Theory of doubly resonant ionization by broad-band radiation applied to the determination of isotopic abundances

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(Received 14 February 1990)

We present a theoretical study of doubly resonant three-photon ionization with radiation of sufficiently broad bandwidth to overlap all hyperfine levels of the resonant intermediate states. We demonstrate that isotopic selectivity in ionization is apt to occur under a variety of circumstances, although the degree may vary from negligible to quite significant, depending on the relative values of atomic and radiation parameters. Our theory provides a satisfactory quantitative interpretation of recent experimental data in Sn.

INTRODUCTION

In a recent paper[1] by two of us (P.L. and A.L.) we provided a theory of resonant two-photon ionization with broad-band radiation, pertaining to applications of this process in the determination of isotopic abundances. Specifically, we demonstrated that isotopic selectivity is apt to result more often than not, even when the bandwidth of the radiation is sufficiently large to overlap the resonant transitions of all isotopes present in the sample. Our results, which provided the explanation for the rather unexpected experimental data of Fairbanks *et al.*,[2] suggested that the phenomenon is to be expected in other schemes of resonance ionization as was also apparent in related experimental data.[2]

The purpose of this paper is to extend our theory to doubly resonant three-photon ionization in an attempt to provide an explanation for observations in Sn. As will be seen below, the analysis of this process is considerably more complex than that of resonant two-photon ionization. The number of levels and consequently of the density-matrix equations is here significantly larger. It represents a process with a complicated set of interactions not lending itself to simple physical pictures; except in one very special case (involving a transition from one $J=0$ to another $J=0$ state for even isotopes) where the transition is totally forbidden, thereby precluding ionization of even isotopes. Clearly, we have 100% selectivity in that case. In general, however, the selectivity will depend on an intricate interplay between atomic and radiation parameters—such as strength of transitions between discrete states as well as between discrete and continuum, hyperfine structure splittings, laser intensity, bandwidth, pulse duration, and frequency. Because of such interplay only detailed analysis can provide a guide as to the suitability and efficiency of a particular process in a particular atom.

As we show in this paper, doubly resonant three-photon ionization exhibits some features that resemble those of resonant two-photon ionization.[1] In particular a range of intensities exists over which the amount of ionization for even isotopes differs from that for odd, but the ratio remains practically constant over that range of intensity. This has the advantage that the outcome of an experiment can thus be predicted without the necessity for knowledge of the laser intensity or bandwidth with extremely demanding accuracy. Typically, that range of intensities extends from about 10^5 W/cm^2 to about 10^7 W/cm^2.

Recall that the initial motivation for the measurements in Refs. 2–6 was the determination of isotopic abundances through resonance ionization; which presupposes that all isotopes of the same atom ionize to the same degree. Our calculations in Ref. 1 and herein have shown why this is not necessarily the case, explaining thus the anomalous ratios of Fairbanks *et al.*[2] As we have pointed out,[1] the method can still be employed in the determination of isotopic abundances, provided one has *a priori* knowledge (presumably through theory or related experiment) of the expected ratios which can be used to calibrate the results. Having, however, shown that selectivity will occur even with broad-band radiation, we can also turn the motivation around. Since selectivity can be adjusted to some degree by varying externally controlled laser parameters, we may now view the process also as a way of separating isotopes without the necessity of extremely narrow-band radiation. Obviously, only a limited degree of selectivity can in general be expected; except in very special cases such as the one mentioned above, where even 100% is feasible.

This is not the place nor do we feel qualified to assess the merits of this scheme as a possible technique of isotope separation in comparison with the more established technique[7,8] based on narrow-band lasers resolving the excitation of one isotope. Its only obvious merit has to be the minimal requirement on laser bandwidth. Whether that in itself makes it an interesting candidate deserving further consideration remains to be seen.

THEORETICAL FORMULATION

Our formulation is quite general and follows the lines presented in detail in earlier publication.[1,9] To avoid confusing the reader with unnecessary generalities we will limit our presentation of the formalism to the specific example in Sn.

