

Selective ionization: Effects of power broadening, laser bandwidth, and interaction time on selectivity

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We present an analysis of the factors that affect selectivity in resonant multiphoton ionization. After a discussion of the formalism in terms of the density matrix in the context of two-photon-resonant three-photon ionization, we apply the theory to Li and Sr, demonstrating the effects of laser bandwidth, power broadening, and pulse duration.

I. INTRODUCTION

Although a substantial body of theoretical work on resonant multiphoton ionization has been published,¹ most of it has been presented in terms of rather general formalisms not directly useful to those experimentalists who are interested in the application of such processes to selective ionization. The role of saturation, ac Stark shift, laser bandwidth, and intensity fluctuations are aspects about which important questions seem to exist among experimentalists active in the field. Moreover, most theoretical papers have concentrated on rate approximations having thus underemphasized the very important role of laser-pulse duration.

Our purpose in this paper is to present a brief discussion of the essentials of the formalism and to show by means of realistic calculations how the above aspects affect isotopic selectivity. We have, in fact, chosen to discuss numerical results on two atoms Li and Sr, upon which experimental interest has recently been focused.²

A typical scheme of resonant multiphoton ionization (RMI) envisaged in connection with isotope separation, measurement of cross sections of excited states, and related problems involves a transition between two bound states $|g\rangle$ and $|a\rangle$ and ionization from the energetically higher of these two states $|a\rangle$. In general, the transition $|g\rangle \rightarrow |a\rangle$ can involve any number of photons as can the transition $|a\rangle \rightarrow \text{continuum}$. No real transitions to other states are assumed. The strengths of the above two transitions are thus determined by the appropriate multiphoton effective matrix elements³ and the laser intensity. Both bound states $|g\rangle$ and $|a\rangle$ will in general undergo ac Stark shifts under the influence of the laser that causes the transition. These shifts are proportional to the intensity of the laser.

If the laser is not monochromatic,⁴ allowance must be made for its finite bandwidth which affects the saturation, the selectivity, the dependence on laser power, etc. If in addition to the nonzero bandwidth, the laser undergoes intensity fluctuations, the ac Stark shift is generally enhanced⁵ by a factor depending on the details of the stochastic behavior of the field. In that case it is not given simply by the polarizability multiplied by the intensity.

Intensity fluctuations do of course affect more than the ac Stark shift. They affect the multiphoton transition rate from $|g\rangle$ to $|a\rangle$ and from $|a\rangle$ to the continuum, the saturation behavior of the process, the total yield, and hence the selectivity.

If maximum ionization is desired (as is the case in connection with isotope separation), a time-dependent analysis of the process is often necessary. In fact, one of the parameters that determine the maximum of ionization, given a desired degree of selectivity, is the interaction time. Obviously, if this time is too long, selectivity will suffer because the off-resonant isotope will also be ionized significantly. Also, if the interaction time is too short, selectivity will suffer because both on- and off-resonant isotopes will be ionized only by a small percentage. The amount of ionization of the on-resonant isotope will then be comparable to that of the off-resonant isotope. There is an optimum interaction time which is related to the saturation of ionization. We must therefore consider the solution of the density-matrix equations incorporating all necessary effects. Under certain circumstances, rate equation approximations to the full density matrix may be useful, at least as a first estimate. In what follows, we discuss examples of such rate equations and the limits of their applicability in the context of two-photon-resonant three-photon ionization.

Power broadening of the intermediate excited state (due to both Rabi oscillations and ionization) has a profound influence on selective ionization. Higher laser intensity helps the ionization but at the cost of selectivity. Good selectivity, on the other hand, requires low intensity in order to avoid power broadening. But low intensity implies sacrifice of ionization. Thus with a single laser, one is forced to a compromise between selectivity and amount of ionization dictated in each case by the magnitude of the atomic parameters. In particular, the relative magnitude of Rabi frequency and ionization of the intermediate states is the most important factor as we will also see in the specific examples of the two atoms examined later on. If, on the other hand, a second laser of larger intensity is employed for the ionization step (with frequency chosen so as to leave the bound-bound transition unaffected) one has the option of increased ionization combined with good

selectivity. In this fashion, the power broadening due to the Rabi oscillation is minimized which is especially necessary when the Rabi-frequency matrix element dominates that of ionization, as is the case with Sr. Of course, this is particularly important in two-photon-resonant three-photon ionization where Rabi frequency and ionization width are both proportional to the laser intensity. Thus an additional aspect analyzed in this paper is the optimization of selectivity and ionization achieved by the use of a second laser. This requires a slight modification of the existing formalism as discussed in the following section.

Our intention in this paper is neither the elaboration of theoretical intricacies of field-fluctuation effects nor the review and evaluation of possible schemes for selective ionization. We aim instead at the demonstration of the relation between theoretical understanding of selective ionization and application to experiments.

II. THE AVERAGED DENSITY-MATRIX EQUATIONS

Let $|1\rangle$ and $|2\rangle$ be the lower and upper resonant states with energies $\hbar\omega_1$ and $\hbar\omega_2$. A laser of frequency ω tunable around the two-photon transition $|1\rangle \rightarrow |2\rangle$ is assumed; which means $2\omega \cong \omega_2 - \omega_1$. The laser is allowed to have a nonzero bandwidth denoted by γ_L . The third photon ionizes the atom in state $|2\rangle$ with a rate denoted here by γ_2 (also referred to as the ionization width of state $|2\rangle$). It is given by the photoionization cross section of state $|2\rangle$ multiplied by the photon flux. If it takes more than one photon to ionize from state $|2\rangle$, γ_2 will be given by the appropriate generalized cross section multiplied by the corresponding power of the photon flux. Certain important aspects of the process depend significantly on whether γ_2 is linear in the photon flux or not. We shall proceed here with the assumption that γ_2 is linear in the flux which is equivalent to considering two-photon-resonant three-photon ionization. The excited state $|2\rangle$ can in general decay back to $|1\rangle$ via a cascade of spontaneous emissions, the net rate of which we denote by Γ_2 .

