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Angular distribution of electrons from two-photon ionization of Ti atoms

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Titanium atoms are excited by light from a nitrogen laser from the $a\ ^3F_4$ state, near the ground state, through the $x\ ^3G_5$ state, to become ^4F ions plus free electrons. The angular distribution of photoelectrons from the process gives limits on the ratio of amplitudes for transitions from the intermediate $4p$ orbital to the final continuum s and d channels. The total number of photoelectrons indicates that the total ionization cross section for the $^3G_5$ state is 1×10^{-18} cm^2. While the method can, in principle, provide relaxation times for angular momentum reorientation (an application of the methods of perturbed angular correlations in atomic processes), the present measurements have been carried out under conditions in which no relaxation occurs.

I. INTRODUCTION

Ionization of atoms or molecules by absorption of two photons is a process from which one can extract data concerning intermediate states. Here we present experimental findings from measurement of the angular distribution of electrons from resonant two-photon ionization. The theoretical basis for interpreting this information has been worked out recently.[1]

The intent of the present paper is primarily to report the successful measurement of the angular distribution of photoelectrons from a resonant two-photon process that is consistent with theoretical calculations, and secondarily to report the measurement of the cross section for photoionization of an atom from an excited state.

The long-term purpose of the work is the development of resonant two-photon ionization as a probe to study excited states of atoms and molecules. In that context, the work described here represents the first demonstration of the practicality of the technique.

Previous work has examined many other aspects of multiphoton excitation. Zernik worked out the explicit angular distributions for nonresonant two-photon ionization of hydrogen atoms.[2] Yatsiv, Wagner, Picus, and McClung observed resonant two-photon absorption to a bound atomic excited state.[3] Bebb determined two-photon ionization rates for alkali atoms and suggested that cesium, excited by a frequency doubled ruby-laser beam, would exhibit a near-resonant process in which a "single" intermediate state dominates the process.[4] Rizzo and Klewe demonstrated multiphotoionization of alkalis[5,6] and Hall[7] and Kishi and co-workers,[8-10] showed that the near-resonant case described by Bebb indeed described the laser-induced photoionization of sodium and cesium. Total cross sections for nonresonant two- and three-photon ionization have been studied experimentally by Fox, Kogan, and Robinson.[11] Lineberger and Patterson observed resonant two-photon photodetachment in C_2^-.[12] Several theoretical analyses of angular distributions in atomic and molecular photoionization are now available for many facets of the subject.[13-20] The most general expression for the angular distribution of photoelectrons from any one-photon process with an isotropic ensemble as target is

$$I_1(\theta)=\alpha+\beta P_2(\cos\theta); \tag{1}$$

this is now very generally known.[21] The angular distribution for two-photon ionization of an isotropic target ensemble has been shown[13,17,20] to be

$$I_2(\theta)=\alpha'+\beta' P_2(\cos\theta)+\gamma' P_4(\cos\theta). \tag{2}$$

In both cases, θ is measured with respect to the unique axis of the radiation: the polarization axis for linearly polarized light; the propagation axis for circularly polarized or unpolarized light. In solving the problem of resonant two-photon ionization one may ask the question, to what degree is the process a succession of independent one-photon processes or, to what degree does the intermediate state "remember" its mode of preparation?. In the limiting stepwise process, $I(\theta)$ is given by (1), with the coefficients α and β determined only by the properties of the second photon and the (isotropic) intermediate state. In the other limit, $I(\theta)$ is given by (2), and the coefficients α', β', and γ' are functions of the properties of both photons, the (isotropic) initial state, and the anisotropic intermediate state.

For atoms, the problem can be put in very simple and explicit terms—for convenience, we suppose the process is carried out with light having a definite axis of polarization. The form of (1) is the result of a P_1 field interacting with an isotropic target. The form of (2) is the result of a P_1 field acting on the *anisotropic* target generated by the action of the first P_1 field. In its initial isotropic state, the target gas has equal populations in all m_l states of its ground n, l level. The selection rules for photon absorption imply that the intermediate level will not, in general, have equal populations in all its m_l states, so its spatial distribution will be anisotropic. (Intermediate states with total-angular-momentum quantum numbers of zero or one-half are exceptions, of course.) If ionization from the intermediate level occurs while its spatial distribution is anisotropic, a distribution of the form (2) occurs. If complete relaxation of the orientation of angular momentum occurs for the intermediate state, then the distribution (1) must be observed.

