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Multiphoton spectroscopy of doubly excited, bound, and autoionizing states of strontium

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We present a theory attempting an interpretation of existing data on three- and four-photon ionization of Sr in the wavelength range 557–575 nm and at 532 nm. Two-photon resonances with bound excited states and three-photon resonances with doubly excited autoionizing states are studied. ac Stark shifts and broadening of resonances, as well as singlet-triplet transitions, are shown to yield interesting new information on atomic structure. The absorption of a fourth photon above the threshold leads to excited final ionic states, with autoionizing states having served as intermediate three-photon resonances. The calculation is based on a configuration-interaction scheme, with singlet-triplet mixing taken into account either through *jl* coupling or phenomenologically by adjustment to some aspects of the data. The apparatus of resonant multiphoton theory is combined with the above scheme. Depending on the quantity in question, the agreement between theory and experiment ranges from good to semiquantitative.

I. INTRODUCTION

This paper presents a theoretical synthesis of experimental observations on three- and four-photon ionization and autoionization of atomic strontium. Although our primary objective has been the interpretation of the data of Petite and Agostini,[1] we have placed equal emphasis upon the data of Feldmann and Welge,[2] so as to unify what has been observed so far. Experimental studies of this type (employing a single laser) in alkaline-earth atoms began almost 14 years ago with the work of Suran and Zapesochnyi[3] and Aleksakhin *et al.*[4] For a number of reasons (including a threshold conveniently located with respect to lasers of readily available wavelengths) Sr attracted more attention.[5–8] Partly as a consequence of this preference by experimentalists, we also employed Sr as a model for a number of our theoretical studies[9–12] dealing with the behavior of doubly excited autoionizing states under strong fields. In the course of such studies, we attempted to incorporate as much experimental evidence as available, an exercise that led to the present manuscript.

Whatever the initial motivation for such experiments may have been (they were most probably undertaken for the classic reason that the atoms and the lasers were there), it soon became clear that they revealed two interesting facets. One has to do with the new manifolds of autoionizing states that become accessible via a multiphoton process. This is quite evident from a simple comparison of the single-photon (uv) photoabsorption spectrum with the equivalent three-photon spectrum (see Fig. 2 of Ref. 2), and is discussed in some detail in the following sections. The second is related to the phenomenon of multiple ionization and represents in fact the first set of observations of the ejection of more than one electron through multiphoton processes at relatively modest intensities, raising also questions as to the underlying mechanism and the possible role of multiply excited states. It was much later that multiple ejection[13–15] in the rare gases was observed at higher intensities.

As to the spectroscopic aspect of these experiments, it is our objective in this work to focus on the richness of information on atomic dynamics that can be extracted. In processes of this type, however, the radiation (laser) is not a simple probe, as is the case in traditional single-photon absorption. Because of the magnitude of the intensity, the laser itself is part of the whole dynamical process and can induce distortion of the atomic structure. This is not necessarily a nuisance, although it does place additional demands on the theoretical analysis. It is because of such effects that certain desirable transitions can occur at all. The ac Stark shift of near-resonant states is the most usual (one might say, standard in the trade) laser-induced distortion which can be exploited so as to provide additional insight into the underlying structure. A case in point is discussed later on in Sec. III B. A further most desirable effect of the intensity in the present context is absorption of one or more additional photons before an autoionizing state can decay by autoionization. This is intimately connected with the possibility of leaving the ion in an excited state, as well as with double-electron ejection. The first part of this aspect is addressed in Sec. III D.

The theory on which the calculations were based is in spirit similar to related recent work[11,12] by two of us (P.L. and X. T.), and we do not include theoretical details here. It is a configuration-interaction formulation suitably extended to incorporate field-induced effects. As in our previous papers,[11,12] we consider a sufficient number of configurations constructed on the potential of the core Sr^{2+} ($1s^2$-$4p^6$) which is held frozen in a single Hartree-Fock configuration. Fine structure, which is necessary for the interpretation of the experiments, has been introduced in part phenomenologically. Clearly, the calculation cannot claim the overall level of accuracy of recent work by Greene and Kim[16] and Aymar *et al.*[17] for single-photon absorption. It must be borne in mind on the other hand that we are dealing with a much more complex situation. It involves many angular momenta (up to $J=4$), summations over infinite (or truncated) sets of intermediate states, resonances with intermediate states and of course related field effects. Although we have recently employed[18,19] multichannel quantum defect theory (MQDT) for multiphoton transitions in the rare gases and have work in progress for a similar approach to two-electron atoms, the present undertaking is for the moment too complex to be treated with MQDT. Then there is the question of double-electron ejection which is not easily accommodated in MQDT. The assessment of how well we have done in the present task must thus rely on how well we can predict the experimental data and on the internal checks and consistency of the model. In view of the rapidly rising interest in related studies[20,21] in Sr as well as other alkaline-earth atoms, we expect to come back with a more complete picture as more data become available.

We must note here that this work, in both experiment and theory, is much different in intention and spirit from the classic studies of Xu *et al.*[22] and Cooke and Cromer,[23] who in a number of papers have studied series of autoionizing states by selective excitation through a two-color technique. By preselecting a two-photon-excited Rydberg state and then exciting the appropriate core state with a second photon, they isolate a particular route of creation of the autoionizing state. Here we are dealing with exactly the opposite situation; excitation and ionization by a single color (laser) which implies the involvement of a number of channels and considerably higher power so that even transitions within the continuum can occur. The problem then is the response of the atom to such an excitation, the possibility of double (or even multiple) ionization, and the more general behavior of a multielectron atom under a strong pulsed laser. And ultimately one hopes to shed some light to the participation of doubly excited states lying high above the first ionization threshold, on the way to understanding the participation of multiply excited states in atoms with more than two valence electrons. In fact, at this time, one of the main motives for studies such as this is the exploration of the conditions under which highly excited two-electron states may be reached through a multiphoton process with a single laser and the concomitant possibility of double ionization via a route of doubly excited states, often referred to as a direct process. As of the writing of this paper, the answer remains as elusive as it has been since the question was posed[3,4,13–15] roughly thirteen years ago.

We should state at the outset that no claim of definitive and final quantitative interpretation of the observations is implied in this paper. We approached this problem the way one approaches a puzzle, having at our disposal only that part of the picture that uv photoabsorption and most recently the calculations by Aymar *et al.* provide. Most of the picture, however, remains unknown. We have done rather well with some quantities (such as three of the four ac stark shifts), reasonably well with relative branching ratios to excited ionic states, and at best semi-quantitatively with relative peak heights of the autoionizing resonances. It remains to be seen how much of this will survive the test of further theory, by us and others, and additional experimental data. For the specialists, we would like to note that we did not include pulse shape and interaction-volume effects because neither theory nor experiment claim that level of accuracy. In one case, namely, the shift of the $5d5d(^1D_2)$, where a major discrepancy appears,[2] we did include a pulse shape (see Sec. III B) and checked whether the volume effect might make a difference. Unfortunately it does not.

The paper is organized as follows. Sections II and III constitute the main body of the paper. The material of Sec. II deals with the modifications that become necessary in formulating multiphoton transitions which include singlet-triplet mixing. Section III is divided in five parts, Secs. III A–III E. Sections III A–III C deal with the analysis of the two-photon resonances, their shifts and widths, and certain aspects of atomic structure to which these quantities appear to be sensitive. Section III D is devoted to the interpretation and assignment of the three-photon autoionizing resonances that have been observed in the range of wavelengths under consideration. In Sec. III E we present a partial assessment of the dependence of branching ratios to excited ionic states on the laser intensity. Finally, in Sec. IV we conclude with a brief discussion and outlook.

II. MULTIPHOTON MATRIX ELEMENTS IN INTERMEDIATE COUPLING

The experimental results discussed and interpreted in this paper require the calculation of three- and four-photon ionization for wavelengths such that three photons are energetically sufficient for ionization (Fig. 1). The fourth photon will therefore be involved in a transition between states above the first threshold with some participation of doubly excited autoionizing states, depending on the photon wavelength. Since two-photon resonances with intermediate bound states are also en-

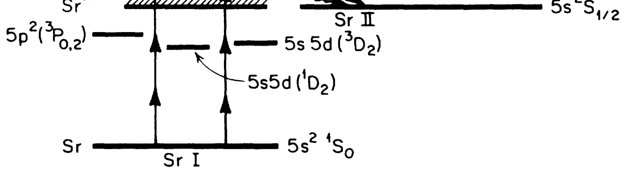

FIG. 1. Schematic level diagram of the transitions studied in this paper.

countered in this wavelength region, the apparatus of resonant multiphoton theory becomes necessary, including the laser-induced ac Stark shifts of the resonant states which, as we shall see below, provide valuable input to the interpretation of the observations. An additional aspect which is indispensable to the interpretation is the singlet-triplet mixing of the atomic states. Its significance is obviously reflected upon the fact that two-photon-resonant transitions to triplet states, such as $5s5d(^3D_2)$ and $5p^2(^3P_{0,2})$, exhibit prominent peaks. Given that the initial (ground) state $5s^2(^1S_0)$ is singlet, only intercombination transitions could account for the presence of these resonances; which can in turn be used as information input in evaluating the strength of singlet-triplet mixing.