First we describe the atomic system. The isotopes of Sn fall into two classes: the even ones, with zero nuclear spin, and the odd ones, with nonzero nuclear spin, $I_N=\frac{1}{2}$. The even ones can be described in a fine-structure basis $|JM_JLS\rangle$ while the odd ones exhibit hyperfine structure (HFS) described in a $|FM_FJI\rangle$ representation. This difference in the atomic structure was found to be the cause for the anomalous response of the two types of isotopes in singly-resonant cases studied before.[1] For the even isotopes the initial state is $|0\rangle=|5p^2\,{}^2P_0\rangle$, the first resonant state is $|1\rangle=|5p6s\,{}^3P_1^\circ\rangle$, excited by a 268-nm laser, and the second resonant state is $|2\rangle=|5s7d\,{}^3D_2^\circ\rangle$, excited by a 615-nm laser. Both frequencies are sufficiently high to ionize the atom above its second fine-structure ionization threshold and no other bound or autoionizing state is directly involved in the process. For the odd isotopes, the situation is more involved. The ground state is (the magnetic sublevel degeneracy not taken into account) characterized by total angular momentum $F=\frac{1}{2}$. However, the resonantly excited intermediate states are now hyperfine multiplets. Specifically, the first resonant state is a doublet with two states characterized by $F=\frac{1}{2}$ and $F=\frac{3}{2}$, which we denote by $|1'\rangle$ and $|1''\rangle$, respectively. It is excited with the uv laser as well. The second resonant state is also a doublet with total angular momenta $F=\frac{3}{2}$ and $F=\frac{5}{2}$ for the states $|2'\rangle$ and $|2''\rangle$, respectively. The visible laser induces the resonant excitation to this doublet. It is assumed that both lasers are sufficiently broad so as to overlap the hyperfine multiplets they excite. This means that all hyperfine levels in both resonant states are excited coherently. Whether this coherence will be destroyed before ionization has occurred depends on the relation between the laser pulse duration and the ionization efficiency on one hand and the hyperfine coupling time ($\sim\Delta_{\rm HFS}^{-1}$) on the other.[1]

The full set of density matrix equations for the odd isotopes has the following form:

$$\frac{d}{dt}\sigma_{00}=-2\sum_k \mathrm{Im}(\Omega_{k0}\sigma_{0k})\quad (k=1',1'')\,, \tag{1}$$

$$\frac{d}{dt}\sigma_{kk}=-\Gamma_k\sigma_{kk}+2\,\mathrm{Im}(\Omega_{k0}\sigma_{0k})-2\sum_l[\mathrm{Im}(\Omega_{kl}\sigma_{lk})](\delta_{l2'}+\delta_{l1''})\quad (k=1',1'';\ l=2',2'')\,, \tag{2}$$

$$\frac{d}{dt}\sigma_{ll}=-\Gamma_l\sigma_{ll}+2\sum_k[\mathrm{Im}(\Omega_{lk}\sigma_{kl})](\delta_{l2'}+\delta_{k1''})\quad (k=1',1'';\ l=2',2'')\,, \tag{3}$$

$$\left[\frac{d}{dt}-i\Delta_k+\tfrac{1}{2}\Gamma_k+2\gamma_L^{\rm uv}\right]\sigma_{0k}=(i/2)\Omega_{0k}(\sigma_{00}-\sigma_{kk})+(i/2)\Omega_{k'0}\sigma_{kk'}+(i/2)\sum_l\Omega_{lk}\sigma_{0l}(\delta_{l2'}+\delta_{k1''})\,. \tag{4}$$

$$(k,k'=1',1'',\ k\neq k';\ l=2',2'')\,,$$

$$\left[\frac{d}{dt}-i(\Delta_l+\delta_k)+\tfrac{1}{2}\Gamma_l+2(\gamma_L^{\rm uv}+\gamma_L^{\rm v})\right]\sigma_{0l}=-(i/2)\sum_k\Omega_{0k}\sigma_{kl}+(i/2)\sum_k\Omega_{kl}\sigma_{0l}\quad (k=1',1'';\ l=2',2'')\,, \tag{5}$$

$$\left[\frac{d}{dt}-i\Delta_l-\tfrac{1}{2}(\Gamma_k+\Gamma_l)+2\gamma_L^{\rm v}\right]\sigma_{kl}=(i/2)\Omega_{kl}(\sigma_{kk}-\sigma_{ll})-(i/2)\Omega_{kk'}\sigma_{k'l}-(i/2)\Omega_{kl'}\sigma_{l'l}$$
$$+(i/2)\Omega_{k'l}\sigma_{kk'}\delta_{l2'}\quad (k=1'',\ k'=1';\ l=2',2'',\ l'\neq l)\,, \tag{6}$$