If we consider the matrix elements $\rho_{ij}(t)$ of the atomic density matrix and introduce the standard transformation $\rho_{12}(t) = \sigma_{12}(t)e^{i2\omega t}$ and $\rho_{jj}(t) = \sigma_{jj}(t)$, $j=1,2$, we can write the equations in terms of the slowly varying quantities $\sigma_{ij}(t)$. The electric field of the laser is written as

$$\mathbf{E}(t) = [\epsilon(t)e^{i\omega t} + \epsilon^*(t)e^{-i\omega t}] \mathbf{e}, \quad (1)$$

where \mathbf{e} is the polarization vector and $\epsilon(t)$ the amplitude whose slow fluctuations (slow compared to $1/\omega$) give rise to the nonzero bandwidth and possible intensity fluctuations. The interaction between atom and field in the dipole approximation is given by $-\boldsymbol{\mu} \cdot \mathbf{E}(t)$ with $\boldsymbol{\mu}$ being the usual dipole operator. Without going into the details of the derivation,⁴ we quote now the equations of motion of the slowly varying density matrix $\sigma_{ij}(t)$.

$$\frac{d}{dt} \langle \sigma_{11}(t) \rangle = \Gamma_2 \langle \sigma_{22}(t) \rangle + 2 \operatorname{Im} \{ \mu_{12}^* \langle \sigma_{12}(t) [\epsilon^*(t)]^2 \rangle \}, \quad (2a)$$

$$\begin{aligned} \frac{d}{dt} \langle \sigma_{22}(t) \rangle = & -(\Gamma_2 + \gamma_2) \langle \sigma_{22}(t) \rangle \\ & - 2 \operatorname{Im} \{ \mu_{12}^* \langle \sigma_{12}(t) [\epsilon^*(t)]^2 \rangle \}, \end{aligned} \quad (2b)$$

$$\begin{aligned} \left[\frac{d}{dt} + i\Delta + \frac{1}{2}(\Gamma_2 + 3\gamma_2 + 2\gamma_L) \right] \langle \sigma_{12}(t) [\epsilon^*(t)]^2 \rangle \\ = i\mu_{12} 2\epsilon_0^4 \langle \sigma_{22}(t) \rangle - \langle \sigma_{11}(t) \rangle, \end{aligned} \quad (2c)$$

where

$$\mu_{12} \equiv \hbar^{-2} \sum_m \frac{\mu_{1m} \mu_{m2}}{\omega_{m1} - \omega} \quad (3)$$

is the usual two-photon effective dipole matrix element,^{3,4} involving a summation over all virtual intermediate states and

$$\Delta = 2\omega - \omega_{21} - 3F_{21} \quad (4)$$

is the dynamic detuning from exact two-photon resonance. It is referred to as "dynamic," because it includes the ac Stark shift F_{21} of the resonance transition. F_{21} is given by the difference $F_1 - F_2$ between the shifts of states $|1\rangle$ and $|2\rangle$, respectively, and is proportional to the laser intensity, the constant of proportionality being the polarizability of the respective state. The detuning from resonance changes, therefore, with laser intensity.

The model on which the above equations are based assumes that the complex amplitude $\epsilon(t)$ of the electric field fluctuates around an average value ϵ_0 . This gives rise to a bandwidth [full width at half maximum (FWHM)] γ_L and in general to intensity fluctuations. The rigorous treatment of the problem including intensity fluctuations is extremely complicated and has been discussed elsewhere in more than one context.^{5,6} Here we adopt a simplified version of the theory which was developed in a much earlier paper⁴ and where some of the details of the derivation can be found. It is simplified in that the effect of amplitude fluctuations is treated perturbatively while that of phase fluctuations is treated exactly. The factors of 3 appearing in front of γ_2 and F_{21} , as well as the factor of 2 in front of ϵ_0^4 in Eq. (2c), have their origin in amplitude fluctuations. They should be replaced by one, if the amplitude is perfectly stabilized. The effect of phase fluctuation, on the other hand, is properly taken into account through the presence of γ_L in Eq. (2c). In this phase diffusion model, the laser spectrum is Lorentzian near the center with FWHM $2b$ and has a cutoff around β ($> b$). The γ_L is expressed as⁷

$$\gamma_L = 2b \frac{\beta^2}{\Delta^2 + \beta^2}. \quad (5)$$

It is for the sake of simplifying the discussion in this paper that we speak of amplitude and phase fluctuations as if they were separate. In general, it is the correlation properties of the complex amplitude that enter through the correlation functions which in turn depend on the origin of the stochastic behavior of the field. The factor of 3 mentioned above is obtained through a model of Gaussian fluctuations for $\epsilon(t)$ corresponding to a chaotic field. It should be noted that the ionization width fluctuates as $|\epsilon(t)|^2$ fluctuates. Thus γ_2 is the average over such fluctuations while the factor of 3 accounts for their effect.

The same holds true for the shift. In general, quantities depending on $|\epsilon(t)|^2$ are affected only when there are amplitude (and hence intensity) fluctuations. They are totally unaffected by phase fluctuations whose sole effect is to add to the width of the resonance, as evidenced by the additive presence of γ_L in Eq. (2c).

