Evidence for Internal Dielectronic Excitation of Slow Highly Charged Uranium Ions

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We have measured x-ray emission from the neutralization of slow U^{q+} ions with charge states $q = 61 - 73$ and energies of $7q$ keV on a Be foil. We were able to resolve M-satellite groups and found an expected increase in M x-ray intensity with increasing number of M-shell vacancies in the incident ions. However, for charge states with no M-shell vacancies, we also observed a significant intensity of M x rays. We take this observation as evidence of an internal dielectronic excitation process occurring during the neutralization of the ions.

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The interaction of slow highly charged ions with solid surfaces has recently drawn considerable interest. These ions have the unique property of high potential energy relative to their kinetic energy. The interaction of these ions with quasifree electrons near a surface results in several interesting effects [1]: emission of a large number of secondary electrons, the formation of a "hollow atom" with many electrons in high-n quantum states, and the possibility of a "Coulomb explosion" of atoms near the point of impact on a nonconductive surface [2]. Experimental evidence for these effects has appeared in measurements of electron [3–6] and x-ray [7–10] spectra resulting from the neutralization of highly charged ions on surfaces.

In most theoretical models of these interactions, the highly charged ions resonantly capture electrons from the conduction band into high-lying Rydberg states as they approach the surface. Some of the excitation energy of these states is emitted by radiation and autoionization, while emitted electrons are replaced by new captures. The rates for these processes, however, are far too low to allow the resulting "hollow atom" to relax before it reaches the surface, so the ion impinging on the surface is a complex multiply excited atomic system.

Both the dynamics of the neutralization process and the atomic structure of the multiply excited states present challenging many-body problems. Atomic structure calculations used to explain the measured electron [11] and x-ray [8, 12] spectra have usually followed the "Hagstrum model" [13] in which electronic deexcitation from the high Rydberg states is dominated by autoionization.

In this Letter we present evidence for a further dielectronic process, derived from the experimental observation of significant M x-ray emission from slow highly charged uranium ions with no M vacancies incident on a surface. In this internal dielectronic excitation (IDE) process, an electron in a high-n state interacts with an M-shell electron to form an intermediate state with an M vacancy, which can subsequently radiatively decay. IDE is analogous to dielectronic recombination in ion-electron collisions [14], and to the process creating so-called "nonequivalent" electrons in slow ion-atom collisions [15]. A similar dielectronic excitation process has been reported in the ion-surface interaction of Ar^{2+} and Pb, in which an intrashell ($3s$-$3p$) excitation by a $4s$-$4p$ transition was proposed [16].

We extracted U^{q+} ions, with charge states from $q = 62$ to $q = 73$, from an electron beam ion trap (EBIT) at the Lawrence Livermore National Laboratory. It produces highly charged ions by sequential ionization in a high-current-density electron beam. The electron-ion interaction energy can be tuned over a wide range to optimize production of any desired charge state. The device is described in detail elsewhere [17]. The ions, with kinetic energies of $7.0q$ keV, were momentum analyzed and focused onto a 25 μm thick Be foil target. X rays from the interaction of the ions with the surface were detected through the foil by a Si(Li) detector with a geometrical solid angle of 0.12 sr and a resolution of 180 eV FWHM at 5.9 keV. The absorption of the 2×25 μm thick Be foil is negligible for x-ray energies above 3 keV. The vacuum in the target chamber was kept in the low 10^{-8} range to prevent spurious events from electron capture in the residual gas.

The x-ray spectra obtained for U^{q+}, $62 \leq q \leq 73$, are shown in Fig. 1, together with calculated transition energies for the transitions predicted to have the highest rates in hollow atoms formed from U^{66+} and U^{73+}. The transition energies were calculated using a j-j averaged Dirac-Hartree-Slater model [18]. The calculations include the effects of finite nuclear size, relaxation, and the Breit interaction. To simulate the many spectator electrons in a hollow atom, we used the present standard picture of hollow-atom formation, which comes from the classical over-barrier model [1, 11]. In this picture, at a