Since we are dealing with a two-electron atom, all states must here be understood as properly antisymmetrized two-electron states. Let us consider, as an example, a two-photon transition from $5s^2(^1S_0)$ to a state of the form $5sns(^1S_0)$. For this simple case of singlet-singlet transition, the usual general expression

$$r_{ba}^{(2)}=\sum_n \frac{\langle b|r|n\rangle\langle n|r|a\rangle}{E_n-E_a-\hbar\omega}$$
$$=\int d\mathbf{r}_2\int d\mathbf{r}_1\psi_b(\mathbf{r}_2)r_2G(\mathbf{r}_2,\mathbf{r}_1;\Omega)r_1\psi_a(\mathbf{r}_1) \qquad (2.1)$$

will involve matrix elements of the type $\langle 5smp|r_\alpha+r_\beta|5s^2\rangle$, where $|5s,p\rangle=\psi_{5smp}(\mathbf{r}_\alpha,\mathbf{r}_\beta)$ are the two-electron (labels α and β) wave functions. Here $G(\mathbf{r}_2,\mathbf{r}_1;\Omega)$ is the Green's function

$$G(\mathbf{r}_2,\mathbf{r}_1;\Omega)=\sum_n \frac{\psi_n^*(\mathbf{r}_2)\psi_n(\mathbf{r}_1)}{E_n-\hbar\Omega} \qquad (2.2)$$

related to the radial Green's function $g_l(r_1,r_2;\Omega)$ through

$$G(\mathbf{r}_2,\mathbf{r}_1;\Omega)=\sum_{l,m}\frac{g_l(r_1,r_2;\Omega)}{r_1r_2}Y_{lm}^*(\theta_1,\phi_1)Y_{lm}(\theta_2,\phi_2)\ . \qquad (2.3)$$

The selection rules for dipole transitions determine which terms survive in the sum over lm. In a three-photon transition, double summation over intermediate states reduces to a triple integration of a product of two Green's functions, and so on.

For purely singlet-singlet transitions, the states $|n\rangle$ in Eq. (2.1) will be of the form $5snp(^1P_1)$. The initial state $5s^2(^1S_0)$ will be (at least) one product of two single-electron wave functions denoted by $\psi_{5s^2}(\mathbf{r}_i)$. The wave function ψ_{5s} appearing in the states $5snp$ and $5sns$, in general, is not the same as $\psi_{5s^2}(\mathbf{r}_i)$. Although in principle every state $5snl$ requires a slightly different $5s$, we take here all such with the same $5s$ within a given series nl. In calculating matrix elements of the form $\langle 5snp|r_\alpha+r_\beta|5s^2\rangle$ between antisymmetrized wave functions, we obtain products of the form

$$\langle\psi_{np}(r_\alpha)|r_\alpha|\psi_{5s^2}(r_\alpha)\rangle\langle\psi_{5s}(r_\beta)|\psi_{5s^2}(r_\beta)\rangle\ ,$$

where the second (overlap) factor is different from unity. For singlet states, the spatial part of the wave function will be symmetric and will have the form

$$\frac{1}{\sqrt{2}}[\psi_{5s}(r_\alpha)\psi_{np}(r_\beta)+\psi_{5s}(r_\beta)\psi_{np}(r_\alpha)]\ .$$

The two-photon matrix element between $|5s^2\rangle$ and $|5s,ms\rangle$ (where $m\neq 5$) is then written as

$$\langle 5s^2|r^{(2)}|5sms\rangle$$
$$=\sqrt{2}\int dr_1\int dr_2\psi_{ms}(r_2)r_2g_1(r_2,r_1;\Omega)r_1$$
$$\times\psi_{5s^2}^*(r_1)\int dr\,\psi_{5s^2}^*(r)\psi_{5s}(r)\ , \qquad (2.4)$$

where the Green's function is evaluated at the appropriate energy $\hbar\Omega=E_{5s^2}+\hbar\omega$. Other two-photon matrix elements (for singlet-singlet transitions) are given by similar expressions differing in the initial and final states and/or the energy of the Green's function.

Because of the relatively high value of Z (38), the distinction between singlet and triplet is not strict in Sr. Stated otherwise, neither LS nor jj coupling is rigorously applicable in the description of all states. We have a case of intermediate coupling[24] and, as shown below, a multiphoton transition is affected in a way much subtler than a single-photon transition. To discuss the necessary modifications of the formalism, let us consider the specific example of states $5snp$ which in pure LS coupling would be separated in groups of singlets $(^1P_1)$ and triplets $(^3P_0,{}^3P_1,{}^3P_2)$. Because of the non-negligible importance of magnetic interactions, these states are coupled, with the consequence that neither $(^1P_1)$ is pure singlet nor $(^3P_1)$ is pure triplet.

Let $\psi(^1L_J)$ and $\psi(^3L_J)$ be the uncoupled purely singlet and triplet states obtained from the configuration $5snp$. As a result of the coupling due to magnetic interactions, two other states which are linear superpositions of the above are generated and can be written as

$$\Psi(^3L_J)=\frac{1}{\sqrt{\alpha^2+\beta^2}}[\alpha\psi(^3L_J)-\beta\psi(^1L_J)]\ , \qquad (2.5a)$$

$$\Psi(^1L_J)=\frac{1}{\sqrt{\alpha^2+\beta^2}}[\alpha\psi(^1L_J)+\beta\psi(^3L_J)]\ , \qquad (2.5b)$$

where α and β are coefficients which contain atomic-structure information. It is these new states that correspond to the (physical) experimentally determined singlet and triplet L_J states. For the specific case of $5snp$ we would have the uncoupled $^1P_1$ and $^3P_0$, $^3P_1$, and $^3P_2$ states. It is the states $^1P_1$ and $^3P_1$ that will be coupled through Eqs. (2.5a) and (2.5b). The coefficients α and β can in principle be obtained through *ab initio* calculations.[24] Approximate expressions for the ratio $(\beta/\alpha)^2$ as a function of experimental energies are often useful. If we consider the levels $^3L_{l+1}$, ^3L_l, ^1L_l, and $^3L_{l-1}$ (obtained from the configuration LS) and label them as 1, 2, 3, and 4, respectively, the approximate value of $\rho=\beta/\alpha$ is given by

$$\frac{1}{\rho^2}=\frac{E_{32}}{\frac{1}{3}E_{14}-E_{24}}-1\ , \qquad (2.6)$$

where E_1, E_2, E_3, and E_4 are the energies of the states 1, 2, 3, and 4. This equation gives a reasonably good result in most cases except those in which the magnetic interaction is extremely weak. The Pauli-Houston equation

$$\frac{1}{\rho^2}=\frac{3}{4}\left[\frac{E_{34}-\frac{1}{3}E_{14}}{E_{14}}\right]^2 \tag{2.7}$$

is then more appropriate. As an example, we note that for the state $5s5p$ of Sr the value of ρ turns out to be 0.03, while for a state like $5s7d$, ρ is about 0.23. Thus $5s5p(^1P_1)$ and $5s5p(^3P_{0,1,2})$ can be considered to be practically uncoupled singlet and triplet states, while $5s7d(^1D_2)$ and $5s7d(^3D_2)$ will be mixtures of singlet-triplet states. It is in general expected that the mixing becomes more pronounced for higher-excited states.

Let us consider now the extension of the formalism necessary for the inclusion of the singlet-triplet mixing in the calculation of a multiphoton transition. We employ again a two-photon matrix element as an example. A two-photon transition from $5s^2(^1S_0)$ to $5p^2(^3P_2)$ is impossible without this mixing. With the intermediate states $5snp$ mixed above, the two-photon matrix element is now written as

$$\sum_n \frac{\langle 5p^2(^3P_2)|\mathbf{r}|5snp(^3P_1)\rangle\langle 5snp(^3P_1)|\mathbf{r}|5s^2(^1S_0)\rangle}{E_n^{(3)}-E_{5s^2}-\hbar\omega}+\frac{\langle 5p^2(^3P_2)|\mathbf{r}|5snp(^1P_1)\rangle\langle 5snp(^1P_1)|\mathbf{r}|5s^2(^1S_0)\rangle}{E_n^{(1)}-E_{5s^2}-\hbar\omega}\ , \tag{2.8}$$

where $E_n^{(1)}$ and $E_n^{(3)}$ indicate energies of singlet and triplet states, respectively. Since each of the states $5snp$ is in general a mixture of both triplet and singlet states, the matrix element connecting it with $5s^2$ is proportional to the coefficient of the singlet component. Thus the matrix element $\langle 5snp(^3P_1)|\mathbf{r}|5s^2(^1S_0)\rangle$ will normally be smaller than $\langle 5snp(^1P_1)|\mathbf{r}|5s^2(^1S_0)\rangle$ because $5snp(^3P_1)$ is mainly a triplet while $5snp(^1P_1)$ is mainly a singlet. The converse holds true for the matrix elements involving the state $5p^2(^3P_2)$. Using the expressions from Eqs. (2.5) for the mixed states, the two-photon matrix-element can now be written as

$$\langle 5p^2(^3P_2)|r^{(2)}|5s^2(^1S_0)\rangle=\sum_n \frac{\alpha_n\beta_n}{\alpha_n^2+\beta_n^2}\left[\frac{1}{E_n^{(1)}-E_{5s^2}-\hbar\omega}-\frac{1}{E_n^{(3)}-E_{5s^2}-\hbar\omega}\right]$$
$$\times\langle 5p^2(^3P_2)|\mathbf{r}|5snp(^3P_1)\rangle\langle 5snp(^1P_1)|\mathbf{r}|5s^2(^1S_0)\rangle\ , \tag{2.9}$$

where we now have only matrix elements between singlet-singlet and triplet-triplet states with only the separate components of Eqs. (2.5) appearing. As expected, this expression shows that if either α_n or β_n is zero, the two-photon transition between a singlet and a triplet state is totally forbidden. It also shows that the importance of a triplet intermediate state $5snp$ is determined not only by the amount of singlet it contains (the coefficient β_n) but also by the proximity of its energy to a single-photon resonance. In fact, the physical singlet and triplet states are equally important in a singlet-triplet two-photon transition, since both terms appear multiplied by $\alpha_n\beta_n$. Thus an intermediate single-photon resonance with a triplet state $5snp$ is as important as a resonance with the corresponding singlet state.