$$\left[\frac{d}{dt}-i\Delta_l'-\tfrac{1}{2}(\Gamma_k+\Gamma_l)+2\gamma_L^{\rm v}\right]\sigma_{kl}=(i/2)\Omega_{kl}(\sigma_{kk}-\sigma_{ll})\delta_{12'}-(i/2)\Omega_{k0}\sigma_{0l}+(i/2)\Omega_{k'l}\sigma_{kk'}$$
$$-(i/2)\Omega_{kl'}\sigma_{l'l}\delta_{l'2'}\quad (k=1',\ k'=1'';\ l=2',2'',\ l'\neq l)\,, \tag{7}$$

$$\left[\frac{d}{dt}-i(\Delta_k-\Delta_{k'})+\tfrac{1}{2}(\Gamma_k+\Gamma_{k'})\right]\sigma_{kk'}=(i/2)\sum_l\Omega_{lk}\sigma_{k'l}-(i/2)\Omega_{k0}\sigma_{0k'}-(i/2)\Omega_{k'0}\sigma_{0k}$$
$$+(i/2)\sum_l\Omega_{lk'}\sigma_{kl}\delta_{l2'}(k=1',\ k'=1'';\ l=2',2'')\,, \tag{8}$$

$$\left[\frac{d}{dt}-i(\Delta_l-\Delta_{l'})+\tfrac{1}{2}(\Gamma_l+\Gamma_{l'})\right]\sigma_{ll'}=-(i/2)\sum_k \Omega_{lk}\sigma_{kl'}-(i/2)\sum_k \Omega_{l'k}\sigma_{kl}\delta_{k1''} \quad (l=2',\, l'=2''; \, k=1',1'') \, . \tag{9}$$

To obtain this compact form of the system of 15 equations we have separated the excited states in two groups, one, labeled by k,k', containing the energetically lower excited doublet and the other, labeled by l,l', comprised of the members of the energetically higher hyperfine doublet. The proper values of the indices are indicated next to the equations. In the above equations, we denote by Ω_{mn} the Rabi frequency between states $|m\rangle$ and $|n\rangle$, and by Γ_m the ionization width of state $|m\rangle$. All Rabi frequencies and ionization widths are single-photon processes in the case under study. The Rabi frequencies between the ground state and the first excited doublet are proportional to $(I_{\rm uv})^{1/2}$, while the ones connecting the first and second excited doublets are proportional to $(I_v)^{1/2}$, where $I_{\rm uv}$ and I_v are the intensities of the uv and visible laser, respectively. The ionization from the first doublet is due to the uv laser, while the upper doublet is ionized by both lasers. Therefore, $\Gamma_{2'}$ and $\Gamma_{2''}$ are obtained by summing up two terms, one proportional to $I_{\rm uv}$ and the other proportional to I_v. The Kronecker delta symbols δ_{ij} ($\delta_{ij}=1$ if $i=j$, otherwise $\delta_{ij}=0$) are used to ensure that within the compact and symmetric, with respect to the states, notation employed no terms representing transitions between $|1'\rangle$ and $|2''\rangle$ have survived. This transition is forbidden by angular momentum selection rules. The detunings, appearing in the equations, are defined as follows:

$$\Delta_k=\omega_{\rm uv}-(\omega_k-\omega_0), \quad k=1',1''$$

$$\Delta_l=\omega_v-(\omega_l-\omega_k), \quad l=2',2''; \quad k=1''$$

$$\Delta'_l=\omega_v-(\omega_l-\omega_k), \quad l=2',2''; \quad k=1'$$

where $\omega_{\rm uv}$ and ω_v are the photon frequencies of the uv and visible laser, respectively.

