\ln E+i\frac{d\delta}{d\tau}\right), \tag{20}$$

where

$$E^2=\mu_{12}^2\epsilon_0^2/4\hbar^2\,.$$

Close to $t=t_0$ or $\tau=0$, one can expand $\delta(\tau)$ as $\tau[d\delta(0)/d\tau]$ and write

$$f(t)=g_0+\frac{i}{2}g_1+\frac{g_1^2}{4}\left(\tau-\frac{i}{g_1}\frac{d}{d\tau}\ln E-\frac{i\Gamma}{g_1}\right)^2, \tag{21}$$

$$g_0=E^2+\frac{1}{2}\frac{d}{d\tau}\Gamma+\frac{1}{2}\frac{d^2}{d\tau^2}\ln E\,, \tag{22}$$

$$g_1=d\delta(0)/d\tau\,. \tag{23}$$

Substituting Eqs. (21)–(23) in Eq. (18) and with the following definitions of z and n,

$$z=\left(\tau-\frac{i}{g_1}\frac{d}{d\tau}\ln E-\frac{i\Gamma}{g_1}\right)g_1^{1/2}e^{-i\pi/4}\,, \tag{24}$$

$$n=ig_0/g_1=q+ip\,, \tag{25}$$

where q and p are real, Eq. (18) reduces to the following equation:

$$(d^2/dz^2+n+\tfrac{1}{2}-\tfrac{1}{4}z^2)A_2=0\,. \tag{26}$$

For a general pulse, n, defined in (25), is time dependent and thus depends on z. Only when n is time independent does Eq. (26) reduce to a Weber equation. However, when the pulse is long, then the smooth peak of the long pulse can serve as a constant field.[20,21] When n is an integer, Eq. (26) has bounded solutions at infinity which are represented in parabolic cylinder functions $D_n(\pm z)$ and $D_{-n-1}(\pm iz)$. In this case, the function g_0 becomes real; and, therefore, q is identically zero. In this limit one can show that the asymptotic probability $|a_2|^2$ is given by[20]

$$|a_2|^2=(1-e^{-2\pi p})e^{-\Gamma\tau}, \tag{27}$$

where

$$p=\frac{E^2}{d\delta(0)/d\tau}\,. \tag{28}$$

It is interesting to note that result (27) predicts a simple and single decay of the population of the excited state. The decay constant Γ defined in Eqs. (12) and (16) involves radiative, collisional, chemical depletion, as well as intensity-dependent ionization. The function p in the constant-field limit depends only on the field intensity, oscillator strength of the transition, and the slope of the difference potential curves of the system. Only when time variation of the field is included will the function p depend on the relaxation parameters through their time variation. We now consider the different time scales encountered in this process.

In the process there are six time scales that are relevant: the time that the single collisional event stays in resonance is of the order of 10^{-14} sec, the collision time is ~10^{-12} sec, the time between collision at an atmosphere of buffer gas is ~10^{-8} sec, the lifetime of the level is ~10^{-7} sec, the exciting pulse width is ~10^{-6} sec. Therefore, during the time of resonance, 10^{-14} sec, either the ionization or the decay is vanishingly small unless the ionization rate reaches 10^{12} sec^{-1}. Otherwise, after the initial population, which takes place during the time of resonance, the system evolves according to the slower processes.

Equation (27) 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 and departing. Since during collision not much decay or ionization takes place unless those rates exceed 10^{12} sec^{-1}, one can show that after two symmetric resonance times $|a_2|^2$ is

$$|a_2|^2 = 2(1 - e^{-2\pi p})e^{-2\pi p}, \tag{29}$$

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. (29). 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. (27)] $|a_2|^2$ 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 the limit of very weak field $|a_2|^2$ again goes to zero, there exists an intermediate field where $|a_2|^2$ maximizes. However, when $2\pi p \ll 1$, then $|a_2|^2$ becomes linear in the field intensity. Expanding the exponential functions in Eq. (29) yields the following:

$$|a_2|^2 = 4\pi p. \tag{30}$$

Far away in the wing—e.g., when the atoms get closer to each other, thus 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 order 10^{12} sec^{-1}; thus, appreciable ionization is achieved before other collisions take place and before the second crossing. This condition requires power densities of the order of 10^{11} W/cm^2 for a photoionization cross section of the order of 10^{-17} cm^2. Such high power will induce power broadening of the order 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 near complete ionization and inversion during the collision, one needs to consider only one crossing as given in Eq. (27).