The physical triplet states (as intermediate states) will also contribute, in principle, to a two-photon transition between two singlet states. For example, the two-photon matrix element $\langle 5s5d(^1D_2)|r^{(2)}|5s^2(^1S_0)\rangle$ is expressed as

$$\langle 5s5d(^1D_2)|r^{(2)}|5s^2(^1S_0)\rangle=\sum_n \frac{1}{\alpha_n^2+\beta_n^2}\left[\frac{\alpha_n^2}{E_n^{(1)}-E_{5s^2}-\hbar\omega}+\frac{\beta_n^2}{E_n^{(3)}-E_{5s^2}-\hbar\omega}\right]$$
$$\times\langle 5s5d(^1D_2)|\mathbf{r}|5snp(^1P_1)\rangle\langle 5snp(^1P_1)|\mathbf{r}|5s^2(^1S_0)\rangle\ . \tag{2.10}$$

Here we see that triplet intermediate states are important only to the extent that β_n is not negligible compared to α_n; unless the photon frequency is so near resonance with a particular triplet state, that the smallness of the energy difference in the denominator makes up for the smallness of β_n.

It should now be evident that if we consider a triplet-triplet two-photon matrix element, the importance of singlet intermediate states is proportional to α_n^2 except for near resonance with one particular state. Such matrix elements will appear later on in connection with the ac Stark shifts of intermediate triplet two-photon resonances. The autoionizing states are also expected to exhibit singlet-triplet mixing which has a fairly important effect on the resonance structure of the three-photon ionization as well as on the ac Stark shifts of some intermediate two-photon resonances.

III. RESONANT MULTIPHOTON IONIZATION

In the range of wavelengths from 557 to 575 nm and intensities $10^{11}-5\times10^{12}$ W/cm^2 employed in this experiment,[1] three- and four-photon ionization of atomic Sr was observable. On the basis of the photoelectron energies three types of resonances were observed. (i) Intermediate two-photon resonances in three- and four-photon ionization. (ii) Intermediate three-photon resonances with an autoionizing state in four-photon ionization. (iii) Three-photon-resonant three-photon ionization through an autoionizing final state. Combinations of the preceding types of resonances can occur either by the accidental presence of an atomic state at the appropriate energy position or the employment of two lasers (usually referred to as two-color experiment), neither of which is the case in this work. Because of the wavelength range employed in these experiments, resonances of type (ii) represent doubly excited autoionizing states above the first ionization threshold.

A. Two-photon resonances

The intermediate two-photon resonances are identified rather easily since they correspond to bound states whose energies are well known and the resulting resonances are strong, narrow, and well resolved. Three such prominent resonances correspond to the excited states $5s5d(^3D_2)$, $5p^2(^3P_0)$, and $5p^2(^3P_2)$, all of which are triplet. Since the two-photon-resonant transition must connect these states with the singlet ground state, singlet-triplet mixing will play a decisive role in this case. Not only the heights but also the positions of the resonant peaks as affected by the ac Stark shifts depend on the singlet-triplet mixing. Additional information on the contribution of these states is obtained from the respective photoelectron angular distributions, the line shape of ionization as a function of frequency around the resonance, and the dependence on the polarization of the radiation. In addition to its importance for the understanding of the overall ionization process, the preceding information provides valuable input to the spectroscopy of these states which cannot be observed by traditional single-proton absorption.

The preceding two-photon resonances as well as the $5s5d(^1D_2)$ have been observed in two experiments.[1,2] The basic structure of the corresponding matrix element for three-photon ionization has been derived and discused in a previous paper[10] including the effect of the laser intensity on configuration mixing in both the ground and the excited (resonant) state. It did not, however, include singlet-triplet mixing, which is one of the objectives of this paper. This mixing is not important for the $5s5d(^1D_2)$ resonance but is absolutely essential for the other (triplet) resonances. In arriving at the mixing coefficients for these states, we combine several pieces of evidence. Among the experimental evidence that must be reconciled with such singlet-triplet assignments are peak heights and ac Stark shifts of these intermediate resonances. The shifts are discussed in considerable detail in Sec. III B. The peak heights as obtained in the calculation for light linearly polarized are shown in Fig. 2, where the $5p^2(^3P_2)$ is found to dominate the other two, which is in reasonable agreement with experiment[2] as far as the relative heights are concerned. To calculate absolute peak heights requires the input of a number of instrumental parameters not available to a sufficient degree of accuracy to make the necessary complicated analysis worthwhile.

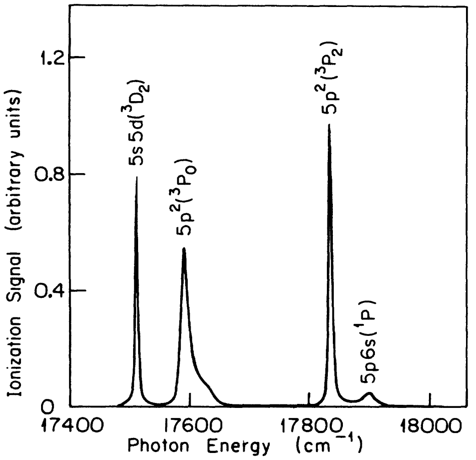

FIG. 2. Relative peak heights of two-photon resonances in three-photon ionization. The peak labeled $5p6s$ corresponds to a three-photon resonance with an autoionizing state not observed in the experiments (see text).

Figure 2 contains also an interesting comparison of the theoretical yield of three-photon ionization at the two-photon resonances with the contribution of the three-photon resonance with the state $5p6s(^1P_1)$, which turns out to be rather small. As discussed in Sec. III D, this resonance was masked by nearby excited states, and this figure gives the reason. In the discussion of the results on three-photon resonances with states of $J=3$ we will see that their contribution is comparable to that of $5p^2(^3P_2)$. Given that singlet-triplet mixing is quite strong in Sr, one should not be surprised that three-photon ionization through what appear to be triplet states is stronger than through a singlet state like $5p6s(^1P_1)$. Although in single-photon uv absorption this state plays a dominant role, in three-photon absorption it appears as a low, broad background dominated by sharp $J=3$ resonances not contributing to simple-photon absorption.

B. Shifts of intermediate two-photon resonances

Throughout the range of intensities (up to 10^{12} W/cm^2) used in the present experiments, the ac Stark shifts were proportional to the laser intensity I. Formally, the shift of state $|a\rangle$ due to radiation of frequency ω is given by

$$S_a=\hbar^{-1}\omega_{ai}\sum_i \frac{|\langle a|\mu|i\rangle|^2}{\omega^2-\omega_{ai}^2} I \ , \tag{3.1}$$

where $\mu=-e(\mathbf{r}\cdot\boldsymbol{\varepsilon})$ is the projection of the electric dipole operator on the polarization vector $\boldsymbol{\varepsilon}$ of the radiation, $\omega_{ai}=\hbar^{-1}(E_a-E_i)$ is the difference of the energies of states $|a\rangle$ and $|i\rangle$, and the infinite summation over i extends over all sets of states to which $|a\rangle$ is connected through a nonvanishing dipole matrix element. Special care is required if $\omega=\omega_{ai}$ for some i, which is not the case here. The states whose shifts are studied in this paper are $5s5d(^1D_2)$, $5s5d(^3D_2)$, $5p^2(^3P_0)$, and $5p^2(^3P_2)$. All four are reached by two-photon absorption from the ground state and since three of them are triplet, intercombination transitions are involved. The heights of the peaks corresponding to $2\omega=\hbar^{-1}(E_a-E_{5s^2})$ will therefore depend on the strength of the respective two-photon matrix elements as well as the ionization widths of these states. The position of the peaks (as functions of ω) are determined by the overall shift which is the difference of S_a from the shift S_g of the ground state which is included in all of our calculations here, although its influence is small. Thus all shifts reported here as referring to a particular two-photon resonance are to be understood as the difference $S_a - S_g$. In calculating spectra and line shapes, these shifts are not calculated separately; they are obtained as part of the diagonalization of a matrix involving the states of interest and their coupling to the field. We will, however, discuss below each of the shifts separately, analyzing the important contributions in each case, in order to elucidate the atomic features that determine such shifts.

The shift of the ground state is straightforward since it is a singlet state, and in the range of wavelengths from 575 to 557 nm there is no near resonance with a singlet $5snp(^1P_1)$ state. The nearest of such states is the $5s5p(^1P_1)$ which is detuned by at least 4000 cm^{-1}. The shift is thus obtained through Eq. (3.1) by summation over all $5snp(^1P_1)$ states including the continuum $5s\varepsilon p(^1P_1)$. The magnitude of this shift turns out to be -0.10 cm^{-1}/GW/ cm^2.

The calculation of the shift of $5s5d(^1D_2)$ is only a bit more complicated. The wavelength of the radiation corresponding to two-photon resonance with this state is 576 nm. Virtual emission and reabsorption of photons of this wavelength falls in a region far from resonance with any bound state, singlet or triplet. Since $5s5d(^1D_2)$ itself is by far predominantly singlet, it is only virtual transitions to singlet states that would contribute to the shift. Virtual absorption and reemission of 576-nm photons, on the other hand, leads to an energy region above threshold where a number of discrete doubly excited states are embedded in the continuum (see discussion in Sec. III D and especially Sec. III D 2). There is no evidence that any of these states is exactly or even very nearly resonant with the absorption of a third photon, but some are sufficiently near to lend some oscillator strength to the infinite summation. This contribution is added to that obtained from the principal value of the integral over the smooth continuum. The resulting total value of the shift is 0.5 cm^1/GW/cm^2. The experimental data, on the other hand, show no shift of the resonance peak but do show substantial asymmetric broadening. This type of broadening is often associated with the presence of a shift due to a near resonant transition. We have not been able to identify such a near resonant state, nor have we been able to obtain a line shape that matches the data. The type of line shape obtained from the theory is shown in Fig. 3. It does exhibit broadening and asymmetry but not in the direction of the data (Fig. 4). Although, under certain special conditions,[25] two-photon-resonant three-photon ionization can exhibit broadening without apparent shifting, we have determined that these conditions are not satisfied in this case. Thus the matter will have to remain unresolved for the time being.

