Electron Shake-Up in Two-Photon Excitation of Core Electrons to Rydberg Autoionizing States

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The results of a theoretical and experimental investigation of satellite line strengths in two-photon transitions to Rydberg autoionizing states in multielectron atoms are presented. In studies of $6snd$-$7sn'd$ two-photon transitions in Ba I, the distribution of line strengths over various final $7sn'd$ states for a given $6snd$ initial state is found to vary dramatically as a function of detuning from intermediate $6pn''d$ autoionizing resonances. These results indicate the influence of electron rearrangement *during* the multiphoton transition.

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Electron shake-up describes two-electron transitions that occur when a core electron makes a transition, changing the potential for an outer electron, thus "shaking" it into a different quantum state. Shake-up may occur either when a core electron is ionized,[1-7] or in the excitation of a core electron to an unoccupied outer orbital.[8,9] In the former case, the outer electrons respond to the increase in effective nuclear charge of +1, while in the latter case, the outer electrons respond to the increase in core size. An important parameter determining shake-up spectra is the time scale of the change in the potential seen by the outer electron. The differences between adiabatic and sudden transitions in shake-up spectra have been considered theoretically[4] and observed experimentally in photoionization of atoms[5] and molecules[6] and in photoemission in solids.[7] These investigations have examined the influence of the velocity of the ejected photoelectron on the final-state potential and have been limited to single-photon excitations.

Here, we report the study of a *two-photon* excitation of the 6*s* core electron in barium starting from $6snd$ Rydberg initial states. (The $6snd$ initial states were first selectively populated from the ground $6s^2$ state by conventional two-step laser excitation.[8]) In the two-photon transition $6snd$-$7sn'd$ the core-size change produces the shake-up of the Rydberg *nd* electron into several *n'd* orbitals. Since this case involves a two-photon excitation there are two separate opportunities for rearrangement of the wave function: in the virtual intermediate state of the two-photon transition as well in the final state. By varying the detuning from $6pn''d$ real intermediate states, the transition time from $6snd$ to $7sn'd$ can be varied from being short compared to the intermediate-state rearrangement time to being much longer. When the detuning from the significant intermediate $6pn''d$ resonances is large compared to the spacing between these states, then the absorption time is short compared to the intermediate-state readjustment time[9] and the observed shake-up spectrum should depend only on the initial $6snd$ and final $7sn'd$ states. We refer to this process as direct shake-up. When the detuning is small compared to the spacing between adjacent $6pn''d$ states, then the absorption process is long compared to the readjustment time, and the observed shake-up spectrum should depend on relaxation in the intermediate state as well (intermediate-state shake-up). For the general case of arbitrary detuning, the observed shake-up spectrum will contain *interferring contributions from both the direct and intermediate-state processes.*

Figure 1 shows the basic excitation diagram for the $6s24d$-$7sn'd$ transitions in Ba I. The laser ω_1 was tuned near the significant $6p_{3/2}n''d$ intermediate resonances ($n''=23$, 24, or 25), or detuned far off (800 cm^{-1}) intermediate-state resonance. The laser ω_2 was tuned so that the two-photon transition reached final $7sn'd$ states for $n'=23$,

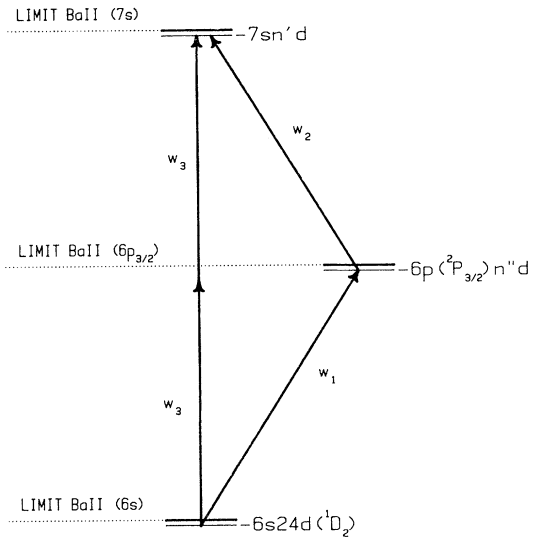

FIG. 1. Diagram of relevant levels for the core excitation $6s24 \rightarrow 7sn'd$. Excitation is either sudden when $\omega_1 = \omega_2$, or dependent upon intermediate-state relaxations when ω_1 is tuned near $6s24d \rightarrow 6p_{3/2}n''d$ transitions.