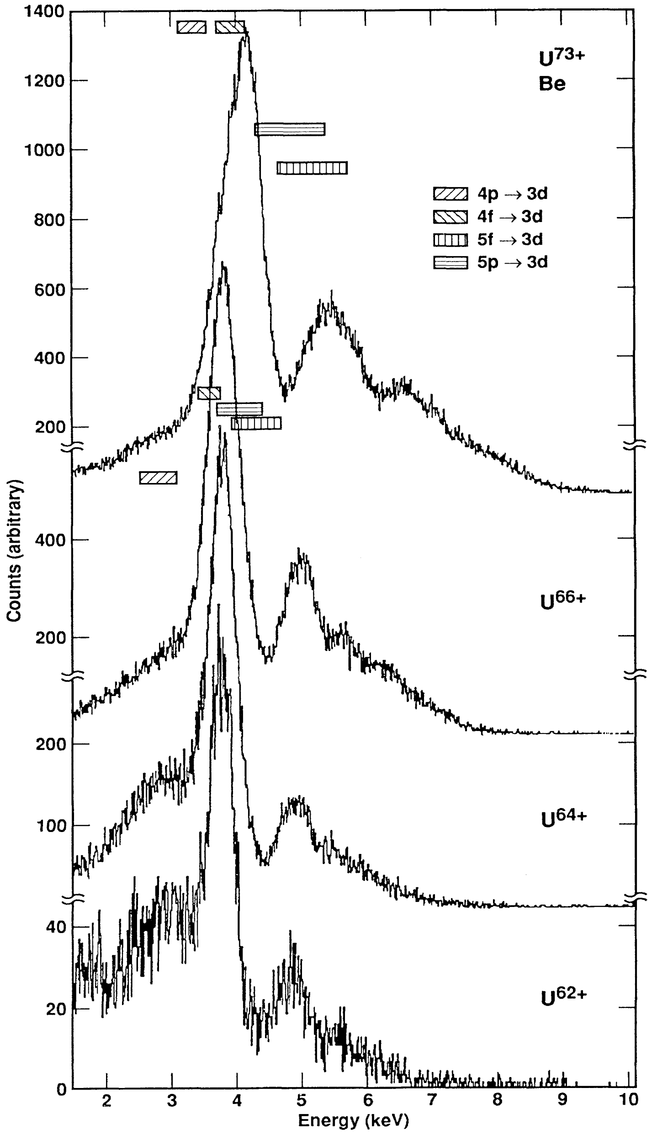

FIG. 1. X-ray spectra for different charge states of U ions incident on a Be foil target. Transition energies shown for U^{66+} and U^{73+} ions are calculated using a Dirac-Slater-Hartree model with spectator electrons distributed statistically into $n = 4$–6 states.

relatively large distance from the surface (approximately 65 a.u. for the case of U^{70+}), electrons emitted from the surface are transferred into high Rydberg states, around $n \approx 60$. Some electrons are deexcited by Auger and photon emission, but the ion is still in a highly excited state when it reaches the surface. When the ion starts to penetrate into the bulk, most of the high-n electrons are stripped off. Closer collisions with lattice atoms transfer electrons into lower states, with $n \approx 8 - 10$. These electrons cascade into inner-shell vacancies, giving rise to M x rays if M vacancies are available. The x rays from transitions into initially empty states of the highly charged ions have been observed in previous measurements [7–10, 12].

In calculating the transition energies, therefore, electrons were statistically distributed in the $n = 4$ to $n = 6$ states for charge states from $q = 15$ to $q = 40$. As a result, the predicted energies fall into bands. A comparison of the measured spectra with the predicted transition energies indicates that most of the observed intensity results from M x rays. As predicted, the centroid of the main peak shifts to higher energy as the initial charge of the projectile is increased.

The most interesting feature of the data in Fig. 1 is the observation of significant M x-ray emission from incident ions with no M vacancies ($q \leq 64$). First, we consider possible explanations for the observation of the anomalous M x rays not involving dielectronic processes. Collisional direct excitation or ionization of M-shell electrons has an extremely low probability, because the velocity of the ions is approximately 0.25 a.u. while the minimum excitation energy for an M-shell electron is more than 220 a.u. We can also exclude molecular orbital promotion in this very asymmetric target-projectile system; vacancy sharing probabilities are estimated to be below 10^{-20} [19].