The role of the laser bandwidth is significant. The model employed to account for the origin of the laser bandwidth is based on phase fluctuations of the laser field.[9] This model does not take into account possible intensity fluctuations due, for example, to multimode structure. But the consistency of the experimental results[2] obtained under conditions that would expose the influence of the above-mentioned laser characteristics on the measurements obtained seems to suggest that they have not played any significant role if at all. The bandwidths (full width at half maximum) of the two lasers are denoted by $2\gamma_L^{\rm uv}$ and $2\gamma_L^v$, for the uv and the visible laser, respectively. The bandwidth as shown in the equations is Lorentzian. This is clearly not realistic and a cutoff parameter β_L could be introduced[10] to ensure that the laser line shape falls off in the wings faster than the Lorentzian. Given that both excited hyperfine doublets are assumed to be totally overlapped by the laser bandwidths and that the separation of the two doublets is enormous compared to the widths of the laser line shapes, the inclusion of β_L does not change anything and was omitted from the equations. Finally, omitted were also the two-photon processes that connect one member of the doublet with the other through both the bound and the continuum part of the spectrum,[11] since they were estimated to be of no importance.

The total ionization is calculated by

$$P(t)=1-\sigma_{00}(t)-\sum_j \sigma_{jj}(t), \quad j=1',1'',2',2''$$

where t is the appropriate interaction time, which in our case is the longest pulse duration τ_L, because both lasers contribute to ionization.

The density-matrix equations for the even isotopes are only nine since now the intermediate excited states are only two, $|1\rangle$ and $|2\rangle$. They can be obtained from the above system of equations by allowing only the values 1 and 2 for the subscripts k and l, respectively.

From the equations for the off-diagonal density-matrix elements (often called coherences in the literature) it is easy to see that they precess at the rate of their energy separation.

$$\sigma_{mn}(t)\sim e^{i(\omega_m-\omega_n)t} \, .$$

For members of the same hyperfine doublet, which are coherently excited, the precession time can be much faster than the laser pulse duration. Therefore the initially established coherence is quickly altered by the hyperfine structure precession. At the same time removal of the system from the states of the hyperfine doublets caused by ionization induces a decay in the same off-diagonal density-matrix elements destroying (and not altering) the coherence. If this happens on a time scale shorter than the hyperfine precession period the measured ionization signal will not be affected by the dephasing effects of the hyperfine precession. Otherwise the ionization signal will monitor the effects of the hyperfine structure although the latter is not energetically resolved.

The above summarize the description of the dynamic part of the calculation. The other very important part of the calculation is the evaluation of the atomic parameters entering Eqs. (1)–(9). The calculation of these parameters for the even isotopes is rather straightforward, since the bound states can be expressed in the representation $|JM_JLS\rangle$ which is convenient for the calculation of both the Rabi frequencies and the ionization widths. For the odd isotopes the angular momentum algebra is more involved. For the calculation of the Rabi frequencies the bound states are expressed in the representation $|FM_FIJ\rangle$. For the ground state $F=\frac{1}{2}$ and $M_F=\pm\frac{1}{2}$. The two magnetic substates are equally populated. The first excited doublet would consist of two states with $F=\frac{1}{2}$ and $\frac{3}{2}$, respectively, and the second one would have $F=\frac{3}{2}$

and $\frac{5}{2}$. Since linearly polarized light is used, the excitation proceeds through the population of the $M_F=\pm\frac{1}{2}$ substates of each resonantly excited state. Thus the problem is completely symmetric with respect to these two substates and they need not be considered separately.

Formally a single-photon electric dipole matrix element for linearly polarized light in the $|FM_FIJ\rangle$ representation is given by

$$\langle IJFM_F|r_0|I'J'F'M_F'\rangle=(-1)^{\Sigma}\delta_{L_cL_c'}\delta_{SS'}\delta_{II'}\begin{pmatrix} F & 1 & F' \\ -M_F & 0 & M_F \end{pmatrix}\begin{Bmatrix} F & 1 & F' \\ J' & 1 & J \end{Bmatrix}\begin{Bmatrix} J & 1 & J \\ L' & S & L' \end{Bmatrix}$$
$$\times\begin{Bmatrix} L & 1 & L' \\ l' & L_c & l \end{Bmatrix}[F,F',J,J',L,L']^{1/2}(l_>)^{1/2}R_{nl}^{n'l'},$$

where $\Sigma=I+S+L_c+l_<+1-M_F$. The symbol

$$[\alpha,\beta,\ldots\nu]^{1/2}\equiv[\alpha(\alpha+1)\beta(\beta+1)\ldots\nu(\nu+1)]^{1/2}$$

