Unexpected X-Ray Emission due to Formation of Bound Doubly Excited States

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A strong emission of characteristic M x rays is observed, without an M vacancy initially present, when slow highly charged ions (Ta^{q+}, $q = 39-48$) capture a single electron in single collisions with rare gas atoms (He). This is explained by the formation of bound doubly excited states through electron correlation. An elaborate theoretical treatment shows that bound doubly excited states are mixed with states where a Rydberg electron is bound in the core of a highly charged ion. It is striking that this occurs with a large probability (close to unity), and one needs to assume that higher Rydberg states are populated than predicted by the overbarrier model in order to explain the experimental results.

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Multielectron effects in time-dependent interactions, such as collisions, have received considerable attention in the past years [1]. This was largely motivated by the interest in the dynamics of the electron-electron (e-e) interaction, which presents a challenging time-dependent many-body problem. In spite of a strong development of many-particle theory, many effects are still quite unpredictable. For instance, multielectron photoionization in strong laser fields has recently shown surprises [2]. The capture cross sections for several electrons by highly charged ions (HCI) can vary widely, dependent on the formation of multiply excited states as well as autoionization or radiative rates for their stabilization. Aside from the fundamental interest in the many-particle aspect, there are several applications of multiply excited atoms and ions. Such atoms and ions exist in plasmas, found, for example, in fusion devices and stars, and have recently been found even in comets [3].

We report here on evidence of a strong dielectronic effect when HCI capture *single* electrons from atoms in the gas phase. The x-ray spectra which are, to our knowledge, observed for the first time for single capture exclusively with slow HCI show interesting cascading features for both an initially filled and unfilled M shell. A key point is that, even when the HCI has an initially filled M shell, one observes intense M x-ray emission in coincidence with singly charged target recoils. A theoretical interpretation of the process and of the observed x-ray spectra will be given here. The Rydberg electron, captured in the collision, is shown to be able to excite the strongly bound core of the highly charged ion in a correlated two-electron process. The M x rays are emitted when these bound doubly excited states decay.

Signatures for a correlated e-e interaction have so far been observed mainly in *double* electron capture of slow highly charged ions by deviations from the independent electron model, i.e., in the population of asymmetric $(n\ell, n'\ell')$ as well as symmetric $(n\ell, n\ell')$ states, where n and ℓ are the principal and orbital angular momentum quantum numbers, respectively. This effect has created controversial discussions as to whether it happens instantaneously, sequentially, or postcollisionally with flourishing activities resulting in subjects such as "autotransfer to Rydberg states," "correlated double capture," and "dielectronic excitation" [4–7].

Another related process is dielectronic recombination (DR) [8], where it is the interaction of the ion with a free electron that populates a doubly excited state. Stabilization then occurs by emission of a photon. The energy of the electron in the continuum is tuned through the resonance of an autoionizing doubly excited state. A similar process has been seen in the stabilization of highly excited electrons which neutralize slow, highly charged ions when impinging on a metal surface. This was discovered by a high intensity of M x rays emitted in slow U^{q+} ($q \leq 64$) surface interactions, in the absence of initial M vacancies in the incident ions [9]. The reason could be "internal dielectronic excitation" (IDE), i.e., that the captured electrons in very highly charged ions can release enough energy to excite an inner-shell electron, even though the kinetic energy is very small [9]. However, contrary to DR, the core-excited state is a bound state. Tuning of the resonance energy has been assumed to occur in the vast amount of configurations [10] which are populated in the HCI-surface interaction. Because of the atomic level structure, the IDE process seems to operate only for exciting the M shell and higher. In fact, K x rays or L x rays were never observed in slow HCI-surface interactions, except when there were vacancies initially in the K or L shell of the projectile [11–13].

In the experiment, ${}_{73}Ta^{q+}$ ($q = 39-49$) ions were obtained with energies of $7 \cdot q$ keV from the J. R. Macdonald Laboratory Cryogenic Electron Beam Ion Source (CRYEBIS). The ion beam was then collimated and directed onto a He gas target. Ion charge states were separated by a 90° sector magnet and calibrated by a He^+ beam impurity overlapping with the 45+ charge component. Recoil ions, due to electron capture by the Ta projectiles, were extracted from the gas cell for time-of-flight analysis. Both recoil-projectile and recoil-x-ray coincidence events give

the number of electrons captured by the projectile. X rays from 1–5 keV were detected at 90° with a Si(Li) detector. The geometrical solid angle was 0.36 sr (2.8% of 4π) and the energy resolution was 180 eV at 5.9 keV and 150 eV at 1.8 keV. Energy calibration was performed by measuring the known K fluorescence lines of Mn (~5.9 keV), Al (~1.5 keV), Si (~1.8 keV), Cl (~2.6 keV), and Ti (~4.5 keV). For the main x-ray intensity detected at about 2 keV, absorption in the 12.5-μm-thick Be window is small and has been corrected. The vacuum in the beam transport system and the target chamber was in the low 10^{-8} mb range, with the gas target on, and thus electron capture on this part of the ion flight path was negligible. Measurements at different target pressures were done for all incident projectile charge states in order to ascertain the linear pressure dependence region for x-ray and recoil ion production. Prior to entering the collision region, M vacancies existed for projectiles with $q \geq 46$ (Ta^{45+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$).