As indicated by the angular brackets in Eqs. (2) it is the averaged, density-matrix elements $\langle \sigma_{ij} \rangle$ that correspond to observable quantities; averaged, that is, over the fluctuations of the field. If there are no fluctuations, which means that the amplitude is perfectly stabilized and the bandwidth is zero (or negligible compared to $\Gamma_2 + \gamma_2$), Eqs. (2) must be modified by setting $\gamma_L = 0$ and replacing $3\gamma_2$, $3F_{21}$, and $2\epsilon_0^4$ by γ_2 , F_{21} , and ϵ_0^4 , respectively. In that case, $\langle \sigma_{ij}(t) \rangle$ is simply replaced by $\sigma_{ij}(t)$ with no stochastic average involved.

Ionization is given by

$$\langle P(t) \rangle = 1 - \langle \sigma_{11}(t) \rangle - \langle \sigma_{22}(t) \rangle \quad (6)$$

$$\frac{d}{dt} \langle \sigma_{11}(t) \rangle = \Gamma_2 \langle \sigma_{22}(t) \rangle + 2 \operatorname{Im} \{ \mu_{12} \langle \sigma_{12}(t) [\epsilon^*(t)]^2 \rangle \}, \quad (7a)$$

$$\frac{d}{dt} \langle \sigma_{22}(t) \rangle = -(\Gamma_2 + \gamma_2 + \gamma_2') \langle \sigma_{22}(t) \rangle - 2 \operatorname{Im} \{ \mu_{12} \langle \sigma_{12}(t) [\epsilon^*(t)]^2 \rangle \}, \quad (7b)$$

$$\left[\frac{d}{dt} + i\Delta + \frac{1}{2}(\Gamma_2 + 3\gamma_2 + \gamma_2' + 2\gamma_L) \right] \langle \sigma_{12}(t) [\epsilon^*(t)]^2 \rangle = i\mu_{12} 2\epsilon_0^4 [\langle \sigma_{22}(t) \rangle - \langle \sigma_{11}(t) \rangle], \quad (7c)$$

where

$$\Delta \equiv 2\omega - \omega_{21} - 3F_{21} - F_{21}' . \quad (8)$$

The dynamic detuning includes the ac Stark shift F_{21} of the resonance transition as well as the ac Stark shift F_{21}' caused by a second laser if present. γ_2' is then the rate of ionization of level $|2\rangle$ caused by the second laser. γ_2' and F_{21}' appear in the equation without the factor 3, because the second laser is involved in the ionization process for $|2\rangle$ to the continuum without participating in the bound-to-bound two-photon-resonance process. Needless to add that although the ionization rate of $|2\rangle$ can be increased in relation to Rabi frequency by introducing a second laser, it cannot be decreased since the laser causing the two-photon transition will inevitably cause ionization, and separating the ions from the two pulses is not a trivial instrumental problem, if possible at all. If both lasers' pulses are much shorter than the lifetime of the excited state, one could delay the second pulse with respect to the first. If the second laser is much stronger than the first, γ_2 can be dominated by γ_2' , and the ionization rate of $|2\rangle$ can, in principle, be approximately independent of the Rabi frequency. Even if the second laser's intensity is comparable to that of the first, we can increase the value $(3\gamma_2 + \gamma_2')$ without increasing the Rabi frequency. Thus we increase the total ionization rate and at the same time we still can have a fairly good selectivity. This result is further discussed in Sec. IV.

and will in general be a complicated function of the time during which atom and radiation interact. This interaction time is either the laser-pulse duration or the time of transit of the atom through the laser beam, whichever is shorter. If certain conditions which are discussed below are met, it may be possible to express $\langle P(t) \rangle$ in the form $1 - e^{-Wt}$ where W is the transition probability per unit time. In that case, the process is describable by a single rate W . Under different conditions, two rate constants may be necessary while in the most general case, $\langle P(t) \rangle$ must be obtained through the complete solution of the density-matrix equations (2).

The rate of ionization can be increased further if a second laser of higher power and different frequency is used for the ionization step. The frequency must be different so as not to affect the two-photon bound-bound transition. With this consideration, taking the stochastic average of the equations of $\sigma_{ij}(t)$ we have

III. RATE APPROXIMATIONS

In order to aid physical insight into the problem and its formulation, we give here a brief summary of certain special cases and the conditions under which they can be obtained from the general equations.

For brevity let us set

$$\Gamma_2 + 3\gamma_2 + 2\gamma_L \equiv \gamma \quad (9)$$

and

$$\langle \sigma_{22}(t) \rangle - \langle \sigma_{11}(t) \rangle \equiv n(t) . \quad (10)$$

Substituting into Eq. (2c) and converting it to an integral equation we obtain

$$\langle \sigma_{12}(t) [\epsilon^*(t)]^2 \rangle = i\mu_{12} 2\epsilon_0^4 \int_0^t dt' n(t') e^{(i\Delta + \gamma/2)(t'-t)} . \quad (11)$$