We come now to the shifts of the triplet states $5s5d(^3D_2)$, $5p^2(^3P_0)$, and $5p^2(^3P_2)$. The two-photon transition to each of these states depends significantly on the singlet-triplet mixing and so do their shifts. Again, we have the virtual transitions into the continuum including the contribution of doubly excited states. Two of these states, namely, the $5p6s(^1P_1)$ and $(^3P_1)$ are particularly important for the shifts of $5p^2(^3P_0)$ and $(^3P_2)$ because the absorption of one photon (of the respective two-photon resonant frequency) from either the $5p^2(^3P_0)$ or the $5p^2(^3P_2)$ leads to the vicinity of $5p6s$. In fact, the absorption of a 562-nm photon from the $(^3P_2)$ leads between the $5p6s(^3P_1)$ and the $5p6s(^1P_1)$, a coincidence that is shown below to play a crucial role on the magnitude of the shift of the $(^3P_2)$.

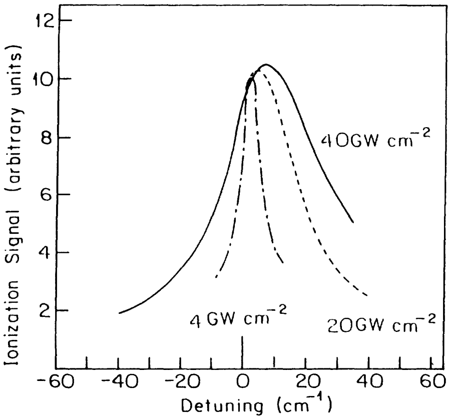

FIG. 3. Theoretical line shapes of the $5s5d(^1D_2)$ two-photon resonance for the different intensities.

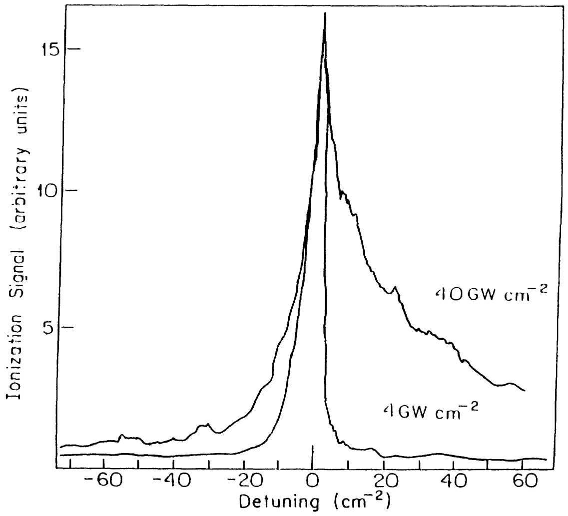

FIG. 4. Experimental line shapes of the $5s5d(^1D_2)$ two-photon resonance for two different intensities.

The importance of the effect of laser intensity in terms of shifts and broadening is illustrated in Figs. 5 and 6. That the shifts are proportional to laser intensity is demonstrated by the data of Fig. 5. Thus the discussion in terms of shifts linear in laser intensity is quite meaningful within the range of intensities of this experiment.

We consider now in some detail each of the shifts of the three triplet resonances. The $5s5d(^3D_2)$ is located so that virtual transitions to the $5s5p(^3P_1)$ make a substantial contribution to its shift (pushing the state up) while the less significant virtual transitions to the doubly excit-

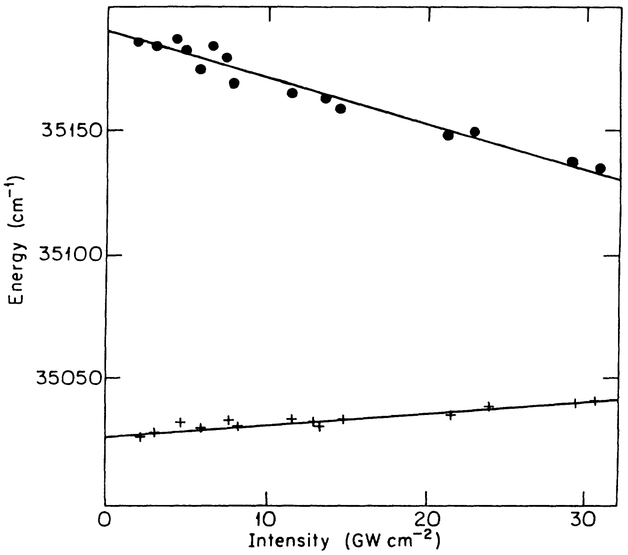

FIG. 5. Experimental position of intermediate two-photon resonances $5p^2(^3P_0)$ (upper line) and $5s5d(^3D_2)$ (lower line) as a function of intensity.

ed states $5p6s$ and $5p5d$ would tend to pull the state down. One might therefore expect a net shift upward whose magnitude would depend on the details of the calculation. The resonance $5p^2(^3P_0)$ is also expected to undergo a relatively strong shift upward owing to virtual transitions to the vicinity of $5s5p(^3P_1)$ and a strong shift downward due to virtual transitions to $5p6s$ and $5p5d$. A relatively strong downward net shift may thus be expected. The autoionizing states $5p6s$ and $5p5d$ are linear combinations of $^3P_1$ and $^1P_1$. In fact the distinction between singlet and triplet becomes rather vague because each of the doublets into which these states split contains as much singlet as it does triplet. We do nevertheless characterize one as triplet and the other as singlet for the purpose of classification. In the case of $5p6s$, the doublet we finally arrive at (see also Sec. III D 2) is

$$5p6s(^3P_1)=\alpha(^3P_1)+\beta(^1P_1)\ , \tag{3.2a}$$

$$5p6s(^1P_1)=\beta(^3P_1)+\alpha(^1P_1)\ , \tag{3.2b}$$

with $\alpha^2=0.536$ and $\beta^2=0.464$. The experimental[26,27] known energy separation is $E(5p6s(^1P_1))-E(5p6s(^3P_1))\simeq 824$ cm^{-1} with $E(5p6s(^3P_1))$ being placed at 52 882 cm^{-1} above the ground state. The number thus obtained for the shift of $5s5d(^3D_2)$ is 1 cm^{-1}/GW/cm^2 as compared to the experimental result of 0.7±0.3 cm^{-1}/GW/cm^2. We do not find any particular sensitivity to any near-resonant doubly excited states. The remaining minor disagreement between theory and experiment is at this point of uncertain origin.

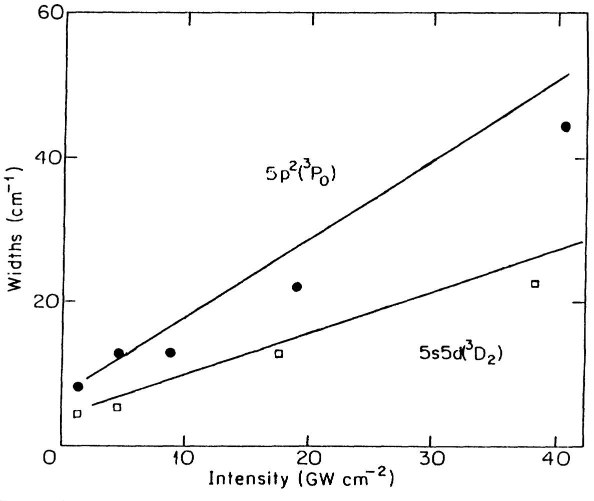

FIG. 6. Comparison between measured (dots) and calculated (solid lines) widths of intermediate two-photon resonances.

The situation with the shift of $5p^2(^3P_0)$ and $5p^2(^3P_2)$ is rather different. The theoretical results are -2.41 cm^{-1}/GW/cm^2 for the $^3P_0$ and -0.023 cm^{-1}/GW/cm^2 for the $^3P_2$ as compared to the experimental values -2.5 ± 0.1 and -0.03 ± 0.01 cm^{-1}/GW/cm^2, respectively. The agreement is quite good and the way we arrive at these numbers illustrates the information one can obtain about atomic structure through this interplay between theory and experiment. Considering first the state $5p^2(^3P_0)$, we note that when two photons are on resonance with the transition $5s^2(^1S_0)\rightarrow 5p^2(^3P_0)$ (which means $\omega=17\,596$ cm^{-1}) the virtual absorption of a third photon leads to an energy about 92 cm^{-1} below the $5p6s(^3P_1)$. We therefore expect a significant contribution to the shift of $^3P_0$ from the presence of $5p6s(^3P_1)$ as well as of $5p6s(^1P_1)$, which is farther away and singlet but contains a substantial component of triplet.