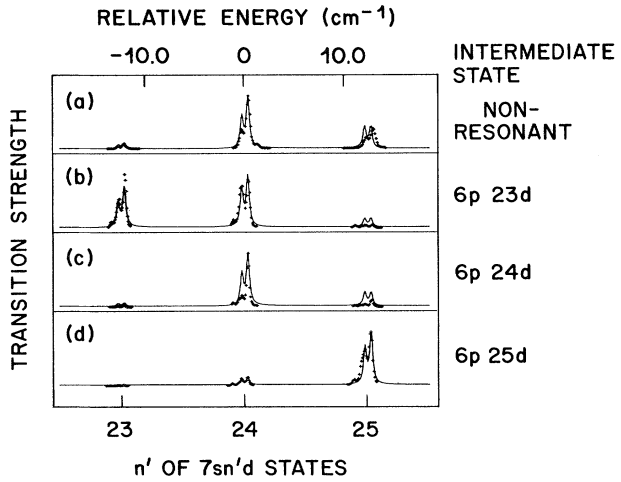

FIG. 2. A comparison of theory and experiment for the observed shake-up spectra for the two-photon transition $6s24d \rightarrow 7sn'd$. In (a), the detuning from intermediate-state resonance is large so that intermediate-state relaxations are negligible. For (b)–(d) the detunings are small, and the various intermediate-state relaxations play a large role in determining the observed shake-up spectra.

24, or 25. The barium atoms in the bound $6s24d$ ($^1D_2$) initial states were prepared by stepwise laser excitation of a barium atomic beam.[8,10] Transitions to the $7sn'd$ states were detected by energy analyzing the electrons emitted following autoionization. Electrons emitted from $7sn'd$ states have energies of approximately 5 eV, whereas electrons produced by single-photon absorption have energies less than 2.5 eV.

Figure 2(a) shows typical data obtained in the far-off-resonance case ($\lambda_1 = \lambda_2 = 472.2$ nm) for the initial state $6s24d$ ($^1D_2$). The binding energy of a Rydberg state is given by $E = -(\frac{1}{2})(n-\delta)^{-2}$, where δ is the quantum defect. For the $6s24d$ state, $\delta = 2.72$.[11] Since the $7s$ core is larger than the $6s$ core, the quantum defects for the $7sn'd$ states are increased to 3.13. Thus the $7sn'd$ Rydberg electron orbital wave functions are not orthogonal to the $6snd$ Rydberg electron orbital wave functions and the distribution of oscillator strengths reflects the direct shake-up process described above.

Figures 2(b)–2(d) show the effect of tuning ω_1 near the intermediate $6pn''d$ states. In these data, the $7sn'd$ shake-up spectra obtained for three discrete detunings from the intermediate $6p24d$ state are shown. (The $6pn''d$ states have a quantum defect[12] of 2.76, and thus these states are not orthogonal to the initial $6snd$ states either.) In Fig. 2(b), ω_1 is tuned to be resonant with the $6p23d$ state, in Fig. 2(c) it is detuned from this resonance to coincide with the $6p24d$ state, while in Fig. 2(d) it is detuned to the other side of the $6p24d$ resonance to coincide with the $6p25d$ state. Note how these spectra, obtained for small detunings from the $6p24d$ intermediate-state resonance, differ significantly from the case of far off resonance shown in Fig. 2(a).