Thus, the coefficients $\alpha' \to \alpha$, $\beta' \to \beta$, and $\gamma' \to 0$, as the system approached complete relaxation in its intermediate state. Specifically, we have shown[1] that the angular distribution of photoelectrons from a two-photon process depends on the matrix elements of the electric-dipole operator R connecting initial states a with intermediate states b, and intermediate states b with final states f, f' and also on a set of coefficients Ξ that contain the angular dependencies and the parameters governing the relaxation process. The coefficients Ξ depend on the initial, intermediate, and final states of the system, on the final state i of the remaining ion, and on the angular momentum states e, e' of the outgoing electron, where f is the direct product of i and e, $f = i \times e$, $f = i \times e'$. The coefficients have the form

$$\Xi = B_{00} + B_{02}(1+\lambda\tau_b)^{-1} + [B_{20} + B_{22}(1+\lambda\tau_b)^{-1}] \times P_2(\cos\theta) + B_{42}(1+\lambda\tau_b)^{-1} P_4(\cos\theta) . \qquad (3)$$

The angular distribution is given by

$$I(\theta) = \sum_{\vec{a},\vec{b},\vec{f},\vec{f}'} \left(\langle f | R | b \rangle \langle b | R | a \rangle \langle a | R^\dagger | b \rangle \langle b | R^\dagger | f' \rangle \times \sum_{\vec{e},\vec{e}',\vec{i}} \Xi(a,b,i,e,f,e',f') \right) . \qquad (4)$$

(We have assumed here that only one final state $\vec{i}$ of the ion is accessible. In the more general case, one must consider contributions from more than one state and the possibility of interferences among those states.) The parameters λ and τ_b are, respectively, the decay rate of the intermediate state and the characteristic relaxation time of the perturbation, which we assume is isotropic. The coefficients B_{ij} of (3) can be obtained for atoms entirely from angular-momentum considerations,[1,22] and have been evaluated[22] for all values of angular-momentum quantum numbers for states a, b, f, f', and i from 0 through 5 and for outgoing total angular momenta from $\frac{1}{2}$ through $\frac{9}{2}$.

One further consideration is required for the general case. Usually, two final channels are open for ionization from a given intermediate state because of the selection rule on the angular momentum of the active electron, $\Delta l = \pm 1$. Hence two final free-electron states e and e' are usually available; often, as in the case we describe below, there is only one initial state a and one intermediate state b. The angular distribution depends on the ratio of the amplitudes of the transition operators $(b|R|f)$ and $(b|R|f')$, corresponding to $(b|R|i,e)$ and $(b|R|i,e')$. We shall call this ratio δ. Apart from an absolute scale factor, then, the angular distribution for two-photon electric-dipole ionization of an isotropic ensemble, capable of undergoing relaxation by an isotropic perturbation in the intermediate state, depends on the amplitude ratio δ, the decay rate λ, and the relaxation time τ_b of the intermediate state.

We should point out that this process is an example in atomic physics of the general set of phenomena usually called "perturbed angular correlations." In the present case, the correlation is that of the polarization or propagation vector of the incoming radiation and the momentum vector of the outgoing electron. In nuclear processes the correlation more commonly involves two final products, such as two γ rays. A striking parallel occurs in the analysis of nuclear resonance processes detected by nuclear radiation.[23] Another powerful use of the correlation properties of multiphoton processes is their application to the spectroscopy of bound states of molecules, as developed by McClain *et al.*[24]

II. EXPERIMENT

We have previously worked out the two-photon process in detail for ionization of sodium,[1] through $^2P_{1/2}$ and $^2P_{3/2}$ states accessible by the yellow doublet, followed by ionization with a 3371-Å photon, e.g., for a molecular nitrogen laser. Sodium is convenient for calculations because the ion state i is a ^1S closed shell, and because the amplitudes of $3pks$ and $3pkd$ photoionization can be determined with some confidence from the quantum-defect method.[25] However, sodium is not the most convenient target from the experimentalist's viewpoint, because it requires photons of two different frequencies.