Considering now the state $5p^2(^3P_2)$, we note that the two-photon-resonant frequency, is $\omega=17\,837$ cm^{-1}. The absorption of a third photon leads to a virtual state between $5p6s(^3P_1)$ and $5p6s(^1P_1)$ at about 194 cm^{-1} below the $5p6s(^1P_1)$. Now the contributions of these two states to the shift of $^3P_2$ will subtract and since they represent substantial contributions, a major effect on the value of the shift is expected. Since the virtual absorption leads near the singlet $5p6s(^1P_1)$ (which contains a smaller component of triplet) the cancellation is more pronounced and it is because of this cancellation of two large contributions that the shift of $^3P_2$ takes the value -0.021 cm^{-1}/GW/cm^2, which is two orders of magnitude smaller than the shift of $^3P_0$.

These shifts provide one opportunity to test the possible presence of the autoionizing state $5p5d$ whose position has been conjectured from data of uv spectroscopy but has never been confirmed. Extrapolation uv data would place such a state to about 57 393 cm^{-1} above the ground state. This would have to be a $^1P_1$ state, if it is to be a member of a series observed in single-photon absorption, and it would make a contribution to the shifts of $5p^2(^3P_0)$ since it would also contain a triplet component. But a configuration like $5p5d$ gives rise to a number of other states such as ^3P, ^1F, ^{3}F, ^{1}D, and ^{3}D which are expected to lie below the ^1P. Most of these states would not have participated in single-photon absorption because they have $J>1$ and would be forbidden by angular momentum selection rules, but they would contribute to three-photon absorption. Evidence form the three-photon absorption spectrum (discussed in Sec. IV) suggests that two such states, namely, $5p5d(^1D_2)$ and $5p5d(^3D_3)$, lie at 53 223 and 53 430 cm^{-1}, respectively, above the ground state, which is also consistent with some of our calculations discussed below. We have explored the effect of these states on the shifts. Although not as decisive as the effect of $5p6s$, it is necessary that they be included; especially for the shift of $5p^2(^3P_2)$ which appears to be rather sensitive to the position of the $5p5d(^3D_3)$. As an example of this sensitivity, we note that if this state is placed at 53 364 cm^{-1} the resulting shift is -0.65 cm^{-1}, while if it is placed at 53 430 cm^{-1} (which is compatible with the experiment) the shift is -0.021 cm^{-1}. In our final calculations of the shifts, all contributions were included at the same time. It is only for the purpose of illustration that we discussed various contributions separately.

To summarize, the shifts of the two-photon-resonant states have been shown to be fairly sensitive to the singlet-triplet mixing and the presence of autoionizing states. A comparison of theory with experiment is summarized in Table I in which the results of various theoretical approximations are also listed.

C. Widths of intermediate two-photon resonances

The width of a two-photon resonance in three-photon ionization can, in principle, contain a number of contributions such as ionization, Rabi oscillation, and laser width. Which of all these effects prevails depends on the atom, the state, and of course the laser. There is in addition a broadening coming from the fact that, exactly on resonance or even at some detuning, and at sufficiently high intensity and sufficiently long pulse duration, all atoms in the interaction volume may be ionized. It is what has been termed instrumental broadening,[28] or depletion broadening as is called in more recent papers.[29] Depending on the main cause of broadening, the dependence of the width on laser intensity may exhibit varying behavior. Under the conditions of this experiment neither laser bandwidth nor depletion broadening have been dominant.

Since the bound-bound transition from the ground state to these resonances is a two-photon process, the resulting Rabi frequency is linear in the laser intensity as is the ionziation width. Thus the dependence of the width on laser intensity cannot distinguish between these two broadening mechanisms. The experimental data (Fig. 6) show a linear dependence on laser intensity. Our calculations obtain the same behavior (Fig. 6), except that the theoretical values are a bit higher than the experimental. We find, moreover, that it is the ionization width and not the Rabi frequency that dominates. The range of intensities shown in Fig. 6 was not therefore sufficiently high to saturate the two-photon transition.

It is of course a peculiarity of two-photon-resonant three-photon ionization that the relation between Rabi broadening and ionization broadening remains independent of intensity since they both are linear in intensity. The ratio depends on the atom and the particular transition. The small discrepancy between theory and experiment in Fig. 6 is really very minor considering the complexity of both theory and experiment.

D. Three-photon resonances

1. General features

In the wavelength range from 559 nm (17 890 cm^{-1}) to 564 nm (17 730 cm^{-1}) several resonance peaks have been observed in three-photon ionization (Figs. 7, 8, and 9). These peaks appear in the ion as well as the electron signal and all but one have also been observed in the experiment of Feldman and Welge.[2] The peaks labeled *A*, *B*, and *D* by Feldmann and Welge correspond to those labeled IV, III, and I by Petite and Agostini,[1] who left unlabeled a shoulder on the long-wavelength side of I. This shoulder labeled VI in this work must correspond to peak *C* of Feldmann and Welge. Peak V is not very pronouced in the data of Feldmann and Welge but has a definite presence in this work.[1] All five of these peaks must correspond to doubly excited autoionizing states above the first threshold $5s$, since no two-photon resonances with intermediate bound states exist at the respective wavelengths. There is one exception to this, namely, peak II, which corresponds to the two-photon resonance with the $5p^2(^3P_2)$ intermediate state discussed in Sec. III C. It has been observed as a pronounced peak in both experiments.[1,2]

Three of the autoionizing peaks, namely, III, V, and VI, have remained unidentified and it is part of our aim in this work to interpret their presence. The other two, namely, I and IV, which have been given certain assignments by Feldmann and Welge are also analyzed here. These assignments which were given on the basis of information from single-photon uv absorption spectra have to be reconsidered as we show below. In multiphoton absorption, owing to the large intensity employed in the experiment, such doubly excited states can contribute not only to ionization through autoionization (three-photon

TABLE I. Observed and calculated coefficients of the shifts ($\text{cm}^{-1}/\text{GW}/\text{cm}^{-2}$): In calculation 1 only the $5pns$ configuration is taken into account for the shifts of the $5p^2$ states. Calculation 2 includes singlet-triplet mixing and calculation 3 includes the configurations $5p5d$ and $4d4f$. For the $5s5d(^3D_2)$ state configurations $5snp$ and $5snf$ have been included.

State	Experiment	Calculation 1	Calculation 2	Calculation 3
$5p^2(^3P_0)$	-2.5 ± 0.5	-4.26	-2.2	-2.41
$5p^2(^3P_2)$	-0.03 ± 0.01	-0.91	-0.021	-0.023
$5s5d(^3D_2)$	0.7 ± 0.3		1	

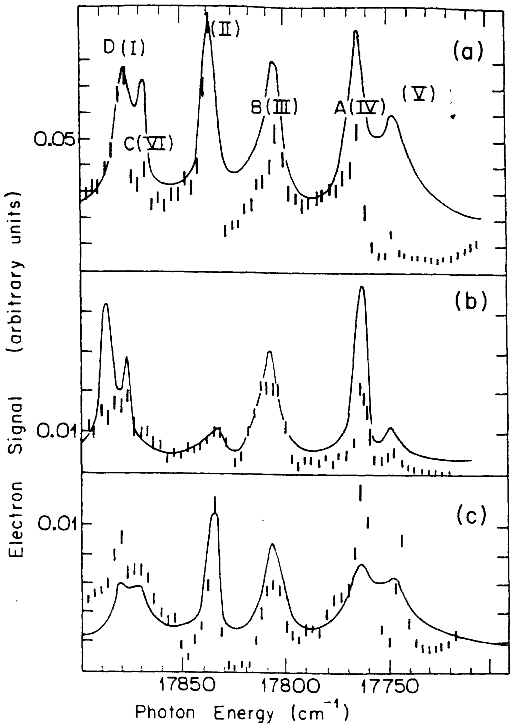

FIG. 7. Experimental (vertical bars) and theoretical (solid line) line shapes of autoionizing three-photon resonances together with the two-photon $5p^2(^3P_2)$ intermediate resonance for linearly polarized light. (a) Ion left in state $5s$, (b) ion left in state $4d$; (c) ion left in state $5p$. The process corresponding to (b) and (c) requires the absorption of four photons.

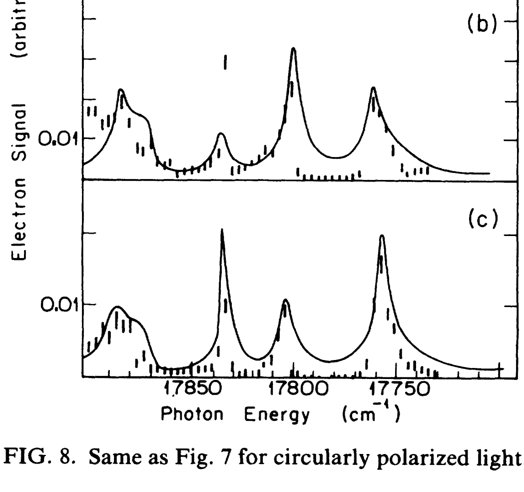

FIG. 8. Same as Fig. 7 for circularly polarized light.

in this case) but can also serve as intermediate states for the absorption of an additional photon thus leading to a different (higher) ionization channel. The residual ion may then be left in an excited state and the photoelectron escapes with a different kinetic energy. Analyzing such processes is also part of our aim in this paper.

In the three-photon energy range under consideration here, namely, from 53 100 to 53 700 cm^{-1} above the ground state, a number of doubly excited states may be expected. To be accessible through three-photon absorption, they must be of odd parity, as in single-photon absorption. In fact, a few such states have been observed (or inferred) as resonances in uv photoabsorption and ionization. On the basis of such information, it is expected that configurations such as $5p6s$, $4d4f$, $4d7p$, and possibly $5p5d$ may give rise to resonances. Whereas any resonance observed in single-photon absorption must have total angular momentum $J=1$, in three-photon absorption, $J=3$ is also available and may in fact have a stronger overall transition strength; other things being equal. We expect therefore that all resonances known from single-photon absorption in principle appear in three-photon ionization. Given, however, that the uv sources employed in single-photon experiments had relatively large bandwidths, even the $J=1$ resonances may exhibit here different profiles, owing to the smaller laser bandwidth, as well as the fact that the same resonance excited by three photons will in general exhibit a different line shape than if excited by a single photon. If a $J=1$ resonance is broad compared to a narrow $J=3$ resonance with which it may overlap, then in three-photon ionization the $J=1$ state may appear as background.