and $l_<\equiv\min(l,l')$, $l_>\equiv\max(l,l')$. The rest of the symbols are the usual 6-j and 3-j symbols.[8] Finally $R_{nl}^{n'l'}$ is the radial matrix element between the one-electron wave functions characterized by the quantum numbers (n, l) and (n',l'), respectively. The assumption behind this formula is that the atomic system consists of a core (whose quantum numbers we denote with the subscript c) that does not participate in the excitation and an electron (whose quantum numbers we denote with lowercase latin characters) that responds to the action of the electromagnetic field. No doubly excited or inner-subshell excited states are involved in the processes discussed here.

The calculation of the ionization widths for the odd isotopes is quite involved. A series of transformations from the $|FM_FIJ\rangle$ representation to other representations, suitable for describing the continuum states of the system, is needed. At first a transformation to the $|JM_JSL\rangle$ representation is performed,

$$|FM_FIJ\rangle=\sum_{M_J}\langle IJFM_F|I,M_F-M_J,JM_J\rangle|IM_I\rangle|JM_JLS\rangle,$$

followed by a transformation to the $|jJ_cJM_J\rangle$ representation,

$$|JM_JLS\rangle=\sum_{j,J_c}\langle sS_c(S),lL_c(L),J|sl(j),S_cL_c(J_c),J\rangle|JM_JjJ_c\rangle.$$

The transformation coefficient are complicated expressions involving 3-j, 6-j, and 9-j symbols.[12] Then it is straightforward to write the ionization width of the $|FM_FIJ\rangle$ state as

$$\Gamma_{FM_F}=\sum_{J_c,M_{J_c}}\sum_{m_s}|\langle Km_s;J_cM_{J_c}|r_0|FM_FIJ\rangle|^2,$$

where K represents the energy of the outgoing electron, m_s the projection of its spin on the polarization axis, and J_c, and M_{J_c} are the quantum numbers of the core (equivalently the ion) left behind by the ejected electron. Since the spin of the outgoing electron is not resolved an incoherent summation over m_s must be performed. At the same time the ion could be left in any of the two fine-structure components of its ground state with $J_c=\frac{1}{2}$ or $\frac{3}{2}$. A second incoherent summation is needed to properly take into account this additional multiplicity of the final, noninterfering states. Needless to say, an enormous amount of angular momentum algebra is involved in performing the above transformations and summations and the separation of the angular from the radial parts of the atomic parameters.

For the purposes of this paper, the radial parts of the matrix elements have been calculated on the basis of single-channel quantum defect theory.[13] For an atom like Sn, with two ionization thresholds due to the fine structure of the ionic core, multichannel quantum defect theory (MQDT) would be more appropriate, especially in regions of the spectrum where channel coupling is important. We did not attempt such an elaborate analysis for a number of reasons. First, we did not expect major channel-coupling effects because the energy of the ejected photoelectron lies well above the second fine-structure ionization threshold where the one-electron continuum is smooth without autoionizing resonances. Second, the uncertainty we expect from single-channel quantum defect theory is not disproportionately large compared to the experimental uncertainties of the data at our disposal, as discussed in some detail in the next section. Third, a MQDT analysis sufficiently extensive to accommodate three-photon transitions—such as the one performed recently for the rare gases[14]—would require spectroscopic data not available to us at the present time. If and when experiments on Sn reach a higher level of accuracy, it may become necessary to undertake a more elaborate calculation of the atomic parameters. For the time being the results and discussion presented in the following section leave no doubt as to the interpretation of the phenomenon under consideration.

RESULTS AND DISCUSSION

To proceed with the numerical solution of the systems of density-matrix equations we must also specify the pa-

rameters of the laser. Following the experimental conditions as described in Ref. 2, we employ an almost Gaussian form for the temporal shape of both pulses and assume 100% temporal overlap between them. For the pulse duration, we have used the value $\tau_L = 5$ ns for both lasers and the values $\gamma_L^{uv} = 0.4$ cm^{-1} and $\gamma_L^{v} = 0.25$ cm^{-1} for their respective bandwidths, all corresponding to the experimental conditions.[2] The hyperfine splittings for the two doublets are $\Delta_{HFS}^{(1)} = 0.25$ cm^{-1} and $\Delta_{HFS}^{(2)} = 0.025$ cm^{-1}, for the first and second excited doublet. The corresponding coupling times are $\tau_{HFS}^{(1)} = 0.02$ ns and $\tau_{HFS}^{(2)} = 0.2$ ns, which satisfy the condition $\tau_{HFS}^{(i)} \ll \tau_L$ ($i = 1,2$). In other words, the laser pulse duration is much longer than the characteristic hyperfine coupling times. This corresponds to the situation which, as discussed at length in Ref. 1, is apt to lead to significant isotopic selectivity.

