Quantum approach to photoelectron recapture in post-collision interaction

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We have performed a fully quantum-mechanical calculation of the partial L_2-hole Ar^+ yield from photoionization of Ar at energies just above the L_2 threshold. The result is in excellent agreement with a recent synchrotron-radiation experiment by Eberhardt *et al.* [Phys. Rev. A **38**, 3808 (1988)], illustrating the importance of the Coulomb interaction between the reaction products in influencing the photoionization cross section and Auger rate near threshold.

I. INTRODUCTION

Inner-shell photoionization followed by Auger-electron decay is an example of a resonant rearrangement collision in which three charged particles, an ion and two electrons, are formed. The mutual Coulomb interaction among the products affects the photoionization cross section and Auger-electron emission rate. It results in deviation from predictions of the usual two-step model in which ionization and decay are treated as distinct processes. The semiclassical approach introduced by Niehaus[1] has been very powerful for the description of this post-collision interaction (PCI) phenomenon.[2] A consistent treatment of threshold phenomena in inner-shell photoionization, however, requires use of scattering theory in its quantal form.[3]

One feature of PCI is the recapture of a photoelectron by the doubly ionized atom at the moment its ionic charge is doubled through the Auger-electron emission. In an inelastic electron scattering[4] and a photoionization experiment,[5] evidence was found for an anomalously large Ar^+ yield just above the Ar L_2 threshold. This phenomenon was attributed to electron recapture by the Ar^{2+} ion,[1,6] in accord with analogous findings in autoionization following electron impact.[7]

Conclusive evidence of the anomalously large Ar^+ yield in photoionization above the L_2 threshold has been presented by Eberhardt *et al.*[8] In Ar^+ yield spectra measured as a function of photon energy across the L_2 threshold, these authors found that the yield gradually decreases in a range of ~ 3 eV above the threshold. The Ar^{2+} yield increases correspondingly. This result is in striking contradiction with the prediction of the conventional two-step model. Since the L fluorescence yield is negligible, the two-step model implies that all excited Ar^+ ions with L_2 holes are converted into Ar^{2+} ions during the lifetime of the L_2 hole. During an interval that corresponds approximately to a hole-state width $\Gamma(L_2)\simeq 0.1$ eV, the Ar^+ yield should therefore drop to zero. An obvious explanation for the discrepancy between this prediction and observation is that just above the L_2 threshold the photoelectron is recaptured into an excited state of the Ar^{2+} ion which then decays to Ar^+ by photon emission. A quantitative comparison of the observations with the prediction of the quantum theory of PCI,[9,10] previously lacking, is the purpose of the present work.

II. QUALITATIVE CONSIDERATIONS

The probability that an Auger electron is emitted in the interval $(t,t+dt)$ can be assumed to be given by the rate equation

$$dP=(1-P)\frac{dt}{\tau_h}\ , \tag{1}$$

where τ_h is the lifetime of the initial hole state and where $1-P(t)$ represents the relative number of atoms which are present at time t with the hole in the inner shell. Equation (1) is based on the assumption that the decay of the hole by fluorescence is negligible. From Eq. (1) we obtain by integration the probability $P(\tau)$ that the Auger electron has been emitted at any time t not longer than τ. We thus have

$$P(\tau)=1-\exp(-\tau/\tau_h)=1-\exp(-\Gamma\tau)\ , \tag{2}$$

where Γ is the width of the hole state. Equation (2) also gives the probability that the photoelectron has been slowed down or recaptured in a time not longer than τ. According to energy conservation we have

$$\omega+E_0=E^{(+)}+E_{\rm exc}=E^{(2+)}+\varepsilon+\varepsilon_A\ , \tag{3}$$

where ω is the photon energy, E_0 the total ground-state energy of the atom, and $E^{(+)}$ and $E^{(2+)}$ are the corresponding ionic energies. Thus, $E_{\rm exc}$ and ε are the kinetic energies of the photoelectron before and after Auger-electron emission, respectively. If the photoelectron is recaptured, however, it has a negative energy $\varepsilon=-\varepsilon_n$, and the Auger-electron energy ε_A is accordingly enhanced. The question now is which time $\tau=\tau(E_{\rm exc})$ should be associated with a given excess energy

$E_{\rm exc}=\omega-E_B$, where E_B is the binding energy corresponding to the hole. Estimates can be made both semiclassically[8] and quantum mechanically.