The effects of intermediate-state shake-up can be modeled by computing the two-photon transition moment in second-order perturbation theory,[13] *allowing total relaxation for each intermediate state,* and summing each state's contribution weighted by the time that the atom spends in that intermediate state. That is, the rate is

$$R = (2\pi/\hbar)|T|^2 A(\Omega), \tag{1}$$

where $A(\Omega)$ is the density of final states and

$$T = \sum_{n''} \langle 6snd | \mu_1 E_1 | 6pn''d \rangle \langle 6pn''d | \mu_2 E_2 | 7sn'd \rangle (\Delta\epsilon_{n''} + i\Gamma_{n''}/2)^{-1}, \tag{2}$$

where $\Delta\epsilon_{n''} = \epsilon_{n''} - \hbar\omega_1$, and $\epsilon_{n''}$ and $\Gamma_{n''}$ are the energy and width of the intermediate states $6pn''d$. This expression may be writtten in an isolated core approximation[8]:

$$T = [\langle 6s | \mu_1 E_1 | 6p \rangle \langle 6p | \mu_2 E_2 | 7s \rangle]_{\text{ion}} \sum_{n''} \langle n | n'' \rangle \langle n'' | n' \rangle (\Delta\epsilon_{n''} + i\Gamma_{n''}/2)^{-1}, \tag{3}$$

where the first term is to be evaluated using Ba^+-ion wave functions, and the Rydberg wave functions $|n\rangle$, $|n''\rangle$, and $|n'\rangle$ are hydrogenic, with effective quantum numbers appropriate for the $6s$, $6p$, and $7s$ cores, respectively. The analytical expression for the Rydberg overlap integrals is[10]

$$\langle n|n''\rangle = \frac{2(n^*n''^*)^{1/2}}{n^*+n''^*}\,\frac{\sin\pi(n^*-n''^*)}{\pi(n^*-n''^*)}, \qquad (4)$$

where n^* and n''^* are the effective quantum numbers of the n and n'' states, respectively.

In the far-off-intermediate-resonance case, $\Delta\epsilon_{n''}$ is large for all n'' and does not vary appreciably in the sum. Under these conditions, Eq. (3) may be evaluated as

$$T = \frac{\langle n|n'\rangle}{\Delta\epsilon}\left[\langle 6s|\,\mu_1E_1|6p\rangle\langle 6p|\,\mu_2E_2|7s\rangle\right]_{\rm ion}. \qquad (5)$$

This is just the prediction that far off intermediate resonance, where the transition is fast compared to intermediate-state relaxations, the shake-up spectrum will depend only on the direct overlap of $|nd\rangle$ and $|n'd\rangle$. When $\Delta\epsilon_{n''}$ becomes small, then intermediate-state relaxation begins to play a role, and T is given by Eq. (3).

The evaluation of T in Eq. (3) is complicated by the fact that all the $6pn''d$ intermediate states are coupled to several continua and are thus autoionizing. This couple has the effect of making all of the energies of the $6pn''d$ states complex, and the overlap integral in Eq. (4) must be evaluated with use of complex effective quantum numbers. Physically this represents the additional phase that the electron accumulates in going through the intermediate states, over and above the phase introduced by the detuning from resonance. The proper way to treat this problem is by using multichannel quantum defect theory (MQDT) where the coupling of the $6pn''d$ states is taken into account at the outset.

An analytical summation of Eq. (3) has been performed with use of MQDT techniques yielding[14]

$$T = T_{\rm ion}'\{\langle n|n'\rangle[A(\omega_1)+B(\omega_2)] - \langle n'|n_p\rangle A(\omega_1)C(n_p,n) - \langle n|n_p\rangle B(\omega_2)C(n_p,n')\}; \qquad (6)$$

here

$$T_{\rm ion}' = (2\pi/\hbar)[\langle 6s|\,\mu_1E_1|6p\rangle\langle 6p|\,\mu_2E_2|7s\rangle]_{\rm ion},\quad A(\omega_1) = [\,2\hbar(\Omega_{(6s-6p)}{}^{\rm ion} - \omega_1)]^{-1},$$

$$B(\omega_2) = [2\hbar(\omega_2 - \Omega_{(6p-7s)}{}^{\rm ion}]^{-1},\quad C(n_1^*, n_2^*) = (n_1^*/n_2^*)^{3/2}[\sin\pi(n_2^* + \delta_i + i\Gamma_i]/[\sin\pi(n_1^* + \delta_i + i\Gamma_i],$$