Two additional types of experimental information are available to us in this work: Peak heights obtained with light circularly polarized, and branching ratios to final states involving excited ionic states by both linearly and circularly polarized light. Due to the selection rule $\Delta M_J=\pm 1$, circularly polarized light can only lead to $J=3$ resonances. Thus any resonance appearing under both polarizations must involve at least one component with $J=3$. Since some of these resonances are fairly broad, it should not be too surprising if $J=1$ and $J=3$ are found to overlap. Photoelectron angular distributions provide a third valuable input. Although not part of this work, such information exists in data obtained by Feldmann and Welge and in calculations by two of us.[30] Parts of such information is therefore taken into account in the course of the present analysis, although not explicitly discussed in this paper.

2. *Theoretical model and wave functions*

The ground state has the configuration $5s^2(^1S_0)$, but as is also the case with the excited states, it is not a single configuration. It also includes $5p^2\,4d^2$, etc. The first set of (virtual) intermediate states for the three-photon transition are of $^1P_1$ or $^3P_1$ character, while the second set of intermediate states of interest in this paper contains members of $^1D_2$, $^3D_2$, $^3P_0$, and $^3P_2$ character. The bound, doubly excited configurations $5p^2$ and $4d^2$ and the singly excited configurations $5snp$, $5snd$, and $5sns$ must be included in the summation over intermediate states. We have shown in previous work[10,11] how the field-free (mixed) configurations can undergo further mixing (at sufficiently high intensity), introducing, for example, states of character $^1G_4$ at the second photon level. Since these effects are not dominant in this work, as far as we can tell from our calculations at this time, we concentrate on the spectroscopy, in terms of configuration mixing free of strong-field effects.

For doubly excited states above the threshold, we begin with the core ($1s^2$-$4p^6$) frozen in single configuration calculated with a Hartree-Fock program. To construct multiconfiguration doubly excited states we consider the configurations $4dnp$, $5dnp$, $4dnf$, $5dnf$, $6dnf$, $7dnf$, $5pns$, $5snp$, $5snd$, $6pns$, $7pns$, $8pns$, $5pnd$, $6snp$, $6snd$, $6pnd$, $7pnd$, and $8pnd$ and perform configuration-interaction (CI) calculations in order to assess the main components of states in the energy range of interest. Since our calculation does not give a very good absolute position of energies, we bias the value of the first excited ionic state $5p$, thus obtaining energies for the atom to within 2–3 % of available experimental values. For example, the experimental energies 54 735 cm^{-1} of $4d7p(^3P_1)$ and 55 249 cm^{-1} of $4d7p(^1P_1)$ are placed at 54 073 and 54 245 cm^{-1} by our calculation. It must be mentioned here and kept in mind throughout this paper that nothing is known experimentally about ^1F_J, ^3F_J, ^1D_J, and ^3D_J states, all of which can contribute to three-photon ionization. This is how we then proceed. (a) We obtain wave functions and energies for all states generated by the preceding configurations and allowed in three-photon absorption. (b) By comparison with all experimental evidence discussed earlier we decide which state to assign to each peak. (c) This decision involves calculating peak heights and branching ratios for which we employ our wave functions with energies taken as in the experiment (i.e., changed by 2–3 %).

We discuss now each peak beginning with (I) (Figs. 3–6) which together with (VI) appear at positions where uv absorption has detected[26,27] a broad feature with two humps. The uv single-photon analysis has placed in that region states containing mainly a superposition of $5p6s$ and $4d4f$ configurations with total $J=1$. Our calculations give the main superposition for such states,

$$5p6s(^3P_1)\simeq 0.56|5p6s\rangle-0.33|4d4f\rangle+0.50|4d7p\rangle$$
$$+0.32|4d5f\rangle-0.32|4d8p\rangle+\cdots\ , \quad (3.3a)$$

$$5p6s(^1P_1)\simeq 0.63|5p6s\rangle+0.31|4d4f\rangle+0.39|4d7p\rangle$$
$$-0.33|4d5p\rangle+\cdots\ , \quad (3.3b)$$

which demonstrates substantial $|4d4f\rangle$ component but also a number of other configurations with $4d$ core. As noted earlier, uv data place $5p6s(^3P_1)$ at 52 882 cm^{-1} and $5p6s(^1P_1)$ at 53 706 cm^{-1} which is compatible with their effect on the ac Stark shifts (Sec. III B). Our calculation, however, places the $(^3P_1)$ at 53 236 cm^{-1} and the $(^1P_1)$ at 51 996 cm^{-1}. Although the error in the energy is about 3%, there is a more serious discrepancy in that we find the singlet below the triplet, in contradiction to the uv assignment.[27] This discrepancy may not be as serious as it looks at first, if we recall that the singlet-triplet mixing is in this case of the order of 60% to 40%. This means that the distinction between singlet and triplet is not very sharp, or said somewhat differently, small changes in the mixing will reverse the assignment. Further work is necessary on this point. Note finally that there is some uncertainty in the literature as to whether $5p6s(^1P_1)$ is at 53 706 cm^{-1} or at 53 648 cm^{-1}; an uncertainty understandable in view of the 800 cm^{-1} autoionization width of this state. It appears therefore that the configuration $5p6s$ should play some role in the region of peaks I and VI, at least as a broad background.

The configuration $4d4f$ is strongly mixed with $5p6s$ as shown in Eqs. (3.3a) and (3.3b) and as also found in uv data.[27] Three such states, namely,

$$4d(^2D_{3/2})nf[\tfrac{3}{2}]_1^0\ ,$$

$$4d(^2D_{5/2})nf[\tfrac{3}{2}]_1^0\ ,$$

and

$$4d(^2D_{5/2})nf[\tfrac{1}{2}]_1^0$$

are placed by uv experiment at 53 253, 53 546, and 53 792 cm^{-1}, respectively. These cannot be the only states of that configuration. A number of others not observable in single-photon ionization should also lie in the vicinity. We have calculated such states and find them strongly mixed with $5p5d$, $4d5f$, and $4d7p$. Two examples are

$$4d4f(^3D_2)\simeq -0.61|4d4f\rangle+0.67|4d5f\rangle$$
$$-0.23|5p5d\rangle+0.22|4d7p\rangle+\cdots\ , \quad (3.4a)$$

$$4d4f(^1D_2)\simeq -0.63|4d4f\rangle+0.66|4d5f\rangle$$
$$+0.23|5p5d\rangle-0.18|4d6f\rangle$$
$$+0.15|4d7p\rangle+\cdots\ , \quad (3.4b)$$

where we show only configurations with coefficients larger than 0.1. Our calculated values for the energies of these states are 53 495 and 53 451 cm^{-1}, respectively; which can be off by a few hundred wave numbers. The $5p6s$ is absent from Eqs. (3.4a) and (3.4b) since it cannot form anything but a P state. We expect then the simultaneous (noninterfering) contribution to three-photon ionization of such states on top of those appearing in uv spectra. In all cases, substantial singlet-triplet mixing is expected.

Singlet-triplet mixing was discussed earlier in connection with bound excited states. The mixing coefficients in that case must come from a diagonalization in the space of a few states with the electrostatic and spin-orbit interactions treated as perturbations in a secular equation. It is the language of intermediate coupling that is appropriate in that case. For doubly excited states above threshold, especially those in which one of the electrons is relatively farther from the core, so that its electrostatic interaction with the core is smaller than the spin-orbit interaction in the core, jl coupling is more appropriate. If S_1 and L_1 are the total spin and orbital angular momenta of the core and l the orbital angular momentum of the electron in the larger orbit, then the angular momentum coupling is denoted by $S_1L_1jl[K]_J$, where $\mathbf{j}=\mathbf{S}_1+\mathbf{L}_1$, $\mathbf{K}=\mathbf{j}+\mathbf{l}$, and the total angular momentum J is formed by combining the spin of the outer electron with K which means $J=K\pm\frac{1}{2}$. States in this coupling can be written through an angular momentum transformation in terms of LS-coupling states which shows the relative singlet-triplet superposition. As an example, we consider the following pair of states, which after the necessary angular momentum algebra are written as

$$|5p(^2P_{1/2})6s[\tfrac{1}{2}]_1\rangle=\frac{1}{\sqrt{3}}|^1P_1\rangle+\frac{2}{\sqrt{3}}|^3P_1\rangle\ , \quad (3.5a)$$

$$|5p(^2P_{3/2})6s[\tfrac{3}{2}]_1\rangle=\frac{\sqrt{2}}{\sqrt{3}}|^1P_1\rangle-\frac{1}{\sqrt{3}}|^3P_1\rangle\ . \quad (3.5b)$$

These are quoted in the uv literature[26,27] as triplet and singlet, respectively. From the relative magnitude of the coefficients dictated by angular momentum considerations alone, it is evident that the singlet-triplet mixing is quite strong when the jl coupling is applicable. Incidentally, the preceding coefficients are fairly close to those required for the correct shift of $5p^2(^3P_{0,2})$ states. The difference between the two sets of coefficients [compare Eqs. (3.5) with Eqs. (3.2)] implies that the electrostatic interaction is not completely negligible compared with the spin-orbit interaction of the core for this particular state. The photoelectron angular distribution is also sensitive to the singlet-triplet mixing. As mentioned above, information on such distributions has been taken into consideration in the assignment of mixing coefficients. In fact, for all five of the peaks appearing as three-photon resonances, as well as those appearing as two-photon intermediate bound-state resonances, singlet-triplet mixing, compatible with photoelectron angular distribution information, has been taken into consideration.