In the semiclassical model,[8] we have $\tau=\tau_P-\tau_A$, where τ_P is the time it takes for the photoelectron to reach the distance R from the nucleus at which point it is overtaken by the fast Auger electron. It is assumed that the Auger electron reaches R in time τ_A. If the electrons are released close to the nucleus with constant velocities, we have approximately $\tau\simeq\tau_P\simeq R/v_P$, since v_A is much larger than v_P. The criterion for recapture of the photoelectron is that $R^{-1}\geq E_{\rm exc}$, where R^{-1} is the energy that the Auger electron receives from the photoelectron at a distance R. Since $v_P\simeq(2E_{\rm exc})^{1/2}$, we obtain that $\tau/\tau_h\simeq\Gamma/(2^{1/2}E_{\rm exc}^{3/2})$ in Eq. (2).

In the quantum-mechanical estimate, τ is replaced by the time during which the photoelectron interacts with the Auger electron. If this interaction is described by a time-independent perturbation, we have approximately $\tau\Delta\varepsilon\simeq 1$, where $\Delta\varepsilon$ is the spread of energies which are released when the photoelectron is recaptured. According to Eq. (3), $\Delta\varepsilon\simeq\varepsilon\geq E_{\rm exc}$. Thus we have $\tau/\tau_h\simeq\Gamma/E_{\rm exc}$ in Eq. (2).

Let the yield of singly ionized ions now be measured in an experiment in which an atomic inner shell is photoionized just above threshold. If the hole decays solely by nonradiative Auger transitions, then it follows from Eq. (2) and from the quantum-mechanical considerations indicated above that

$$P(E_{\rm exc})\simeq 1-\exp(-\Gamma/E_{\rm exc}) \tag{4}$$

represents the probability of producing singly ionized ions in the recapture process. The semiclassical considerations predict a qualitatively similar but somewhat broader distribution. Equation (4) indicates that the yield of singly ionized ions as a function of $E_{\rm exc}$ never drops to zero within the range of Γ, as predicted by the two-step model. The distribution always has a tail with a half-width which is approximately given by $E_{\rm exc}=\Gamma/\ln 2$, as long as the hole is predominantly filled by nonradiative transitions. This tailing is analogous to production of molecular x rays with energies that exceed the united-atom limit in ion-atom collisions.[11] In both cases the phenomenon can be looked upon as being a consequence of the uncertainty principle.

The approximate formula (4) shows that the distribution of singly ionized ions is rather sensitive to the width Γ. In the present applications we have chosen $\Gamma(L_2)=0.126$ eV which is the value recommended by Krause and Oliver[12] for Ar. In their work Eberhardt *et al.*[8] used $\Gamma(L_2)=0.185$ eV, taken from their own measurements. They noted, however, that agreement between their semiclassical model and experiment would be less good if the width $\Gamma(L_2)=0.116$ eV of King *et al.*[13] were used.

III. QUANTUM-MECHANICAL CALCULATION AND DISCUSSION

The present calculations are based on lowest-order PCI theory.[9] As shown in detail in Ref. 9, this theory leads to the relativistic cross section

$$\frac{d\sigma}{d\varepsilon}=\frac{\pi}{3\omega\alpha}\sum_{lj,l_A,j_A}[\Gamma_{l_Aj_A}(\varepsilon)|\langle(E_{\rm exc}+\varepsilon_A^0-\varepsilon)lj|\tau_0\rangle|^2+\Gamma_{l_Aj_A}(E_{\rm exc}+\varepsilon_A^0-\varepsilon)|\langle\varepsilon lj|\tau_0\rangle|^2]\ , \tag{5}$$

where $\Gamma_{l_Aj_A}$ are the partial Auger rates and where

$$|\tau_0\rangle=\int\frac{|\tau lj\rangle\left\langle[n_il_ij_i]\tau lj,J=1\left|\left|\sum_\nu\boldsymbol{\alpha}\cdot\mathbf{A}^{(e)}(\mathbf{r}_\nu)\right|\right|J=0\right\rangle}{E_{\rm exc}-\tau+i\Gamma/2}d\tau \tag{6}$$