We next derive the ionization yield. Since the continuum states were eliminated from the coupled equations by introducing a shift and a decay of the excited state, one can use this scheme to calculate the total ionization probability. From Eq. (11) and from the result that the decay of the excited state into the continuum is given by $\gamma_1(\epsilon_0^2)$ [Eq. (16)], one writes the total probability of ionization (r) as follows:

$$r = \int_{-\infty}^{\infty} \gamma_1 |a_2|^2 dt. \tag{31}$$

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

$$r = \frac{\gamma_1(1 - e^{-2\pi p})}{\gamma_0 + \gamma_1}\{1 - \exp[(\gamma_0 + \gamma_1)\tau]\}, \tag{32}$$

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

$$r = (1 - e^{-2\pi p}). \tag{33}$$

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

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. (32) 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 then evolves according to the slower processes 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 is adequate for the processes between collision. In order to do so, one has to write 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. (30); therefore, the cross section σ is

$$\sigma = 4\pi \int_0^{R_0} 2\pi b\, db\, p, \tag{34}$$

where R_0 is the internuclear separation where absorption takes place,

$$\sigma = 8\pi^2 \frac{\mu_{12}^2}{4\hbar^2} \frac{dR^0}{d\delta} \epsilon_0^2 \int_0^{R_0} \left(\frac{dR}{dt}\right)^{-1} b\, db, \tag{35}$$

$$\sigma = 4\pi^2 \frac{\mu_{12}^2}{4\hbar^2} \epsilon_0^2 \frac{dR^0}{d\delta} \frac{R_0^2}{v}. \tag{36}$$

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

$$k = N(8KT/\pi\mu)^{1/2}\,\bar{\sigma}\,, \tag{37}$$

where

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

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. This results in

$$k = \frac{8N\pi^2}{3}\,\frac{\mu_{12}^2}{4\hbar^2}\,\frac{dR^{03}}{d\delta}\,\epsilon_0^2\,. \tag{38}$$

Note that k can be written $I\bar{\sigma}$, where I is the flux 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 result [Eq. (38)] was derived on the assumption that $2\pi p \ll 1$ in Eq. (29), we predict the statistical arguments will fail as the intensity of light increases such that $2\pi p \sim 0.1$. 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. (30). This in turn requires somewhat steep potential curves. Therefore, in an intermediate region one will find that higher orders of $2\pi p$ will be important and, therefore, higher powers of the configuration space become important, resulting in temperature-dependent rate constants.

With the absorption rate (38), one can write the rate equations describing the two-photon ionization. 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

$$\frac{dn_0}{dt} = -\sigma_a I n_0 + \sigma_a I \frac{g_1}{g_0} n_1 + \gamma_0 n_1\,, \tag{39}$$

$$\frac{dn_1}{dt} + \gamma_0 n_1 = \sigma_a I n_0 - \sigma_a I \frac{g_1}{g_0} n_1 - \sigma_i I n_1\,, \tag{40}$$

$$\frac{dn_e}{dt} = \sigma_i I n_1\,, \tag{41}$$

where σ_a, σ_i are the absorption and ionization cross sections, respectively; I is the photon flux; g_0, 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

$$\left[\frac{d^2}{dt^2} + \left(\sigma_a I + \sigma_a I\frac{g_1}{g_0} + \sigma_i I + \gamma_0\right)\frac{d}{dt} + \sigma_a I\left(\gamma_0 + \sigma_a I\frac{g_1}{g_2} + \sigma_i I\right) - \sigma_a^2 I^2 \frac{g_1}{g_2} - \sigma_a I \gamma_0\right] n_1 = 0\,. \tag{42}$$