The target we selected for our first venture was atomic titanium, because it is particularly simple from an experimental viewpoint. The relevant

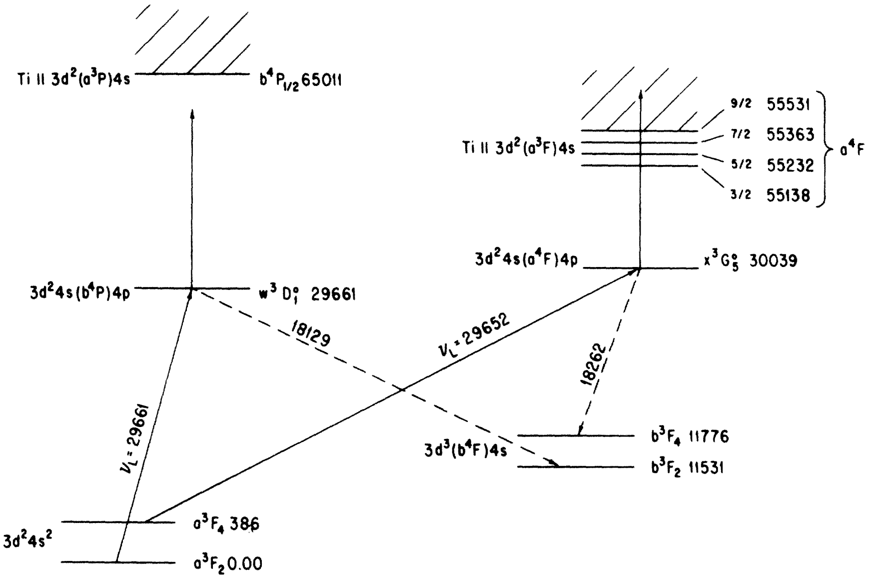

FIG. 1. Level scheme for atomic Ti.

part of the level scheme of Ti appears in Fig. 1. It is possible to excite Ti atoms from the $3d^2 4s^2$, $a\,^3F_4$ level to the $3d^2 4s4p$, $x\,^3G_5$ level with the light of a nitrogen laser, 29 652 cm^{-1} (3371 Å), and then to ionize the excited atoms from their $^3G_5$ state with a second photon of the same frequency to produce Ti^+ in its $3d^2 4s$, $a\,^4F$ state and set free an electron with zero or two units or orbital angular momentum and 4562 cm^{-1} (0.565 eV) of kinetic energy. The ground state, $3d^2 4s^2$, $a\,^3F_2$, can be excited by light from the N_2 laser to the $3d^2 4s4p$, $w\,^3D_1$ level, but cannot be ionized with a second photon of wave length 3371 Å.

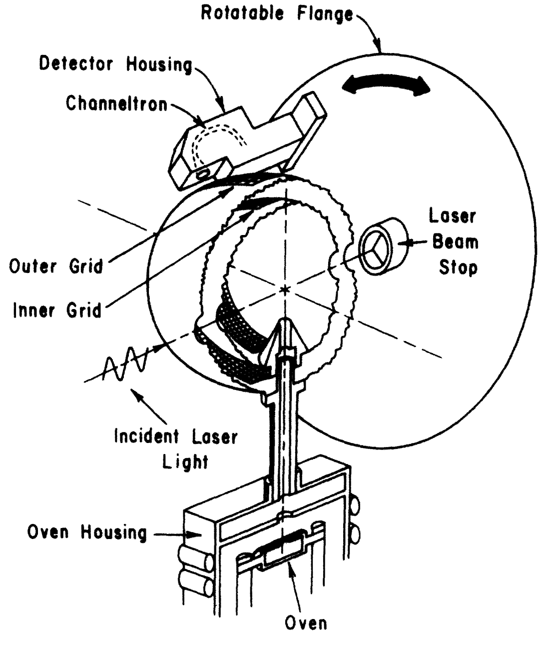

FIG. 2. Schematic representation of the apparatus. The axis of polarization of the incident laser beam rotates continuously about its propagation axis.