involves the reduced $E1$ dipole many-electron matrix element in the Coulomb (velocity) gauge and square brackets denote hole states. In Eq. (5), $\varepsilon_A^0=E^{(2+)}-E^{(+)}$ is the nominal Auger-electron energy. The photoelectron orbitals $|\varepsilon lj\rangle$ and the Auger-electron orbitals $|(E_{\rm exc}+\varepsilon_A^0-\varepsilon)l_Aj_A\rangle$ are evaluated in the field of the doubly ionized ion, whereas the intermediate-state orbitals $|\tau lj\rangle$ are obtained in the field of the singly ionized ion with the hole in the subshell $n_il_ij_i$. If $\varepsilon>0$, the photoelectron ends up in a continuum state $|\varepsilon lj\rangle$, and if $\varepsilon=-\varepsilon_n<0$, it ends up in an excited bound state $|nlj\rangle$. In Eq. (6), $|\tau\rangle$ is either a discrete or a continuum orbital. The contribution from the continuum with $|nlj\rangle$ as final state corresponds to the recapture process. It follows from Eq. (6) that the first term in the sum of Eq. (5) peaks in the vicinity of $\varepsilon=\varepsilon_A^0$, whereas the second term contributes to the region around $\varepsilon=E_{\rm exc}$. Since we have $\varepsilon_A^0\gg E_{\rm exc}$ in the present application, we only need to evaluate the latter term which gives the photoelectron distribution.

Equation (5) does not account for the "no-passing" effect[14,15] which is a consequence of the mutual screening of the ionic core by the photoelectron and the Auger electron in the final doubly ionized state.[10] As shown by Armen *et al.*,[10] however, the modification of the cross section (5) by this screening effect is negligible provided the so-called dynamic charge $Q_d=1-(E_{\rm exc}/\varepsilon_A^0)^{1/2}$ is close to unity. This condition is fulfilled in our application.

The present calculations were performed with Dirac-Fock wave functions; relativity is not essential here, but was included for convenience. We considered $L_2\rightarrow M_{2,3}M_{2,3}$ transitions with an initial $2_{p_{1/2}}$ hole ($E_B=250.5$eV) and two $3_{p_{3/2}}$ holes in the final state. In Eq. (5), l and j were restricted to $l=2$ and $j=\frac{3}{2}$. The intermediate one-hole states thus were $2_{p_{1/2}}^{-1}\tau d_{3/2}$, $J=1$

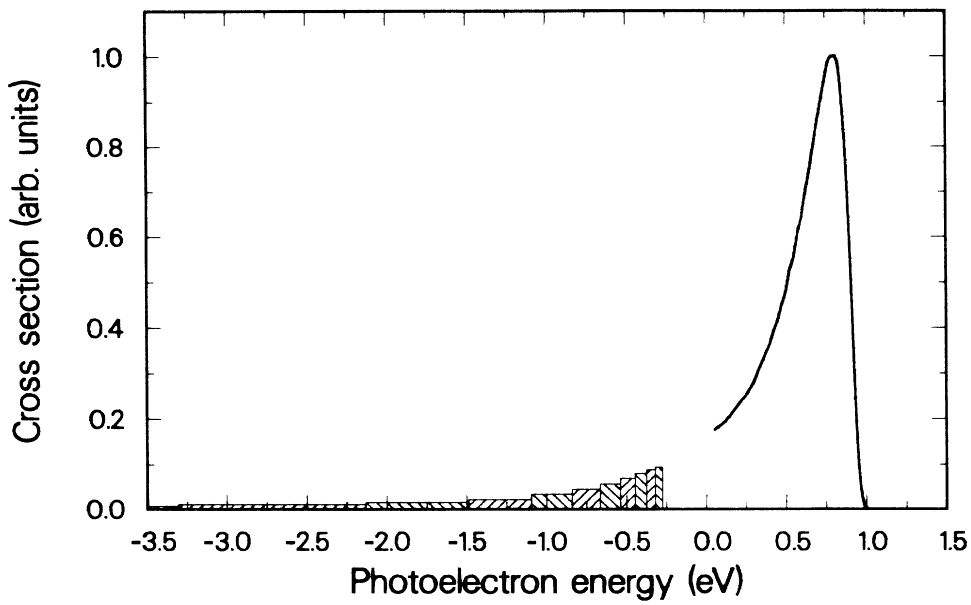

FIG. 1. Partial photoelectron cross section accompanying the formation of the Ar $2p_{3/2}^{-2}(J=2)$ double-hole states, as a function of the photoelectron energy, for $E_{\rm exc}=1.0$ eV. The blocks represent recapture into $|nd_{3/2}\rangle$ states, with n ranging from 3 to 14.