Two further aspects of experimental information which is part of this work and must be reconciled with state assignments are the resonance peak structure under excitation by light circularly polarized and branching ratios to the ionic excited states $4d$ and $5p$ after the absorption of a fourth photon, as shown in Figs. 7–9. The data under circular polarization imply that all peaks observed in Fig. 8 must correspond to states with $J=3$; and that is a rigorous requirement. Since in the region of the peaks I and IV at least one peak appears quite prominently under circular polarization we must account for at least one $J=3$ state, which cannot come from the configuration $5p6s$. We know, on the other hand, that all evidence points to strong $4d4f$ presence in that region as also confirmed by all of our calculatons. This requires that at least one of the two peaks, namely, VI, is a $4d4f$ with $J=3$ and that even at the position of I, another $4d4f$ with $J=3$ is contributing substantially. The data of Petite and Agostini[1] are not completely unequivocal on this point since peak VI is not very prominent, while the data of Feldmann and Welge[2] show two well developed peaks for linear as well as for circular polarization. Three $4d4f$ states, namely, $4d4f(^3D_3)$, $(^1F_3)$, and $(^3F_3)$ may lie in that region, in addition to the presence of $4d4f(^1P_1)$ and $(^3P_1)$. The available data do not allow an unequivocal assignment of one of the $J=3$ states, but with all evidence considered (including angular distributions) we conclude that $4d4f(^3D_3)$ contributes to both I and VI. Consistent with the expected ordering and the photoelectron angular distributions, we assign state $4d(D_{3/2})4f(\frac{5}{2})_3$ to peak I and state $4d(D_{5/2})4f(\frac{5}{2})_3$ to peak VI. According to our calculations peak IV is then identified with $4d(D_{5/2})4f(\frac{7}{2})_3$, which in LS coupling would be labelled as $4d4f(^1F_3)$. One of the reasons that make these assignments compelling is the preference for the $4d$ ionic state (upon the absorption of a fourth photon) as compared with the $5p$ (Figs. 7 and 8). This can be understood on the basis of Eqs. (3.4a) and (3.4b), which show that the $4d$ is quite susbstantial in all states of the type $4d4f(^{1,3}L_J)$. This is not a tautology because the core states $4d$ and $5p$ are in many cases present simultaneously.

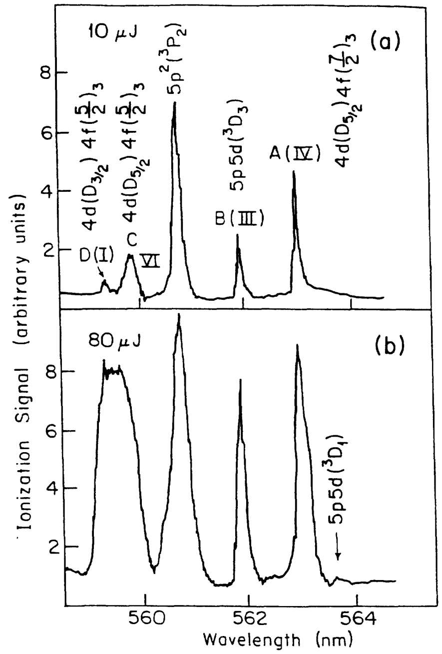

FIG. 9. Experimental three-photon-ionization signals for two laser intensities in the region of autoionizing resonances. For the discussion of peaks assignments, see text.

We come now to peaks III and IV. The latter is absent from the spectrum with circular polarization. Thus for peak V, the two important facts are that it is totally absent under circular polarization and it appears very prominently in the signal which leaves the ion in the $5p$ state [Fig. 7(c)]. It follows, therefore, that it must have $J=1$ and its configuration should contain $5p$. Peak III, on the other hand, must have $J=3$ as well as a significant $5p$ component. Both of these peaks, but especially III, contribute significantly to the $4d$ ionic state [Fig. 7(b)]. As noted above, states that contain $5p$ contain also $4d$ to a significant extent. It is thus to be expected that states contributing to the $5p$ ionic states will also contribute significantly to the $4d$ ionic state. A further illustration of the simultaneous presence of $5p$ and $4d$ is provided by the following two states as obtained in our calculations:

$$5p5d(^3D_2)=0.76|5p5d\rangle-0.33|4d6p\rangle -0.42|4d7p\rangle+0.28|4d4f\rangle\ , \quad (3.6a)$$

$$5p5d(^1D_2)=0.78|5p5d\rangle+0.34|4d6p\rangle +0.46|4d7p\rangle-0.18|4d4f\rangle\ , \quad (3.6b)$$

with calculated energies at 54 627 and 54 544 cm^{-1}, respectively. These are states that, at least for the sake of terminology, we would call $5p5d$, but it obvious that the $4d$ is as significantly present. The preceding calculated energies differ by about 2% from the positions of peaks III and V. For the energy range of interest here, comparison of Eqs. (3.3a) and (3.3b) and (3.4a) and (3.4b) confirms the simultaneous presence of $4d$ and $5p$, a point most recently emphasized by Aymar *et al.*[17] From the data of single-photon uv spectroscopy,[27] the presence of a state $5p5d(^1P_1)$ at 57 393 cm^{-1} has been conjectured by extrapolation of quantum defects. Our calculations space all states from the configuration $5p5d$ within about 2000 cm^{-1}. Thus although we cannot match the energies better than 2%, considering all evidence, such as ionic final states and photoelectron angular distributions we identify peak III with $5p5d(^3D_3)$ and peak V with $5p5d(^3D_1)$. As noted earlier, these triplet states contain substantial amounts of singlet components.

With the preceding assignments and wave functions calculated as discussed, we calculate the resonance absorption peaks shown in Fig. 7, where the peak positions have been matched to the experimental values. The general behavior is reproduced, although relative peak heights show discrepancies which could be eliminated by adjustments of the theory. We chose not to do that, however, because further data would be necessary for such an adjustment to be meaninful. Despite these discrepancies, we have been able to demonstrate at a quantitative level that given sufficient intensity, it is possible to absorb at least one additional photon thus forcing an autoionizing state to avoid autoionization at the lowest level which is the ground state of the ion. This is equivalent to saying that a four-photon absorption has taken place through a doubly excited autoionizing state as an intermediate state.

Peak III which has been observed quite clearly in both experiments corresponds to the two-photon resonance with the bound doubly excited state $5p^2(^3P_2)$. Its shift was discussed in Sec. III B. Its presence under circular polarization is to be expected since it has $J=2$. Upon the absorption of two more photons, the $5p$ ionic state is obtained with substantial probability. Relative to the other peaks, its presence in the $5p$ ionic state is more pronounced than in the $4d$ [compare Figs. 7(b) and 7(c)]. This is consistent with the strong presence of the core $5p$ in the intermediate state. But since $4d^2$ is also present we expect a transition to the $4d$ ionic state as well. Both of these features are reproduced by the theory, as seen in Figs. 7(b), 7(c), 8(b), and 8(c). The theory on the other hand retains this preference for a $5p$ ionic state even under circular polarization while the data seem to show a rather sharp peak for the $4d$ core [compare Figs. 7(b) and 7(c) with 8(b) and 8(c)].

The four-photon absorption via doubly excited intermediate states (either at the two-photon level via the $5p^2$ or the three-photon level via the autoionizing states), and the branching ratios to the three ionic states raise a number of interesting questions. First, one may wonder whether it is the configuration of the intermediate state that mainly determines these branching ratios or the configuration mixing of the initial (ground) state that also plays an important role. On the basis of our calculations and their correlation with the data, it is clear that the intermediate state is the dominant factor. By contrast, in single-proton absorption the ground state plays the most important role, especially for certain configurations. Consider, for example, the state $4d4f(^1P_1)$ which can be reached by either single- or three-photon absorption. If the ground state were pure $5s^2$, this transition would not take place by a single photon. It would, however, take place with three photons through an intermediate state (real or virtual) like $5p^2$, *provided* it is not pure $5p^2$ but contains $4d^2$. For a case of extreme contrast between single and multiphoton absorption, consider now the state $5p5d(^1P_1)$. In single-photon absorption, the transition is possible only to the extent that the initial state contains $5p^2$ or the final state is mixed with a *ps* configuration. In three-photon absorption, on the other hand, it can take place even in an independent-particle approximation where initial, intermediate, and final states are pure (single) configurations; it requires no correlation at all. This comparison shows that correlation[31] plays a different role in a multiphoton transition and that its importance can be deemphasized by the appropriate choice of the transition. It follows then that in an isoelectronic sequence certain multiphoton transitions will not decrease as fast with Z if they are such that they do not require correlation.

E. Intensity dependence of branching ratios

A second question is whether and how the branching ratios to the various ionic states depend on the laser intensity at a given frequency. At relatively low intensity, these ratios are determined solely by intra-atomic interactions. Since final excited ionic states in this experiment require the absorption of at least a fourth photon, the corresponding transition probability is proportional to the fourth power of the intensity. Ground-state ions are created either by a three- or a four-photon process. We expect therefore that the branching ratios will change with increasing intensity, favoring the higher-order processes if the pulse is not too slow. These branching ratios are determined experimentally by photoelectron energy spectroscopy, because transitions to different ionic states lead to electrons of different energies. Agostini and Petite[1] have presented such photoelectron spectra, but the energy resolution did not allow the separate identification of all channels, because groups of electrons from different channels overlapped. For example, at 532 nm, three-photon ionization leaving the ion at the $5s$ state and four-photon ionization producing Sr^{2+} from the $5p$ excited ionic state produce electrons of kinetic energy partially overlapping within the resolution of that experiment. We shall not attempt here a detailed theoretical discussion of this effect since new experimental data of higher resolution are being obtained. We shall postpone the presentation of the related theory to a followup paper with the new data. We do, however, present below certain general features emerging from our calculations.