Metastable states in the incoming ions also cannot explain the observed spectra. It is known that very few ions in metastable states are produced from an electron beam ion source, such as EBIT [17]; however, we have independently verified the lack of metastable contributions to the observed M x-ray spectra. First, the yield of M x rays varies smoothly for charge states with $q \leq 64$, while the probability of metastables would not. Second, we performed a test in which we reduced the electron beam energy to below the ionization energy for $q = 65$. This procedure should dramatically alter any metastable fraction, but we observed no change in the M x-ray yield.

The integrated intensity of the main M x-ray peak normalized to the number of incoming ions is shown as a function of incoming ion charge state in Fig. 2. The M x-ray yield increases monotonically with charge state, but with different slopes above and below $q = 64$. The approximately linear relationship of x-ray yield with charge state for $q \geq 65$ is the expected variation as the number of M vacancies in the ion increases. The slope for $q \leq 64$, however, seems to reflect the number of N-shell vacancies, indicating a mechanism for creating M-shell vacancies using N-shell vacancies.

A process that could give rise to photons at approximately the measured energies with an intensity proportional to the number of N vacancies is radiative electron capture into the N shell. Such a process has been observed in high-resolution x-ray measurements of $K\beta$ lines in the neutralization of Ar^{17+} ions [10]. However, these photons cannot be responsible for the measured signal. First, they would not produce the observed line struc-

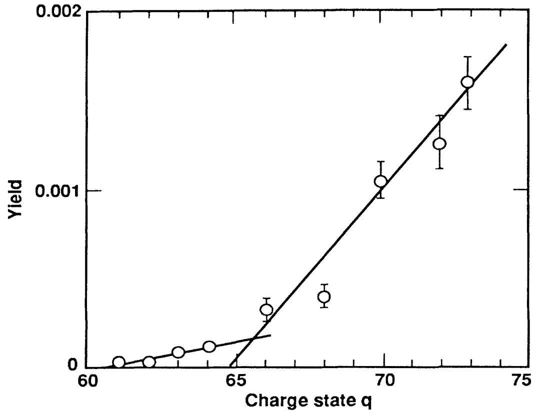

FIG. 2. Integrated intensity of the main peaks of M x rays (see Fig. 1) normalized to the number of incoming ions as a function of the ion charge state.

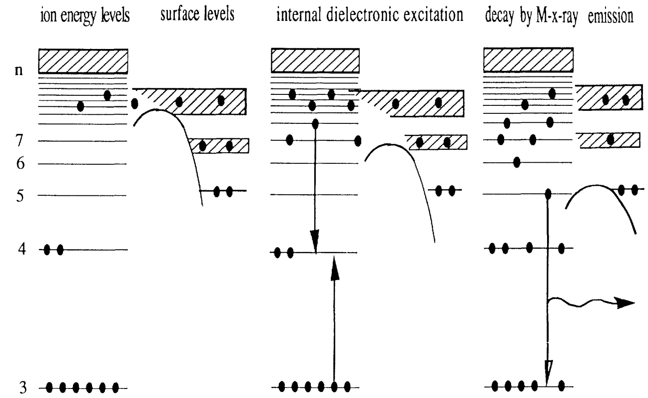

FIG. 3. Schematic of the different steps of the internal dielectronic excitation process in the neutralization of a U^{62+} ion at a surface.

ture. Second, the ionization potentials of U^{61+} and U^{63+} ions are 4.3 keV and 4.6 keV, respectively. These energies represent the maximum energies for photons from radiative capture to charge state $q = 62$ and $q = 64$; they are lower than some of the lines observed to vary with charge state. The low-energy portion of the radiative capture spectrum is visible in our x-ray spectra as a shoulder on the low-energy side of the main M x-ray peak.

We propose a mechanism for production of M-shell vacancies by "internal dielectronic excitation." If a $3\ell n\ell'$ state is energetically degenerate with a doubly excited $4\ell 4\ell'$ state, then a resonant transition between the states is possible. The resulting intermediate $4\ell 4\ell'$ state may decay either radiatively to a $3\ell 4\ell'$ state or nonradiatively back to a $3\ell n\ell'$ state. In the former case, an M x ray is observed. The steps leading to M x-ray emission by this mechanism are shown in Fig. 3. Given the presence of such an energy degeneracy, the rate for formation of the intermediate state with an M-shell vacancy is expected to be quite large compared to other decay rates in the hollow atom. In the system we studied, the formation of a $4\ell 5\ell'$ or higher intermediate state is not energetically allowed.