If $n(t')$ does not change much over times for which $\gamma t \gg 1$, i.e., for times larger than $1/\gamma$, then it can be replaced by $n(t)$ and pulled outside the integral. The integration can then be performed, and in the limit $\gamma t \rightarrow \infty$, we are left with the approximate expression

$$\langle \sigma_{12}(t) [\epsilon^*(t)]^2 \rangle = 2\mu_{12} \epsilon_0^4 \frac{\Delta + i\frac{1}{2}\gamma}{\Delta^2 + \frac{1}{4}\gamma^2} n(t) \quad (12)$$

which can now be substituted into Eqs. (2a) and (2b). If we also introduce the definitions

$$\Omega \equiv 4 |\mu_{12}|^2 \epsilon_0^4 \frac{\frac{1}{2}\gamma}{\Delta^2 + \frac{1}{4}\gamma^2} \quad (13a)$$

and

$$\Omega_0 \equiv 4 |\mu_{12}|^2 \epsilon_0^4 / \frac{1}{2}\gamma. \quad (13b)$$

Equations (2a) and (2b) become

$$\left[\frac{d}{dt} + \Omega \right] \langle \sigma_{11}(t) \rangle - (\Gamma_2 + \Omega) \langle \sigma_{22}(t) \rangle = 0, \quad (14a)$$

$$\left[\frac{d}{dt} + \Gamma_2 + \gamma_2 + \Omega \right] \langle \sigma_{22}(t) \rangle - \Omega \langle \sigma_{11}(t) \rangle = 0. \quad (14b)$$

Is it useful to note the relation

$$\Omega = \Omega_0 \frac{\frac{1}{4}\gamma^2}{\Delta^2 + \frac{1}{4}\gamma^2} \quad (15)$$

from which it is evident that $\Omega_0 = \lim_{\Delta \rightarrow 0} \Omega$.

We have thus arrived at two rate equations in which Ω represents the rate with which atoms are stimulated to make the transition $|1\rangle \leftrightarrow |2\rangle$. Thus Ω is the equivalent of a Rabi frequency, but a two-photon Rabi frequency. It includes, however, the effect of the laser bandwidth, of the broadening of level $|2\rangle$ (owing to spontaneous decay and ionization) as well as of the detuning. It is perhaps more proper to reserve the term Rabi frequency for Ω_0 which is independent of the detuning Δ , a convention that we adopt in the remainder of this paper.

The above rate equations with the initial conditions $\langle \sigma_{11}(0) \rangle = 1$ and $\langle \sigma_{22}(0) \rangle = 0$ can be solved exactly by taking the Laplace transforms, finding the roots and calculating the inversion integrals. The result is

$$\langle \sigma_{11}(t) \rangle = A e^{S_1 t} + (1-A) e^{S_2 t}, \quad (16a)$$

$$\langle \sigma_{22}(t) \rangle = \frac{\Omega}{S_1 - S_2} (e^{S_1 t} - e^{S_2 t}), \quad (16b)$$

where

$$S_{1,2} = \frac{1}{2} (2\Omega + \Gamma_2 + \gamma_2) \times \left[-1 \pm \left[1 - \frac{4\gamma_2 \Omega}{(2\Omega + \Gamma_2 + \gamma_2)^2} \right]^{1/2} \right] \quad (17)$$

are the roots resulting from the solution of the Laplace transformed equations, and

$$A \equiv \frac{S_1 + \Omega + \Gamma_2 + \gamma_2}{S_1 - S_2}. \quad (18)$$

It will be useful to also note the relation

$$S_1 - S_2 = (2\Omega + \Gamma_2 + \gamma_2) \times \left[1 - \frac{4\gamma_2 \Omega}{(2\Omega + \Gamma_2 + \gamma_2)^2} \right]^{1/2}. \quad (19)$$

If instead of spontaneous radiative decay, state $|2\rangle$ undergoes transitions into other channels (e.g., dissociation in a molecule) the equations are still valid with the modification that Γ_2 should be omitted from Eq. (14a) since

the decay out of $|2\rangle$ does not return the system to $|1\rangle$. It is also worth noting that different relaxation times for the diagonal and off-diagonal matrix elements of ρ can be accommodated in the equations (the well-known T_1 and T_2). This is accomplished by replacing Γ_2 in Eq. (9) by another constant Γ_{21} independent of Γ_2 . The latter still appears as the relaxation constant in the diagonal matrix elements; that is, $\Gamma_2 = 1/T_1$ and $\Gamma_{21} = 1/T_2$.

The solutions (16a) and (16b) of the rate equations show that in general two rate constants S_1 and S_2 determine the evolution of the populations. In certain special cases, only one of these constants may be important in the description. This would be the case if one of the two rate constants is much larger than the other. Then one of the exponentials decays very fast, leaving only the one with the small decay constant to determine the rate of ionization. As the simplest example, let us consider the case of weak field in the sense that $\Omega \ll \gamma_2$. From this inequality, it follows that the fraction inside the square root in Eq. (17) is much smaller than unity. Using the approximation $(1 + \chi)^{1/2} \approx 1 + \frac{1}{2}\chi$ and making repeated use of $\Omega \ll \gamma_2$ we arrive at $S_1 \approx -\Omega$ and $S_2 \approx -(\Gamma_2 + \gamma_2)$. Obviously, on the basis of our assumption we have $|S_2| \gg |S_1|$. Thus $-\Omega$ is the smallest root which means that state $|1\rangle$ is depleted according to $A e^{-\Omega t}$, its rate of depletion being Ω which is now recognized as representing a special case of two-photon-resonant three-photon ionization. It reduces to the most conventional form if we take γ_2 to dominate both Γ_2 and γ_L , in which case γ reduces to $3\gamma_2$ and from Eq. (13a) the rate of ionization becomes

$$\Omega = 6 \epsilon_0^4 \frac{|\mu_{12}|^2 \gamma_2}{\Delta^2 + \frac{9}{4}\gamma_2^2}. \quad (20)$$

Since γ_2 is an ionization rate, it is proportional to ϵ_0^2 , which makes Ω proportional to ϵ_0^6 or the third power of the intensity. Also $|\mu_{12}|^2$ combined with the square of the bound-free matrix element yields a three-photon matrix element with a resonance denominator, as expected, since only one state reachable by two photons has been considered, namely $|2\rangle$, and Δ is the detuning from that state. Finally, the factor 6 in front arose from the amplitude fluctuations which had been incorporated in our initial equations for the density matrix. It can be traced to the combination of the factor 3 in front of γ_2 in Eq. (2c) with the factor 2 in front of the right-hand side of the same equation. It is the well-known 3! coming from the effect of intensity fluctuations (photon statistics).³ This effect can be present even in the absence of any bandwidth effects, as in fact happened in Eq. (20) which is obtained in the limit of negligible bandwidth.