The experiment was carried out using the apparatus sketched in Fig. 2. The N_2 laser provided a total peak power of 130 kW in pulses of 20-nsec duration. The line at 29 652.46 cm^{-1} provided the excitation to the $x\,^3G_5$ state. The light was polarized by a calcite prism and then rotated with a revolving half-wave plate. The firing of the laser was synchronized with the rotation of the plate. Photoelectrons were counted at six angles of the polarizer, from 0° through 90°, for each of several fixed positions of the detector.

The titanium source was a tantalum tube oven heated resistively with 60-Hz half-wave rectified current. The laser was fired during the "off" interval of the oven current, to eliminate effects of the magnetic field of the oven current. The typical operating temperature of the oven was 1800℃, which produced a beam flux in the target region of about 2×10^{12} atoms/cm² sec or a density of 2×10^{7} atoms/cm³. At this temperature, about 40% of the atoms are in the $a\,^3F_4$ state, which lies only 387 cm^{-1} above the ground state. Dimer concentrations are negligible at 1800℃.[26]

The main chamber was mounted in the center of three pairs of Helmholtz coils with mutually perpendicular axes. The residual field in the chamber was about 15 mG. Two concentric copper spheres, with median zones of high-transmission screen, surrounded the interaction region. The negatively biased inner sphere served as a Faraday cage; the grounded outer sphere accelerated the electrons radially toward the Bendix Channeltron electron multiplier. The multiplier, 3 in. from the interaction region, had an active area subtending 5.2×10^{-3} sr about the interaction region. The detector could be moved to almost any position on the equatorial circle about the interaction region in the plane perpendicular to the propagation axis of the laser beam. Since pressure in the chamber was below 10^{-6} Torr during experiments, collisions did not contribute to the relaxation time τ_b.

The detector output gate to the counting circuity was open for 0.5 μsec after initiation of the laser pulse, essentially eliminating stray electrons as a noise source. The signal-to-noise ratio was about 20 : 1. Because the recovery time of the Channeltron circuit is considerably longer than 0.5 μsec, only one electron could be identified with each laser pulse. The counting rate was kept low enough that only pulses from single electrons were detected. The pulse repetition rate was 60 Hz.

To demonstrate that we were producing electrons by the desired two-photon process, we carried out two consistency checks. We observed fluorescence at both the resonance frequency and at 18 262 cm^{-1}, corresponding to the decay $x\,^3G_5 \rightarrow b\,^3F_4$, which demonstrated that we were exciting the correct intermediate state. We also measured the dependence of the photoelectron current on light intensity. At full laser intensity, the initial $^3F_4 \rightarrow x\,^3G_5$ transition should be nearly saturated, and the photoelectron current we observed under this condition varied linearly with light intensity. When the laser light was attenuated by an order of magnitude, we observed the photoelectron current I_e to vary as $I_{\text{light}}^{\alpha}$, where $\alpha = 1.9 \pm 0.2$.

We measured the angular resolution of the apparatus and its susceptibility to stray fields by measuring the electron current from a highly collimated (1° angular spread), low-energy (<1.5 eV) electron gun. With the Helmholtz coils activated, the detected current exhibited the 7° spread characteristic of the angular resolution of the detector. This result was independent of quadrant, and independent of whether the detector or source was moved. Hence the center of the distribution was at the center of the interaction region, where the electron gun was located, and indeed the electrons did travel along radial trajectories. With no current in the Helmholtz coils, the electron distributions were considerably flattened and shifted. The experiments with the electron gun also demonstrated that the grids had the same transmission in all four quadrants.

Measurements of photocurrents were made with the detector in several different positions. Most of these were made in the two quadrants in which the residual fields were smallest. The results were independent of detector position, within the uncertainties of the measurements.