Note that $\sigma_i I$ is not equal to the isolated pair ionization rate $\gamma_1\epsilon_0^2$ [Eq. (31)] because here ionization takes place during collisions. During collision, quantum substates are mixed. It is taken here that σ_i includes the degeneracy of the excited state. Equation (42) can easily be shown to have the following solution:

$$n_1 = [N_0\sigma_a I/(f_2 - f_1)]\,(e^{-f_1 t} - e^{-f_2 t})\,, \tag{43}$$

where

$$f_1 = \alpha - \beta, \quad f_2 = \alpha + \beta \tag{44}$$

and

$$\alpha = \tfrac{1}{2}[\sigma_a I(1 + g_1/g_0) + \sigma_i I + \gamma_0]\,, \tag{45}$$

$$\beta = \{\tfrac{1}{4}[\gamma_0 + \sigma_a I(g_1/g_0) + \sigma_i I - \sigma_a I]^2 + \sigma_a^2 I^2 (g_1/g_0) + \sigma_a I \gamma_0\}^{1/2}\,. \tag{46}$$

Therefore, the ionization yield can be derived from Eq. (41):

$$N_e = \sigma_i I \int_0^\tau n_1\,dt\,, \tag{47}$$

where τ is the pulse length. Substituting Eq. (43) in Eq. (47), we get

$$N_e = \frac{N_0\sigma_a I}{f_2 - f_1}\,\sigma_i I\left(\frac{1 - e^{-f_1\tau}}{f_1} - \frac{1 - e^{-f_2\tau}}{f_2}\right)\,. \tag{48}$$

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 and, 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,

$$N_e = N_0[1 - (\sigma_i e^{-\sigma_a I\tau} - \sigma_a e^{-\sigma_i I\tau})/(\sigma_i - \sigma_a)]\,, \tag{49}$$

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

$$N_e = N_0(1 - e^{-\sigma_a I\tau})\,. \tag{50}$$

Expressions (48) and (50) 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

$$N_e/N_0 = \sigma_a I\tau\,. \tag{51}$$

Equation (51) shows linear dependence on buffer-gas pressure and on the light intensity. The dependence on the detuning enters in σ_a. Substituting for σ_a the velocity averaged cross section (38), we get

$$\frac{N_e}{N_0}=\frac{8N\pi^2}{3}\frac{\mu_{12}^2}{4\hbar^2}\epsilon_0^2\frac{dR^3}{d\delta}. \tag{52}$$

For interaction potential of the type c_6/R^6, $\delta=c_6/\hbar R^6$; therefore, the absorption goes like $\delta^{-3/2}$:

$$\frac{N_e}{N_0}=\frac{4N\pi^2}{3}\frac{\mu_{12}^2}{4\hbar^2}\epsilon_0^2\left(\frac{c_6}{\hbar}\right)^{1/2}\delta^{-3/2}. \tag{53}$$

At a particular intensity, $\log(N_e/N_0)$ vs $\log\delta$ is a straight line with slope $-\frac{3}{2}$ and intercept that depends on c_6 and the other parameters; therefore, an accurate measurement of the slope and intercept determines the interaction force. For interaction potential of type b/R^3, the absorption goes like δ^{-2}:

$$\frac{N_e}{N_0}=\frac{8N\pi^2}{3}\frac{\mu_{12}^2}{4\hbar^2}\epsilon_0^2\frac{6}{\hbar}\delta^{-2}. \tag{54}$$

The slope of $\log(N_e/N_0)$ vs $\log\delta$ for b/R^3 is -2.

Note that at higher buffer-gas pressures, $\sigma_a I\tau$ can become greater than unity; therefore, saturation of the absorption can take place even in the wing. Closer to the line center, saturation of the absorption can be achieved easily.

In conclusion, we have derived expressions for two-photon ionization of a gas mixture in both regimes: the ionization during collision where dephasing does not take place and ionization between collisions where dephasing does take place. In both, the dependence of the ionization yield on the details of the interaction of the colliding system is derived. The temperature dependence is also derived, and deviation from the results of statistical theories are derived.

Since saturation of the ionization is attainable with available dye lasers, this derivation is of interest to studies of line broadening[22]; and the two-photon ionization process provides a sensitive method for monitoring the broadening process since detecting a small number of electrons is easier than detecting the same number of absorbed or emitted photons.

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†Address after August 15, Dept. of Physics, Yale University, New Haven, Conn. 06520.

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