The basic assumption $\Omega \ll \Gamma_2 + \gamma_2$ has the implication that the field is sufficiently weak for the transitions $|1\rangle \leftrightarrow |2\rangle$ to be much slower than all other rates in the process. As a consequence, atoms are pumped from $|1\rangle$ to $|2\rangle$ very slowly, thus leaving the population difference $\langle \sigma_{11}(t) \rangle - \langle \sigma_{22}(t) \rangle$ relatively unchanged over time periods of the order $1/\gamma$, which is consistent with the step taken from Eq. (11) to Eq. (12).

Another special case of the solutions (16a) and (16b) corresponds to the opposite limit, i.e., $\Omega \gg \Gamma_2 + \gamma_2 + \gamma_L$.

Taking again, for simplicity, $\gamma_L = 0$ and observing that

$$\frac{4\Omega(\gamma_2 + \Gamma_2)}{(2\Omega + \Gamma_2 + \gamma_2)^2} \ll 1 \quad (21)$$

the two roots are $S_1 = -\frac{1}{2}(\Gamma_2 + \gamma_2)$ and $S_2 = -2\Omega$, where now $|S_2| \gg |S_1|$ and the resulting populations are $\langle \sigma_{11}(t) \rangle \cong \langle \sigma_{22}(t) \rangle \cong \frac{1}{2}e^{S_1 t}$. The rate of depopulation here is $\frac{1}{2}(\Gamma_2 + \gamma_2)$ which implies that, because of the strength of Ω the populations of the two resonant states are almost equalized very quickly [compared to times $1/(\Gamma_2 + \gamma_2)$]. Ionization then proceeds slowly with the rate γ_2 and decay with the rate Γ_2 . Again, $\langle \sigma_{11}(t) \rangle - \langle \sigma_{22}(t) \rangle$ changes very slowly, after a rapid change occurring over a period of the order of $1/\Omega$, which also makes it consistent with the step from Eq. (11) to Eq. (12). Note that in the previous case, excitation to $|2\rangle$ proceeds very slowly and subsequent ionization (relatively) very fast. It goes without saying that, in the case of quick saturation of $|1\rangle \rightarrow |2\rangle$, the single-rate approximation would not be valid over short time periods of the order of $1/\Omega$. The full set of equations must be solved in that case. The full set of equations is especially necessary when Ω and γ are of comparable magnitude in which case none of the above approximations is valid, not even Eq. (12) which leads to the rate equations. Of course even in that case, the oscillations of the populations tend to be damped over times long compared to $1/\gamma$. Over such times simple rate equations do again give good approximations to the ionization rate.

IV. APPLICATIONS

We consider now the application of the preceding theory to the problem of isotopic selectivity² in two-photon-resonant three-photon ionization of atomic Li and Sr.

In Li, we assume that the laser is tunable around the two-photon resonance $2s \rightarrow 4s$ corresponding to an energy difference of $35\,012.06 \text{ cm}^{-1}$. The isotopic shift between ${}^6\text{Li}$ and ${}^7\text{Li}$ is $\Delta_I = 12 \text{ GHz}$. In Sr the two-photon resonance is $5s^2 {}^1S_0 \rightarrow 5p^2 {}^1S_0$ corresponding to an energy difference of $37\,160.278 \text{ cm}^{-1}$, the isotopic shift between ${}^{88}\text{Sr}$ and ${}^{90}\text{Sr}$ being 700 MHz .² The other atomic parameters necessary for the calculations are listed in Table I.

Let the laser be tuned exactly on resonance with the above transition in one isotope. We use as a measure of selectivity the ratio of ionization of the off-resonant isotope to that of the resonant. In terms of the preceding formalism, we need to calculate the ratio of ionization at a two-photon detuning equal to the isotopic shift, to ionization at a detuning equal to zero. We will agree in advance

that the detuning is to be understood as dynamic which includes the ac Stark shift for a given laser power. The laser frequency is assumed tuned exactly on resonance to the shifted two-photon transition. At that power, the same resonance transition for the other isotope is detuned by an amount approximately equal to the isotopic shift. A small correction, due to a difference between the ac Stark shifts in the two isotopes, is totally imperceptible and negligible for all practical purposes of the type discussed in this paper. Let us call \mathcal{S} the selectivity as defined above. Using the definition of total ionization given by Eq. (6), \mathcal{S} can be written as

$$\mathcal{S} = \frac{P(\Delta_I, T)}{P(0, T)}, \quad (22)$$

where $P(\Delta_I, T)$ is total ionization at detuning Δ_I and after interaction time T . It is obvious that the smaller the value of \mathcal{S} , the better the selectivity will be. If the parameters are such that P is expressible in terms of a transition probability per unit time W , then $P = WT$ and \mathcal{S} is independent of time. But even in that case, the linear dependence in time holds for short times, i.e., $WT \ll 1$. For longer times or for situations in which the transition probability per unit time is not constant, we expect a complicated and substantial time dependence of \mathcal{S} .