III. RESULTS

The results of the experiment are these: (a) It is feasible to measure angular distributions of photoelectrons from resonant two-photon ionization. (b) The photoelectrons produced by two-photon ionization of Ti atoms, through the $(rs \rightarrow rp \rightarrow ks, kd;\ a\,^3F_4 \rightarrow x\,^3G_5 \rightarrow a\,^4F + e)$ process, have an angular distribution that is nearly isotropic, within an uncertainty of 10%. (c) The measured photoionization cross section of the $x\,^3G_5$ excited state is $1\times10^{-18\pm1}$ cm^2, compared with a cross section of 2.1×10^{-18} cm^2 from calculations based on the quantum-defect method.[22]

The photoionization cross section of the $x\,^3G_5$ state is based on the observation of 5 ± 2 electrons/sec, corresponding to 190 electrons/pulse going into 4π sr. The photon flux is $5.0(\pm1.5)\times10^{21}$ $\text{photons/cm}^2\,\text{sec}$. If the effusing beam of Ti from the oven is in thermal equilibrium, 40% of the atoms would be in the $a\,^3F_4$ state initially; following optical excitation, under saturation conditions, about 20% of the atoms, or about 4×10^6 atoms/cm^3, would be in the $x\,^3G_5$ state. The deviation from this population figure is, at worst, a factor of 3. If we replace integration over the overlap region of the two beams with the simple product resulting from the assumption of uniform beam densities, then the photoionization cross section σ, for the $x\,^3G_5$ state, is given in terms of N_e, the number of detected electrons/sec, the photon flux ϕ, the particle density N of $^3G_5$ atoms, and T, the pulse duration: $\sigma = N_e(\phi N T)^{-1}$. Using the measured values for N_e, ϕ, N, and T, we obtain $\sigma = 1\times10^{-18}$, with a factor-of-3 uncertainty from the mean values of these parameters. We estimate that the error introduced by using these numbers, rather than integrated beam overlaps, is no more than another factor of 3.

Finally, we turn to the interpretation of the angular distribution. The final state of the system can involve Ti^+ in its ^4F level with $J = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$, and $\frac{9}{2}$, and the outgoing electron as a $ks_{1/2}$, $kd_{3/2}$, or $kd_{5/2}$ wave. The selection rules on total final angular momentum restrict this quantum number to 4, 5, and 6. The separations of the ^4F states of the ion are of order 25–30 cm^{-1}, far more than the width of the exciting laser line. The four final ion states can all be produced, but they will each contribute independently to the final angular distribution, with no interferences. Moreover, our experiment cannot distinguish electrons associated with the four final ion states; this could