δ_i and $n^{*3}\Gamma_i$ are the quantum defect and width of the intermediate $6p_{3/2}n''d$ states, $\Omega_{(6s-6p)}{}^{\rm ion}$ is the frequency of the $6s$-$6p_{3/2}$ ion transition, $\langle n_1|n_2\rangle$ is given by Eq. (4), and n_p is the effective quantum number corresponding to the energy to which ω_1 is tuned $[1/(2n_p{}^2) = \Omega_{(6s\ 6p)}{}^{\rm ion} + 1/(2n^{*2}) - \hbar\omega_1]$. For tunings of ω_1 far away from the ion $6s$-$6p_{3/2}$ transition, $\langle n'|n_p\rangle = \langle n|n_p\rangle = 0$ and T depends solely upon $\langle n|n'\rangle$ in agreement with Eq. (5). Further, this expression demonstrates explicitly that near intermediate resonance, $|T|^2$ will evidence *interferences between the direct and intermediate-state processes.*

The solid curves shown in Fig. 2 show the calculated shake-up spectra using the explicit summation in Eq. (6). Good agreement between the theory and experiment is obtained, apart from the ratio of the intensity of the doublet-structure peaks in each $7sn'd$ peak. (This doublet structure is due to singlet-triplet mixing in the $7sn'd$ states.) Note that there is the substantial asymmetry in the observed and computed spectra between the detunings on the red and blue of the $6p24d$ intermediate-state resonance. This asymmetry is due to the interference between the direct and intermediate-state shake-ups.

The interferences can be seen most dramatically by using Eq. (6) to calculate the shake-up spectra for various detunings on the red and blue side of the $6p24d$ intermediate state. These results are shown in Fig. 3. We have recorded shake-up data at many detunings: In all cases, the data are in good agreement with the calculations shown in Fig. 3.

Two-photon excitation of core autoionizing states to observe selected shake-up processes is a powerful tool to investigate the structure of atoms with two or more electrons promoted to highly excited states. This work demonstrates, however, that intermediate-state relaxations can play a significant role in determining the observed spectra. By varying the detunings from the intermediate states, the time allowed for the intermediate state to undergo relaxation is changed. The spectra and theory presented here clearly show how relaxation dynamics *during* the multiphoton transition can affect the observed shake-up spectra.

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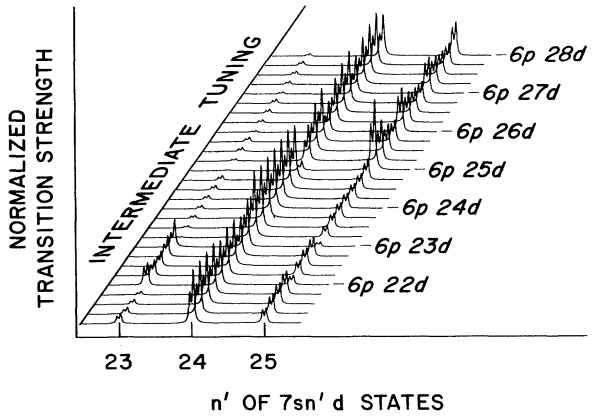

FIG. 3. A calculation of the shake-up spectra in the $7sn'd$ states for various detunings from the $6p24d$ state. The integrated transition strength for each intermediate detuning has been normalized to 1. "Intermediate tuning" is the tuning of the laser at ω_1. Note the large asymmetries which vary as a function of tuning and indicate interference between the direct and intermediate-state processes.

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