The problem involves many parameters and it is not *a priori* obvious which combination is the optimum. Certain general statements, however, corresponding to limiting values of particular parameters can be made. For example, for interaction times sufficiently long, selectivity will deteriorate because both isotopes will ionize. How fast is this deterioration of selectivity depends on laser power. Determining the optimum combination of time and power is one aspect of the problem. Consider also the question of laser bandwidth. The excited state has some field-free width which, in a collisionless atomic beam, is determined by the spontaneous radiative decay. In a molecule, this width is usually dominated by intramolecular processes. As the laser intensity increases, ionization may eventually become stronger than other depopulation mechanisms and it is the ionization width that may then dominate. The laser bandwidth, on the other hand, is determined and limited by instrumental factors. Moreover, narrowing the laser bandwidth entails some sacrifice of laser power. It is evident that narrow bandwidth helps in improving selectivity, while large laser power increases the ionization yield. We have again two competing factors whose optimal combination constitutes another aspect of the problem.

The natural width Γ_2 of the excited state $4s$ of Li is about 25 MHz . A state-of-the-art laser in this wavelength

TABLE I. Atomic parameters of Li and Sr. I is the laser intensity in W/cm^2 .

	Spontaneous width of excited state (MHz)	Ionization width of excited state (Hz)	Two-photon Rabi frequency (Hz)
Li	25	$3.00I$	$7.85I$
Sr	9	$1.53I$	$3.01 \times 10^2 I$

TABLE II. Isotopic selectivity in Li. One laser of bandwidth $\gamma_L = 50$ MHz; interaction time $T = 30$ ns.

Laser intensity I (W/cm ²)	10^7	3×10^7	5×10^7
Ionization P (%)	19.91	67.98	86.78
Selectivity \mathcal{S}	1.98×10^{-4}	1.84×10^{-3}	7.11×10^{-3}

region ($17\,506\text{ cm}^{-1}$) could deliver an intensity of the order of 10^7 W/cm^2 within at best a bandwidth of $\gamma_L = 50$ MHz. We begin our exploration around this range of laser intensity and bandwidth. Although the pulse duration is more or less fixed by the type of the laser, we will let it vary from a few nanoseconds to about 50 ns in order to demonstrate its effect on the process under consideration. The actual pulse duration of the laser contemplated for such experiments is within the above range. We explore first the range of intensities between 10^7 W/cm^2 and $5 \times 10^7\text{ W/cm}^2$. The two-photon Rabi frequency as well as the ionization width vary linearly with laser intensity, the Rabi frequency being 2.6 times larger. Independently of the intensity therefore, ionization will always be slower than the Rabi oscillation if only one laser is employed. Within the above range of intensities, the Rabi frequency varies from 79 to 392 MHz while the ionization width ranges from 30 to 150 MHz. With a laser bandwidth 50 MHz, none of the important parameters dominates the others. Thus we are in a situation in which a single-rate approximation is not expected to be reliable especially for a certain range of interaction times. We proceed with the solution of the complete set of the density-matrix equations showing at the same time when rate approximations give reasonably accurate results. The first set of results is shown in Table II where for each intensity we have the amount of ionization of the resonant isotope and the selectivity at the laser is tuned around the two-photon resonance.

It is evident that increasing laser intensity helps in getting more ionization but at the cost of deteriorating the selectivity. Table III is the result of a rate-approximation calculation. In the calculation, we keep two rate constants S_1 and S_2 . The result is close to that of the density-matrix method especially for the high-intensity case.

In the calculation for the case of two lasers, we assume that synchronized pulses are applied. We choose the second laser's intensity such that $\gamma'_2 = \gamma_2$, and $\gamma'_2 = 2\gamma_2$, respectively. The result is compared with that of the one-laser case, in Table IV.

In the first example, the intensity of the second laser is

TABLE III. Isotopic selectivity in Li. Rate-approximation result. One laser of bandwidth $\gamma_L = 50$ MHz; interaction time $T = 30$ ns.

Laser intensity I (W/cm ²)	10^7	3×10^7	5×10^7
Ionization P (%)	25.51	67.57	86.28
Selectivity \mathcal{S}	1.72×10^{-4}	1.90×10^{-3}	7.39×10^{-3}

TABLE IV. Isotopic selectivity in Li. Two-lasers: intensity of the first laser $I_1 = 10^7\text{ W/cm}^2$, bandwidth of the first laser $\gamma_L = 50$ MHz, ionization width caused by the first laser $\gamma_2 = 30$ MHz, interaction time $T = 30$ ns.

Ionization width caused by the second laser γ'_2	$\gamma'_2 = 0$	$\gamma'_2 = \gamma_2$	$\gamma'_2 = 2\gamma_2$
Ionization P (%)	19.91	50.12	51.60
Selectivity \mathcal{S}	1.98×10^{-4}	1.84×10^{-4}	2.57×10^{-4}

chosen so as to have $\gamma'_2 = \gamma_2$ while the Rabi frequency remains unchanged. As a result, the amount of ionization increases from 19.91% to 50.12% and the selectivity is also improved. If we increase the intensity of the second laser further by taking, for example, $\gamma'_2 = 2\gamma_2$ as in the last column of Table IV, the amount of ionization increases to 51.60% but selectivity deteriorates. How strong the second laser should be depends on the combined consideration of ionization and selectivity. It will be different from case to case. Nevertheless the above example shows that using a second laser provides the option to increase ionization and retain at the same time rather good selectivity.