states with $|\tau d_{3/2}\rangle$ incorporating both discrete ($n=3,\ldots,8$) and continuum states calculated at intervals $\Delta\tau=0.015$ eV up to $\tau=30$ eV and with $\Delta\tau=0.05$ eV up to $\tau=80$ eV. As pointed out earlier, the L_2 width was taken to be $\Gamma=0.126$ eV.[12] The final photoelectron orbitals consisted of $|nd_{3/2}\rangle$ ($n=3,\ldots,14$) discrete and $|\varepsilon d_{3/2}\rangle$ continuum states coupled to $2p_{3/2}^{-2}(J=2)\varepsilon_A f_{5/2}$, $J=\frac{1}{2}$ states. The solution of the corresponding Dirac-Fock equations was obtained, however, for both the $d_{3/2}$ and $f_{5/2}$ orbitals in the field of the $2p_{3/2}^{-2}$, J state averaged over all possible total J values. Both the reduced $E1$ matrix elements and the Auger rates were calculated with Dirac-Fock many-electron wave functions. The Auger rates were calculated with the $2p_{1/2}^{-1}$, $J=\frac{1}{2}$ initial state and $2p_{3/2}^{-2}(J=2)\varepsilon_A f_{5/2}$, $J=\frac{1}{2}$ final states, such that $\varepsilon+\varepsilon_A=E_{\rm exc}+\varepsilon_a^0$, where $\varepsilon_A^0=210$ eV. The Auger rates corresponding to $j_A=\frac{3}{2}$ and to $2p_{3/2}^{-2}$, $J=0$ core states with $l_A=1, j_a=\frac{1}{2}$ were not taken into account because they would not influence the shape of the cross section (5) as a function of $E_{\rm exc}$. This is also true for $l=2$ and $J=\frac{1}{2}$. The $3p_{1/2}^{-1}3p_{3/2}^{-1}$ and $3p_{1/2}^{-2}$ final states were neglected for the same reason. Furthermore, the summation over $2p_{1/2}^{-1}\varepsilon s_{1/2}$, $J=1$ intermediate states was not taken into account because they contribute little to the cross section (5).

The cross section for emission of photoelectrons at $\varepsilon\simeq E_{\rm exc}$ was calculated for $E_{\rm exc}$ between 0.25 and 2.5 eV in steps of 0.25 eV. As an example we show in Fig. 1 the cross section as a function of ε for $E_{\rm exc}=1.0$ eV. The solid curve, which represents final continuum states of the photoelectron, shows the well-known asymmetry and PCI shift of the maximum towards energies below $E_{\rm exc}$.[9,10] The discrete final states corresponding to principal quantum numbers n in the range from 3 to 14 are represented by blocks. They were constructed using the quantum-defect method of Fano and Cooper[16] so that the area of each block represents the contribution of a particular state $|nd_{3/2}\rangle$ to the cross section. In this method, the continuous and discrete parts of the photoelectron distribution merge at $\varepsilon=0$, which allows for an extrapolation of the discrete part into the continuum. The ratio between the discrete part and the total area under the curve including the blocks is thus taken to be the recapture probability $P=P(E_{\rm exc})$, listed in Table I. This interpretation is justified since an examination of the summation over the intermediate states in Eq. (5) shows that the contribution from discrete intermediate states is negligible.

As pointed out above, it is adequate to take the photoelectron distribution corresponding to $l=2, j=\frac{3}{2}$ and $l_A=3, j_A=\frac{5}{2}$ to represent the relative probability of the entire L_2 recapture process. This approach is consistent with the qualitative considerations in Sec. II and with our previous work on PCI,[9,10] which shows that the

TABLE I. Calculated recapture probability $P(E_{\rm exc})$, as a function of excess energy $E_{\rm exc}$ above the Ar L_2 threshold.