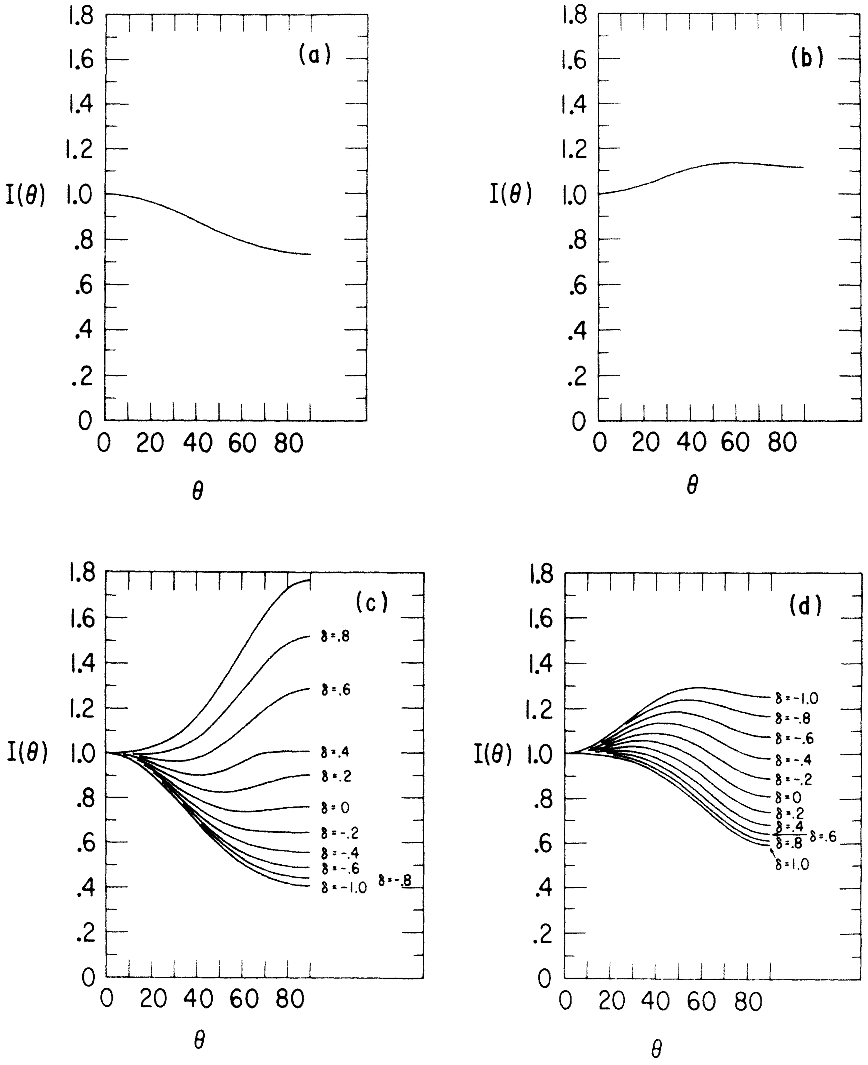

FIG. 3. Angular distribution of photoelectrons from the production of Ti^+ in (a) ${}^4F_{3/2}$ state; (b) ${}^4F_{5/2}$ state; (c) ${}^4F_{7/2}$ state; (d) ${}^4F_{9/2}$ state. All distributions are shown normalized to $I(\theta)=1$ when $\theta=0$. For the $\frac{7}{2}$ and $\frac{9}{2}$ channels, the curves for $\delta=0$ correspond to the outgoing electrons, being in pure d waves.

be done in principle with very high resolution of electron velocities. We find only one Ξ contributing to the ${}^4F_{3/2}$, that corresponding to a $d_{5/2}$ outgoing wave; there are six contributing Ξ's associated with formation of ${}^4F_{5/2}$, three of them with $d_{5/2}$ and three with $d_{3/2}$ outgoing waves. Twenty-one Ξ's are associated with production of ${}^4F_{7/2}$, and 36 Ξ's contribute to the formation of ${}^4F_{9/2}$. Both the ${}^4F_{7/2}$ and ${}^4F_{9/2}$ final ion states may be associated with outgoing s and d waves. It is necessary to include the interferences between outgoing s and d waves associated with any given final ion state; this is done by inclusion of the appropriate Ξ's with different final e states, but the same i state. The angular distribution to a specific final ion state, including both s- and d-wave contributions, can be expressed as

$$I_i(\theta)=I_{is}R_s^2+I_{id}R_d^2+I_{isd}R_sR_d\;, \tag{5}$$

if we take the continuum functions real, as is sometimes done.[27] Strictly, the final state should be a traveling wave,[28] so that (5) would only be valid if the s and d waves had equal phase shifts; otherwise, the third term would contain the cosine of the difference of the phase shifts. Hence our calculations must be considered illustrative rather than exhaustive. We abbreviate the elements as R_s and R_d, for outgoing s and d waves, respectively. We call the ratio

$$\delta=R_s/R_d\;.$$

We assume that the radial transition-matrix elements connecting ${}^3G_5$ with all outgoing s waves is R_s, and for all outgoing d waves is R_d, independent of total J or final ion state. Then the angular distributions for production of ${}^4F_{3/2}$ and ${}^4F_{5/2}$ ions are independent of δ, but those for ${}^4F_{7/2}$ and ${}^4F_{9/2}$ depend on δ. These separate angular distributions are shown in Figs. 3(a)–3(d). Note that the individual distributions clearly exhibit a dependence on $\cos\theta$ higher than quadratic.

Now, if we assume that the final states are all equally probable (i.e., levels of different J have relative probabilities given by their degeneracies), then we can predict the total observed angular distribution for different values of δ, and find what range of values for δ is compatible with our observations.

The distributions associated with different final states of the ion tend to cancel each other, as Fig. 3 shows: The ${}^2F_{3/2}$ and ${}^2F_{5/2}$ contributions vary in opposite directions with θ, and the contributions from the ${}^2F_{7/2}$ and ${}^2F_{9/2}$ also tend to cancel. They vary in opposite ways as functions of δ. The net result is a prediction of final angular distributions which tends towards isotropy for all values of δ. Figure 4(a) shows the distributions we predict and typically observed points; Fig. 4(b) shows a magnified view of the predicted distributions.