We limit the discussion of this issue to radiation of wavelength 532 nm for which some data have been obtained. There is no exact intermediate resonance at this wavelength. The nearest two-photon resonance with a singlet state [the $5p^2(^1S_0)$] is 434 cm^{-1} away. The nearest doubly excited autoionizing resonance at the three-photon level is even farther away. We have therefore three-photon and four-photon nonresonant processes, in which the fourth photon is absorbed within the continuum in an above-threshold ionization (ATI) process except that there are so many autoionizing states in the vicinity that the strength of the transitions comes from them even though nonresonant. If we denote by $\sigma^{(N)}(nl)$ the generalized cross section for N-photon ionization leading to the nl state of the ion, we obtain the following values (in units of $\text{cm}^{2N}\text{s}^{N-1}$): $\sigma^{(3)}(5s)=3.1\times10^{-78}$; $\sigma^{(4)}(5s)=5.8\times10^{-109}$; $\sigma^{(4)}(4d)=6.81\times10^{-110}$; and $\sigma^{(4)}(5p)=2.32\times10^{-109}$. In the paper of Agostini and Petite,[1] these channels have been numbered as (1), (2), (3), and (4), respectively, and for convenience we shall follow their convention (see Fig. 1 of Ref. 1). At low intensity (almost up to 10^{11} W/cm^2) channel (1) dominates by far since it represents a lower-order process. The other channels, however, increase with intensity faster (being proportional to the fourth power). To actually calculate the number of ions produced in each channel, we must integrate over the time of the pulse because at different parts of the pulse different processes are favored, owing to the nonlinear dependence on intensity. The proper calculation is performed by employing the generalized cross sections in a system of kinetic equations as in Ref. 15. For low intensity (say, 10^9 W/cm^2) and a 20 ps pulse corresponding to the experiment of Ref. 1, we obtain essentially 100% of the ions into channel (1). At 10^{12} W/cm^2 we still have 90.31% into channel (1). But we also have 2.48% into (2), 0.22% into (3), and 6.99% into (4). This shows a propsensity for transitions into the $5p$ excited ionic state, as soon as the fourth-order processes acquire significance. The calculation further shows that for a slight increase of the intensity, say, by a factor of 2, there is a dramatic change, with channel (1) and (2) sharing almost equally the production of about 97% of the ions, with about 2.8% going into (4) and about 0.1% into (3). This result cannot be taken literally because when the fourth-order channel (2) becomes comparable to the third-order channel (1), we must include five-photon processes and so on. From the experimental results we know that five-photon absorption plays an important role at that intensity range. Moreover, we must include the depopulation of the final states of channels (1) to (4) by multiphoton processes leading into Sr^{2+}. These processes represent the production of Sr^{2+} via sequential transitions and have been catalogued by Agostini and Petite.[1] A complete quantitative analysis will be presented in the follow-up paper. The point to be made for the time being is that around 10^{12} W/cm^2 for a 20-ps pulse (because the pulse duration is as important as the intensity[15]) we expect to see significant departure of ion branching ratios from those of the field-free atom. This correlates well with the data[1] which show that between 5×10^{11} and 10^{12} W/cm^2, the production of Sr^+ saturates, and at 3×10^{12} W/cm^2 the production of Sr^{2+} is more than that of Sr^+ (Fig. 6 of Ref. 1).

The preceding results on the populations of excited ionic states contain the following interesting conclusion: The population of Sr^+ $(5p)$ reaches a maximum value at some intensity of the order of 10^{12} W/cm^2; this maximum value being about 7% of the atoms in the interaction volume. Below that intensity, not much reaches that state as everything goes into the ground state of Sr^+ via the three-photon process. Above that intensity, the population of $\text{Sr}^+(5p)$ is drained into Sr^{2+} by a further four-photon process. This conclusion is the sort of information one seeks in the contemplation of creating inverted ionic populations by single-beam multiphoton pumping.

As we noted above, at this wavelength (532 nm), there is no resonance with any intermediate bound or autoionizing state. Then at what stage is the propensity for the $5p$ as compared to the $4d$ created? It is at the virtual intermediate state superposition which represents a linear combination of interfering channels. One should be able to change that by varying the wavelength. We already know from Figs. 7 and 8 that $4d$ is favored on some of those wavelengths, except that in that case we had resonance autoionizing states at the three-photon level. It would be interesting to explore this question further experimentally at different wavelenths and different alkaline earth atoms. Related data for Ca have recently been obtained[21] extending previous limited data by Agostini and Petite.[32]

VI. CONCLUDING DISCUSSION

The analysis has concentrated on two-photon-resonant intermediate states, three-photon-resonant autoionizing states, and branching ratios to excited ionic states after the absorption of a fourth photon. Our calculated values for the ac Stark shifts of the intermediate bound resonances are in excellent agreement with the experiment; with the exception of the shift of $5s5d(^1D_2)$, which remains a bit of a mystery; especially since all wave functions came from the same calculation. We have found that the spectum at the three-photon level has been dominated by $J=3$ resonances. Although we have assigned configurations to these resonances, the assignments have to be taken more as bookkeeping labels since configurations appear strongly mixed as is evident in the equations of Sec. III D 2. The branching ratios to excited ionic states as obtained in the calculation were found to be in reasonable agreement with the experiment. As will be shown in a separate paper,[30] photoelectron angular distributions are consistent with and lend support to the interpretation and the state assignments. Given that our theory involved small adjustments of the values of the calculated energies, the comparison with many aspects of more than one set of data has been very valuable in strengthening our confidence in the theoretical model. The relative peak heights of the three-photon resonances agree only semiquantitatively with the experiment. Spatiotemporal pulse effects probably play a role here and should be included eventually. The overall agreement between theory and experiment, in view of the complexity of both, should at this point be considered as satisfactory. Time will tell how far this approach can go as an interpretative and predictive tool.

All transitions leading to excited ionic states involved the absorption of a fourth photon above the first ionization threshold. As such they represent above threshold ionization (ATI), but differ from the popular variety[33] in that two electrons were involved in the transitions. In fact some of these, if not all, can be considered to be at least in part direct two-electron four-photon transitions. Take, for example, the transition to the excited state $Sr^+(4d)$ via the doubly state $5p^2(^3P_2)$ [Fig. 7(b)]. It surely takes a direct two-electron two-photon transition to reach the intermediate state and a two-electron transition to autoionize at the $4d$ of the ion from the $5p^2(^3P_2)$. One might argue, however, that since $5p^2(^3P_2)$ also contains $4d^2$, a two-photon single-electron transition would still lead to $Sr^+(4d)$. But a $4d$ orbital of the $4d^2$ atomic configuration is not the same as a $4d$ orbital of the ion Sr^+. Thus in any case, one must think of such transitions, which lead to excited ionic state, as predominantly direct two-electron transitions.

As noted earlier in Sec. III D, the role of correlation in a multiphoton process is quite different from its role in single-photon transitions, in that N electrons can be raised into the continuum even if independent, as long as the order of the transition is equal to or larger than N. Pursuing then a bit further a variation of the above example, one would expect that a four-photon process of the type $5s^2 \rightarrow 5p^2 \rightarrow 4d\varepsilon d$ [leading to an excited ion Sr^+ $(4d)$] to be much stronger than other channels leading to $Sr^+(4d)$, since it does not require correlation. There are a number of questions of this type worth investigting, which pertain also to the problem of maximization of transitions to a particular ionic state or to a particular doubly excited state above the first threshold. A partial estimate has been obtained in this work, but we are far from complete understanding.

We have, nevertheless, shown that four photons can be absorbed via a three-photon resonance to a two-electron state like $4d4f$, $5p5d$, etc. Now we may ask the following: if a state like $5d^2$ or $5p6p$ lies (let us say by coincidence) at the appropriate number of photons above the $5p5d$, will that additional transition occur with any probability of significance? If yes, can it be maximized by adjusting the intensity? What are the main experimental features that would identify such additional absorptions? Finally, under what conditions can two-electron transitions be pushed all the way to direct double ionization? Although the evidence until now points to severe limitations, owing to the presence of increasingly large numbers of competing channels leading first to the single ion, the matter is far from closed. There seems to exist experimental hints on both sides of the argument. Most recently, for example, Eichmann *et al.*[34] have found in studies of Ba that even if a second laser is employed, still doubly ionized ions are generated by series of sequential processes via a number of excited states of Ba^+. On the other hand, the behavior of the older data on Ca by Agostini and Petite[32] contain some evidence for a contribution to Ca^{2+} by a direct two-electron ejection, with a doubly excited autoionizing state near resonant at the three-photon level, in an overall eight-photon two-electron ionization. The existing data as well as additional results soon to be available on Sr represent perhaps the most complete experimental investigation, at least with a single laser. Although the analysis of the production of Sr^2 remains to be completed, no compelling evidence for direct two-electron transitions to Sr^{2+} has been uncovered so far. It should, however, be kept in mind that only frequencies within a very limited range have been employed.

With a number of further experiments in Sr, as well as Ca, Mg, and Ba in progress, and continuing analysis, some of the preceding questions may yield to answers in the near future. In the process, substantial new territory of the structure of these atoms will have been explored.

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