$E_{\rm exc}$ (eV)	$P(E_{\rm exc})$ (%)
0.25	82.5
0.50	50.0
0.75	33.4
1.00	24.6
1.25	19.0
1.50	15.3
1.75	12.5
2.00	10.5
2.25	9.0
2.50	7.7

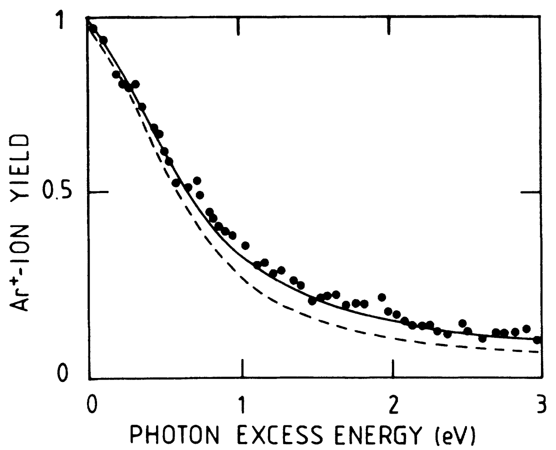

FIG. 2. Measured and calculated Ar^+ yields above the L_2 threshold, as a function of the photon excess energy E_{exc}. The solid curve represents the quantum-mechanical calculation whereas the dashed curve was obtained using the semiclassical model of Ref. 8. In both cases, the hole-state width is taken to be $\Gamma(L_2)=0.126$ eV.

phenomenon is rather insensitive to details of atomic structure. Since we have neglected correlation and the term dependence of the interaction between the ion and the ionized electrons, the individual n-dependent recapture probabilities are less accurate, however, than the total ion-yield ratio. It is also safe to neglect any production of singly ionized ions by the nonradiative decay of $2p_{1/2}^{-1}nd_j$ resonant states in which the nd_j electron either stays as a spectator during the first stage of the decay or directly participates in the Auger-electron emission. The primary reason for this circumstance is that the dominant low-n states do not contribute very much in the above-threshold region, due to the narrowness of the width Γ.

Calculations of $P(E_{exc})$ with $\Gamma=0.185$ eV for a few values of E_{exc} indicate that an estimated ±0.02 eV uncertainty in Γ changes $P(E_{exc})$ by less than 15% in the significant region of E_{exc}. This leaves us with the last source of uncertainty in our calculation. It stems from the fact that the L_3 recapture tail contributes to the production of singly ionized ions in the energy region of interest, since the energy difference between the L_2 and L_3 thresholds is only 2.05 eV. This background effect can, however, be taken into account by assuming that the ratio between the L_3 and L_2 cross sections is 2, and that the dependence of P on E_{exc} is the same for L_2 and L_3. The theoretical curve with the tail correction included is then finally convoluted with the Gaussian instrumental function which accounts for the monochromator resolution.[8] The result, which has been renormalized to unity at the L_2 threshold, is shown in Fig. 2 together with the experimental points. Also shown is the corresponding semiclassical recapture-probability curve, subject to the same corrections as the quantum-mechanical curve.

There is a distinct difference between the quantum-mechanical and semiclassical results in Fig. 2. In the semiclassical model, $P(E_{exc})$ depends critically on τ_P. It does not, however, depend very much on the time τ_A which it takes for the Auger electron to pass the photoelectron, as long as we have $E_{exc} \ll \varepsilon_A^0$ which is the case in the present application. This result is consistent with the quantum-mechanical interpretation in which there is no need to take into account the screening of the nucleus by the Auger electron. It follows that in the semiclassical model R is simply the critical distance at which the photoelectron is still recaptured due to the release of the Auger electron, rather than being the passing radius. If, however, τ_P is taken to be $\tau_P \simeq R/v_P$ with $R^{-1}=E_{exc}$ in Sec. II, the quantum-mechanical result is overestimated rather than underestimated by the semiclassical approach.

IV. CONCLUSION

The present quantum-mechanical analysis of the Ar^+ yield as a function of photon energies close to the L_2 threshold shows that in general there is a considerable probability that the photoelectron is recaptured by the atom in inner-shell threshold photoionization followed by radiationless transitions. Consequently, the yield of singly ionized ions is enhanced in the energy region just above threshold, in contrast to what would be expected on the basis of the lifetime of the inner-shell hole. This post-collision interaction phenomenon should be observable not only in Ar but in other atoms and molecules as well.

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