The conclusion we draw is that, from the nonrelaxed condition in which we observe the photoionization, the angular distribution implies that $0.4 \leqslant \delta \leqslant 1.0$ or $-0.9 \geqslant \delta \geqslant -1.0$. The implication, then, is that the total outgoing wave contains a significant contribution of s wave.

It may be possible to evaluate the parameter δ from a microscopic model, such as one obtains from a Hartree-Fock or Herman-Skillman atomic wave function. The angular distributions obtained thus far indicate that the Hartree-Fock picture gives a reasonably good representation of the still-meager data, and that the Herman-Skillman approximation reproduces the correct form and magnitude of the energy variation of the observed angular asymmetry, for single-photon ionization of rare gases.[29] For single-photon ionization of the valence electrons of alkali atoms by one or many photons, we can be sanguine about the utility of the calculations. In the case of the alkalis, we can use a quantum-defect model with considerable confidence.[1] However, we must be cautious about using highly approximate methods to treat the resonant two-photon ionization of an atom as complicated as Ti. We can expect significant amounts of configuration mixing with the $3d^24s4p$ excited configuration, particularly because of the likelihood of large *angular* correlations among the electrons. This consideration, together with the large atomic number of Ti and the consequent relativistic effects in the inner shells, must make us wary of calculating *angular distributions* from Hartree-Fock models, and especially from models such as the Herman-Skillman wave functions generate, in which the nonlocal exchange potential is replaced by an effective local potential. It will be worthwhile testing such simple models against more accurate approaches and against experiment. For this purpose, atoms other than titanium should be used; the near-isotropic distribution coming from the (currently) unresolvable states of the ${}^2F$ term of Ti$^+$ is not a good test of a theoretical mod-

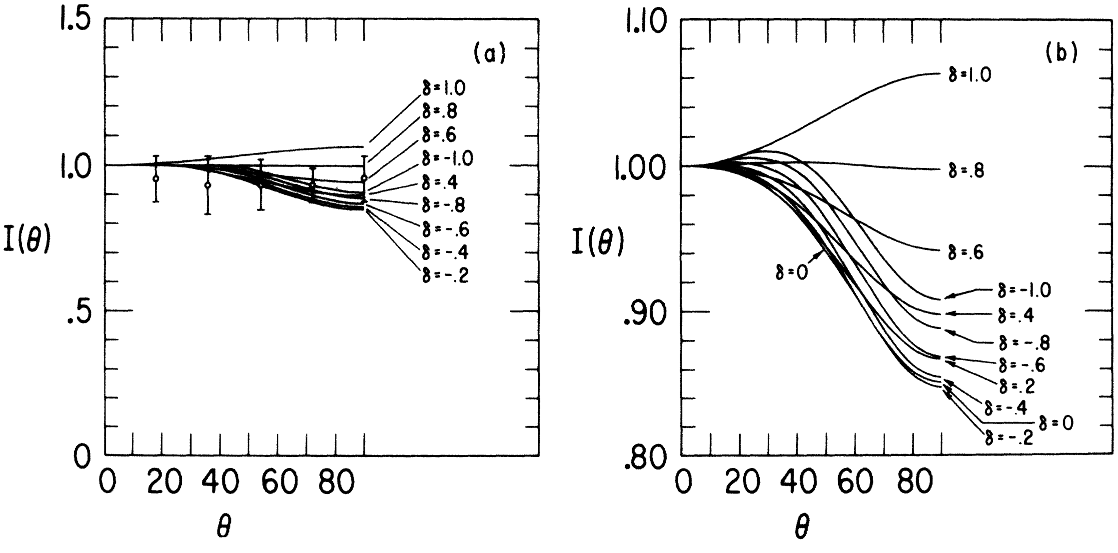

FIG. 4. (a) Predicted angular distributions of photoelectrons (and typical observed points) with all final ion states included; (b) predicted curves on an expanded vertical scale. Error bars correspond to 1 standard deviation in the measurements.

el. It is probably easier to find another complex atom and use a two-frequency excitation system (or a different laser system altogether) than it would be to resolve the states of the Ti^+, ^2F term, in order to get a proper test of a microscopic theory.

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