Using the calculated atomic parameters and the pulse characteristics described above, we calculate the ionization P for the even isotopes and P' for the odd ones. From these, we calculate the quantity $\beta \equiv (P' - P)/\frac{1}{2}(P' + P)$ (%), which we plot as a function of either I_{uv} or I_v, with the other intensity held at a constant value.

Let us begin the discussion of our results with Fig. 1, in which the quantity β (%) is plotted as a function of I_v with $I_{uv} = 400$ W/cm^2. Under these conditions almost all ionization is produced by the visible laser, while the uv laser simply excites atoms slowly to the first intermediate resonant state. One can distinguish three different regions in the plot as the intensity I_v is increased from 10^4 all the way up to 10^8 W/cm^2. At low intensities ($< 5 \times 10^4$ W/cm^2), β is negative and rising towards zero and positive values. This means that, at these intensities, the even isotopes ionize more than the odd. Experimental data from intensity-dependence studies[15] at $I_v = 2 \times 10^4$ W/cm^2 (with $I_{uv} = 400$ W/cm^2) confirm these predictions. This result, surprising to some extent, can be understood as a consequence of an interplay between excitation and ionization efficiencies of the two types of isotopes for this range of intensities. Somewhere around $I_v \approx 1.5 \times 10^4$ W/cm^2 the quantity β reaches the zero value (at which point the ionization faithfully reproduces the natural isotopic abundances) but continues to increase to higher positive values. For 5×10^4 W/cm$^2 < I_v < 10^7$ W/cm^2 there is a relatively flat region of values for β, whose variation is confined between 0.02 and 0.025. Similar regions of nearly constant value for β were also found in our study[1] of singly resonant two-photon ionization. It may well be that this behavior is quite general, probably not depending on the particular scheme.

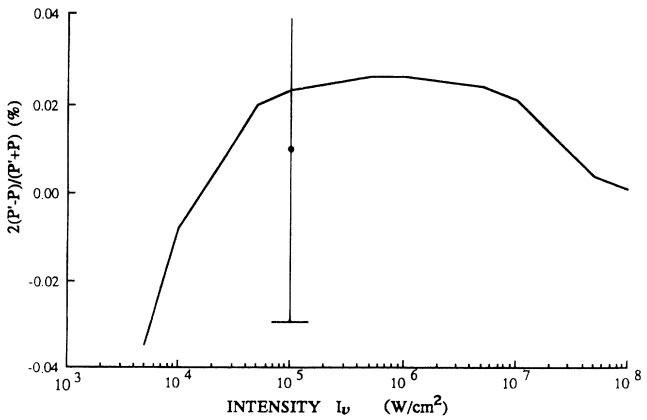

FIG. 1. Fractional difference in ionization as a function of the intensity of the visible laser, I_v. The intensity of the uv laser $I_{uv} = 400$ W/cm^2. The laser pulse duration is $\tau_L = 5$ nsec and the laser bandwidths are $\gamma_L^v = 0.25$ cm^{-1} and $\gamma_L^{uv} = 0.4$ cm^{-1}. The experimental result, shown for comparison, is taken from Ref. 2.

For $I_v > 10^7$ W/cm^2, the values of β start decreasing, and within an order of magnitude for the intensity, the zero value for β is again approached. Because of the very low intensity of the uv laser, the total ionization at the end of the interaction is less than 1% and saturation cannot be the cause for the gradual decrease of β with increased intensity. It is rather solely due to the fact that the rate of ionization is competing with the rate of hyperfine coupling at the upper doublet (states $|2'\rangle >$ and $|2''\rangle >$) and in fact at $I_v = 10^8$ W/cm^2 they are almost comparable.