The energy degeneracy condition requires that some electrons in a high-n state have a transition to the N shell with an energy that exactly corresponds to a transition energy between the M and N shells. While this condition might at first seem difficult to satisfy, the large number of captured electrons cascading through the closely spaced high-n states, together with the large number of satellites for both the M-to-N transitions and the high-n states, make it quite possible. The situation is illustrated in Fig. 4, which shows binding and transition energies calculated using the Dirac-Hartree-Slater model [18]. As with the calculations of the expected x-ray energies, spectator electrons were statistically distributed in $n = 4 - 6$ states. From this figure, it is apparent that for certain populations of spectator electrons there are $4\ell 4\ell'$ states degenerate with $3\ell n\ell'$ states for $n \geq 8$.

Additional evidence for our proposed mechanism comes from the nonobservation of analogous L x rays in a previous measurement of slow, highly charged, near-neon-like Xe ions incident on a metal surface [12]. In this system, the IDE excitation of an L-shell electron is energetically forbidden because the L-to-M transition energy is always greater than the M-shell ionization energy. The nonexsisting direct excitation, ionization, and electron promotion contribution are verified here too, because ion velocity and L-to-M excitation energy were very similar

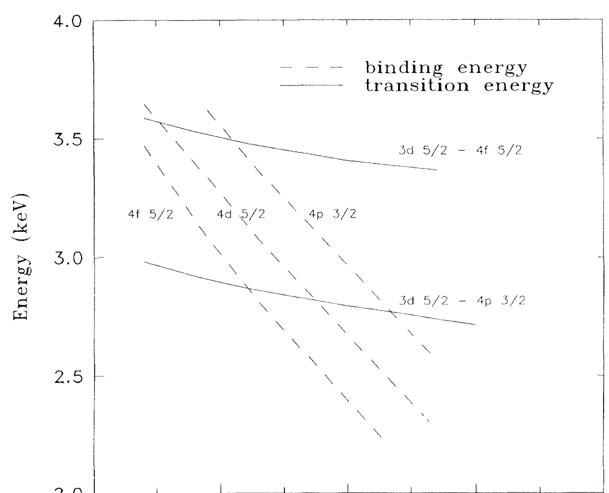

FIG. 4. Binding and transition energies of U ions with a nickel-like (64+) core and spectator electrons distributed statistically into $n = 4$–6 states.

to the ion velocity and the M-to-N excitation energy in the present U case.

We can make a rough estimate of the probability for IDE in highly charged uranium ions from our experimental results. For ions with $q \geq 65$, the M x-ray yield is given by

$$Y_{\mathrm{RAD}} = N_M \omega_M \Omega, \tag{1}$$

where N_M is the number of M-shell vacancies, ω_M is the fluorescence yield for M x-ray emission, and Ω is the detector solid angle. The yield for M x-ray production via IDE can be approximated in a similar manner:

$$Y_{\mathrm{IDE}} = P_{\mathrm{IDE}} \omega_X \Omega, \tag{2}$$

where P_{IDE} is the probability of generating an M-shell vacancy via IDE and ω_X is the fluorescence yield for this vacancy. In general, we expect $\omega_X < \omega_M$, since the state in the former case has a natural nonradiative decay, i.e., back via the incoming channel. However, we can obtain a lower limit by approximating $\omega_X \approx \omega_M$. Given this assumption, we obtain a P_{IDE} of about 0.83 for U^{64+} from Eqs. (1) and (2) and the values given in Fig. 2.

In conclusion, our observation of M x rays emitted during neutralization of slow highly charged U^{q+} ions incident on a solid surface has shown two sigificant features: first, an expected increase in the M x-ray yield as a function of the number of M-shell vacancies in the incident ion, and, second, an unexpected yield of M x rays for incident ions with no M-shell vacancies. The latter observation constitutes good evidence for an internal dielectronic excitation mechanism occurring with a high probability during neutralization. This process must be included in any complete description of the neutralization of ions on surfaces.

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