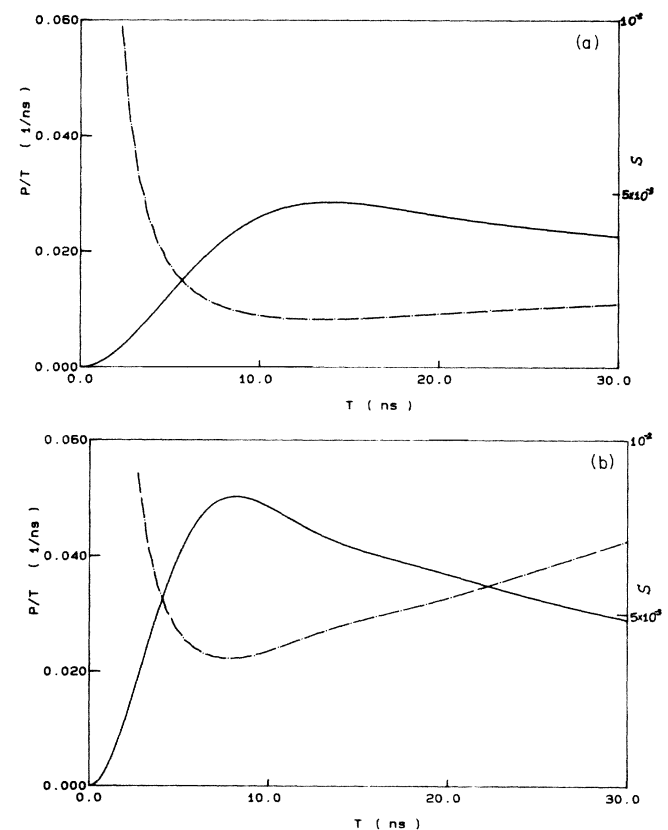


FIG. 1. Time-dependent analysis of the isotope separation in Li. The solid line represents the average ionization rate P/T and the dotted-dashed line represents selectivity \mathcal{S} . $\Gamma_2 = 25$ MHz, $\gamma_L = 50$ MHz. One laser is used; its intensity is (a) $3 \times 10^7\text{ W/cm}^2$ and (b) $5 \times 10^7\text{ W/cm}^2$.

TABLE V. Laser-bandwidth effect. One laser of intensity $I = 10^7$ W/cm², interaction time $T = 30$ ns.

Laser bandwidth γ_L (MHz)	0	5	50	500	5000
Ionization P (%)	24.81	24.21	19.91	7.21	0.99
Selectivity \mathcal{S}	1.59×10^{-4}	1.63×10^{-4}	1.98×10^{-4}	5.50×10^{-4}	3.06×10^{-2}

To demonstrate the laser-bandwidth effect on the isotope separation process, we let γ_L vary from 0 to 5000 MHz and calculate the ionization and selectivity, although it is technically difficult for such intense lasers to have bandwidths even as small as a few MHz. Some results are shown in Table V.

The result is as expected. The narrower the bandwidth the better the separation effect will be. But it is worth mentioning here, that from 50 MHz to 0, the separation effect does not improve dramatically.

To explore the important role of interaction time in the isotopic separation process, we calculate the evolution of ionization and selectivity with the pulse duration. What interests us in this process is the total amount of ionization $P(\Delta=0)$ and selectivity \mathcal{S} at time T . The aim is to calculate the cumulative quantities rather than the instantaneous quantities. In Fig. 1, we present P/T versus T and \mathcal{S} versus T curves. The laser intensities are 3×10^7 W/cm² in Fig. 1(a) and 5×10^7 W/cm² in Fig. 1(b). In both cases one laser is used to ionize Li atoms. According to the results of our calculation, $P(\Delta=0)/T$ is much larger than $P(\Delta=12 \text{ GHz})/T$. Although $P(\Delta=12 \text{ GHz})/T$ increases with the duration time T , it does so very slowly. The range of variation for $P(\Delta=12 \text{ GHz})/T$ is much smaller than that for $P(\Delta=0)/T$. So \mathcal{S} basically depends on $P(\Delta=0)/T$. As we can see from Fig. 1, at the beginning of the process, \mathcal{S} is very large, implying a poor selectivity. This is because $P(\Delta=0)/T$ is still small and comparable to $P(\Delta=12 \text{ GHz})/T$. With the increase of $P(\Delta=0)/T$ the selectivity is improved. After a certain interaction time, the average ionization rate $P(\Delta=0)/T$ increases to a maximum and almost at the same time the selectivity coefficient \mathcal{S} decreases to a minimum. This time could be thought of as the optimal interaction time. After the optimal time, $P(\Delta=0)/T$ decreases. Physically this means that the ionization process slows down. On the contrary, as far as $P(\Delta=12 \text{ GHz})/T$ is concerned, because of the large detuning, the amount of ionization is still very small at that time and the ionization is far from saturation. So $P(\Delta=12 \text{ GHz})/T$ still increases with time even though very slowly. As a result \mathcal{S}

will increase after the optimal time. Comparing Figs. 1(a) and 1(b) we find that with the increase of laser intensity the optimal interaction time becomes shorter. When a strong laser field is applied, the ionization rate will increase rapidly, saturate, and then decrease very fast. Generally speaking, the selectivity with a stronger laser field is worse than that with the weaker laser field. In addition, the \mathcal{S} versus T curve has a deeper dip for the stronger laser field than that for the weaker one. When the laser is not so strong, it may be sufficient to choose the interaction time so as to be a bit larger than the optimal time. For example, while the interaction time is about 10 ns longer than the optimal time in the weak-field case, the selectivity does suffer but not much. When the strong laser field is used, however, the interaction time would be a very significant controlling parameter in the isotope separation process.