To compare with published experimental results,[2] we have to look for that point on the plot which corresponds to $I_v = 10^5$ W/cm^2. The value of β we read off the plot, $\beta = 0.023$, agrees quite well with the experimental value, given the experimental uncertainty. The agreement with the mean experimental value, $\beta = 0.01$ can be further improved if two of the four bound-free radial matrix elements entering the expression for the ionization widths are changed by about 30%. As a result, the widths change only slightly but this is enough to give us $\beta = 0.018$ at the experimental value for I_v. This agreement can be further improved, but such an attempt is not meaningful given the quoted[2] experimental uncertainty limits. The variations of the ionization widths are not arbitrary. They satisfy certain constraints imposed by the atomic structure of Sn and are well within the limits of accuracy expected from quantum defect calculations for atoms like Sn.[1] The curve β versus I_v for $I_{uv} = 400$ W/cm^2, calculated with the altered widths has the same general features as the one on Fig. 1. Therefore, the main points of the discussion on Fig. 1 remain valid and their generality is once more verified from another point of view this time.

Another set of results is presented in Fig. 2. Now the intensity of the visible laser in held constant at $I_v = 10^5$ W/cm^2 and the intensity of the uv laser is varied between 400 and 10^7 W/cm^2. In this case the magnitude of the effect is larger, except for the intensity range around $I_{uv} = 400$ W/cm^2 that corresponds to the experimental observations. As the I_{uv} is further increased the magnitude of β reaches values almost one order of magnitude larger than in Fig. 1. This means that the response of the different isotopes, as monitored by the ionization, reflects now the structure associated with the first intermediate resonant state rather than the second.

To explain this qualitatively, we note that for sufficiently large uv intensity singly resonant two-photon

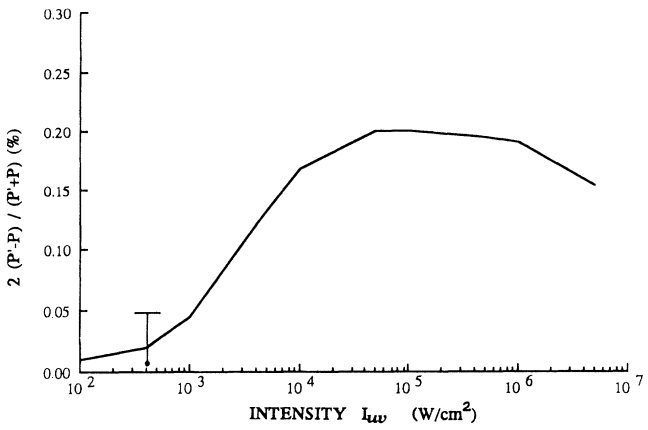

FIG. 2. Fractional difference in ionization as a function of the intensity of the uv laser, I_{uv}. The intensity of the visible laser is fixed $I_v = 10^5$ W/cm^2. The laser parameters are the same as in Fig. 1. The experimental result, shown for comparison, is taken from Ref. 2.

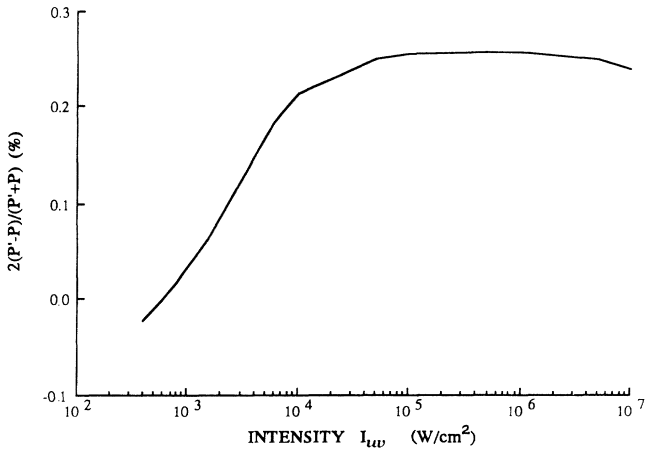

FIG. 3. Fractional difference in ionization as a function of the intensity of the uv laser, I_{uv}. The intensity of the visible laser is fixed $I_v = 400$ W/cm^2. The rest of the parameters are the same as in Fig. 2.

ionization (involving the absorption of two uv photons) competes with the doubly resonant three-photon ionization (involving one uv and two visible photons). Increasing, therefore, the intensity of the uv laser, the population of the first resonant hyperfine doublet and the ionization produced from it tend to dominate the process, minimizing thus the contribution of the second resonant hyperfine doublet which in contrast dominates the process in Fig. 1. But the most important factor for the enhancement of the odd-even difference is the much shorter hyperfine coupling time associated with the lower hyperfine doublet. As the contribution from this doublet to the total ionization signal is increased, the difference in the odd-even response is dominated by its very fast (compared to all other relevant time scales) hyperfine precession. A comparison with our earlier results[1] in two-photon ionization, through the same resonant hyperfine doublet, further supports the arguments given above, although exact agreement is not expected since the effect of the second resonant state is not negligible in the results presented in Fig. 2. However, the general features of the plot seem to agree with those found before.[1] The most obvious of these persistent features is the relatively flat portion of the curve, extending beyond $I_{uv} = 10^4$ W/cm^2, in which β is confined to values around 0.2.

The final figure, Fig. 3, essentially provides a consistency check for the calculations performed so far, connects the present results with those of Ref. 1, and clarifies the effect of the two different light intensities on the magnitude of the anomaly in the response of the different isotopes. By fixing $I_v = 400$ W/cm^2 we minimize its influence in the excitation and ionization processes. By varying I_{uv} we recover almost exactly the results obtained before[1] in the singly resonant scheme with the $6s\ ^3P_1^0$ as the intermediate resonance. The presence of the second resonance has become almost negligible. For very low intensities, $I_{uv} < 10^3$ W/cm^2 (a range of intensities not investigated before[1]) the quantity β becomes negative.

We have now a rather complete picture. For $I_{uv} \ll I_v$, the magnitude of the odd-even anomaly depends on the structure and properties of the upper hyperfine doublet; for $I_{uv} \gg I_v$ the structure of the lower doublet dominates the effect. When $I_{uv} \approx I_v$ both resonant states contribute to the anomalous response but one might dominate as is the case in the present study.

In summary, we have demonstrated beyond any doubt that broad smooth pulses will, as a rule, not ionize all isotopes exactly equally. Different resonance ionization schemes could enhance or minimize the even-odd differences, depending on the choice of the intermediate resonances and the intensity and duration of the laser pulses. For the doubly resonant scheme in Sn studied here, conditions have been found under which the even-odd difference is almost negligible or, alternatively, enhanced to the maximum. One can therefore contemplate a potential application in which a resonance ionization scheme, carefully chosen after proper theoretical analysis, implemented and performed under well controlled experimental conditions, can provide either accurate measurements of isotopic abundances, or, by varying an externally controllable parameter (e.g., laser intensity), isotope separation as well. The nearly constant value that β can have over a fairly broad range of intensities (almost three orders of magnitude), can be useful in optimizing the separation of odd and even isotopes, without severe demands on the accuracy with which the laser intensity and bandwidth need to be known.

Finally, a brief comment on the agreement between theory and experiment is perhaps useful before closing. The error bars of the two experimental points shown in Figs. 1 and 2 are relatively large. The reason of course is that the experiments[2] were designed to test the existence of gross departures from zero and not to obtain very accurate values of the parameter β. One may wonder therefore whether the agreement between theory and experiment is the fortuitous result of the large error bars. First we must note that, as for example Figs. 2 and 3 show, the effect can rise to 25% which is almost one order of mag-

nitude larger than the error bar of Fig. 1. And we know that values of β as large as 30% have in fact been measured[2] in other atoms. Second, theory shows that β is sensitive to a number of atomic and laser parameters. In fact, by changing some of these parameters, we were able to produce effects as large as 80% in our earlier paper.[1] Our study of the sensitivity of the theory to the parameters of the problem has shown that agreement with data is very unlikely to be fortuitous even if the error bars are relatively large. Having now demonstrated the existence of the effect and elucidated the physics of its origin, we hope to have the opportunity in the near future to test the theory against data of higher accuracy.

ACKNOWLEDGMENTS

We gratefully acknowledge a number of useful discussions with W. M. Fairbank, Jr. as well as the communication of his results prior to publication. This work has been supported by the U. S. Department of Energy, Grant No. DE-FG03-87ER60504.

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