The general qualitative features of isotope separation in Sr are similar to those in Li. For Sr, the Rabi frequency of two-photon resonance transition $5s^2^1S_0 \rightarrow 5p^2^1S_0$ as well as the ionization width of $5p^2^1S_0$ state also vary linearly with laser intensity. Unlike Li, however, the ratio between them is quite large. As shown in Table I, the ionization width is $1.53I$ Hz and the Rabi frequency is $301.57I$ Hz, the latter being almost 197 times larger than the former. Usually a strong laser would be preferable for more ionization. But for Sr, the large Rabi frequency will cause broadening of the excited state, leading to deterioration of the selectivity. What makes the separation more difficult in this case, is the small value of the isotopic

TABLE VI. Isotope selectivity in Sr. One laser of bandwidth $\gamma_L = 7$ MHz; interaction time $T = 50$ ns.

Laser intensity I (W/cm ²)	10^5	10^6	10^7
Ionization P (%)	0.18	3.68	31.83
Selectivity \mathcal{S}	7.09×10^{-3}	2.64×10^{-1}	9.78×10^{-1}

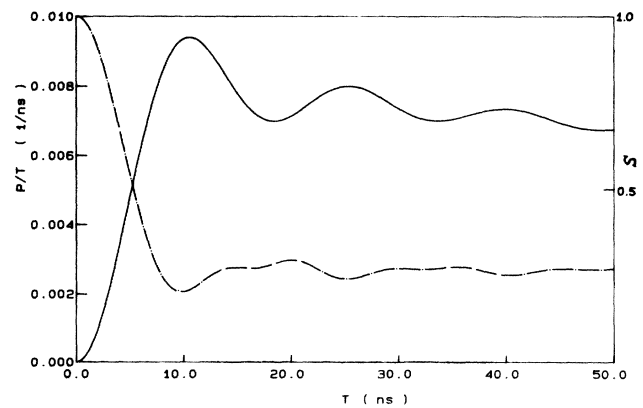


FIG. 2. Time-dependent analysis of the isotope separation in Sr. The solid line represents the average ionization rate P/T and the dotted-dashed line represents selectivity \mathcal{S} . $\Gamma_2 = 9$ MHz, $\gamma_L = 7$ MHz. Two lasers are used; the first laser's intensity is 10^6 W/cm², the second laser's intensity is chosen to be such that $\gamma'_2 = 10\gamma_2$.

TABLE VII. Isotopic selectivity in Sr. Two-lasers: intensity of the first laser $I_1 = 10^5 \text{ W/cm}^2$, bandwidth of the first laser $\gamma_L = 7 \text{ MHz}$, ionization width caused by the first laser $\gamma_2 = 30.16 \text{ MHz}$, interaction time $T = 50 \text{ ns}$.

Ionization width caused by the second laser γ'_2	$\gamma'_2 = 0$	$\gamma'_2 = 10\gamma_2$	$\gamma'_2 = 50\gamma_2$	$\gamma'_2 = 100\gamma_2$	$\gamma'_2 = 200\gamma_2$
Ionization P (%)	0.18	1.96	8.18	14.29	22.44
Selectivity \mathcal{S}	7.09×10^{-3}	7.17×10^{-3}	7.50×10^{-3}	7.98×10^{-3}	9.17×10^{-3}

shift between ^{88}Sr and ^{90}Sr which is only 700 MHz. Thus with a single laser, good selectivity requires low intensity at the cost of amount of ionization. Table VI shows that the amount of ionization is very small when the selectivity is acceptable. If on the other hand, a second laser of much higher power is used for the ionization step, and its frequency is chosen to be sufficiently different from that of the first so that it does not affect the two-photon transition, then the ionization step and the two-photon excitation step could match each other. In Table VII we show examples for the two-laser case. As long as we keep the first laser at low intensity and increase the intensity of the second laser, total ionization increases and the selectivity remains almost unchanged. Even when the intensity of the second laser is so large that $\gamma'_2 = 200\gamma_2$, which indicates that it is roughly about 200 times stronger than the first one, the selectivity remains in the same order. In other words, using a laser of 10^5 W/cm^2 in the excitation step and a second laser of $2 \times 10^7 \text{ W/cm}^2$ in the ionization step, we can obtain 22.4% ionization and have a selectivity as good as 0.009. From the calculation of this case, we see how the use of a second laser may be imposed by the atomic parameter.

When two lasers are adopted, the interaction time still plays an important role. In Fig. 2 we present P/T versus T and \mathcal{S} versus T curves for Sr isotope separation. The

first laser's intensity is 10^6 W/cm^2 while that of the second is chosen so that γ'_2 is 10 times larger than γ_2 . The large Rabi frequency causes the P/T to oscillate and as a result the selectivity varies with interaction time. However, as Fig. 2 shows, \mathcal{S} reaches a dip when the P/T is near the peak. In this special example, the optimal interaction time is about 10 ns.

V. CONCLUSION

In isotope separation, both maximum ionization and best selectivity are desired. Many parameters are involved in this type of problem. We have presented a discussion of the essentials of the density-matrix equation formalism which incorporates all necessary effects. Using this formalism we have obtained detailed results for Li and Sr. Aspects such as laser intensity dependence and laser-bandwidth effects are discussed. Also the time dependence of the process has been analyzed and realistic calculations show that there is an optimal interaction time for isotope separation. A second laser for the ionization step leads to maximum ionization and improved selectivity.

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