Figure 1 shows x-ray spectra for several charge states of Ta^{q+} ions in coincidence with He^+ recoil ions, i.e., for single capture. A peak at about 2 keV can be identified as due to transitions in the M shell (Ta^{49+} has 4 M vacancies). However, we observe such x rays also for a q of 43, where the M shell is initially closed. The shape of the spectra does change quite a bit from $q = 43$ to $q = 46$, but not when the number of M shell vacancies increases ($q = 49$).

The fact that we observe M x rays for Ta^{43+} ions after single capture, is at first very surprising. The ionization potential of the M shell is approximately 4.5 keV. At a projectile velocity of $v = 0.28$ a.u., collisional excitation or ionization of M-shell electrons by impact with He atoms can be excluded. One can also exclude molecular orbital promotion mechanisms [14] of the M-shell electron in this very asymmetric target-projectile system (Ta-He). Metastable ions are eliminated by the production of the ions in the CRYEBIS. However, we have checked for the possibility of a contribution from metastable states by varying the charge state of the incident ion from 39+ to 44+. The flight time from the source to the target is on the order of 4 μs. If metastable states with vacancies in the M shell existed, there should be drastic changes in the yield of M x rays. However, no dramatic change in the yield was observed.

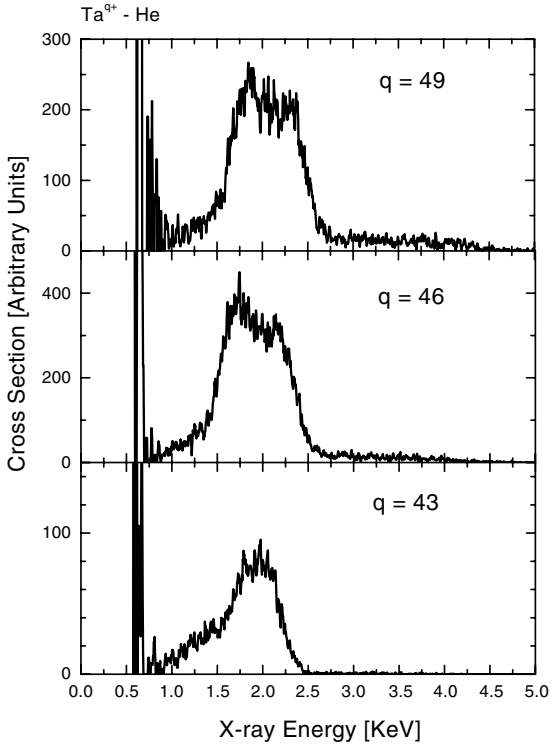

FIG. 1. X-ray spectra for different charge states of Ta^{q+} ions in coincidence with single-electron capture from He gas atoms.

In order to understand the measured spectra we consider first the case of Ta^{46+} capturing a single electron from He. With one M vacancy, and with selection of a single capture, one ensures that relaxation can only occur by photon emission, and hence the fluorescence yield should be unity. At least one M x ray should be emitted per capture event. The rate of this radiative deexcitation depends on the n and ℓ initially populated, and the total spin S for the transition to the ground state. If ℓ is high, the cascade will be in small steps and very slow.

The classical overbarrier model (OBM) [15] has been proven to give quite accurate predictions for electron capture by HCIs at low velocity. It predicts that capture from He occurs at a distance R, of 20 a.u., into quantum states of $n = 16$–17 in Ta^{q+} with q about 43–46. Using this value of R and mv, where m is the electron mass, one finds that the electron should be captured into an ℓ of 4. In a cascade calculation on Ta^{46+}, the dipole transitions from $n = 17$ to $n = 3$ for selected populations of ℓ varying from 0 to 8 were considered with energy levels calculated within the Dirac-Fock approximation. Coupling of the spin of the captured electron to that of the Ta^{46+} ion was neglected. This gives a total cascade time of below 100 ps. The observation time in the experiment was 15 ns. All transitions for these ℓ should thus be seen, with the exception of intercombination lines.

Figure 2 shows the results from cascade calculations for Ta^{46+} for a population of $n = 17$ and $\ell = 0$–8, folded with a Gaussian of 150 eV FWHM. Different distributions of the quantum number m were tested and the results showed essentially no M dependence. It is striking, however, how sensitive the spectral shape is on the selection of ℓ. One can identify the n of initial and final states for individual transitions in the measured spectrum (Fig. 2). Cascading transitions in high n give the intensity at low energy. At about 1 keV the $n = 5$ to $n = 4$ transitions appear. Below 1 keV (e.g., for $n = 6$ to $n = 5$), the detector is not sensitive to photons. The main intensity in the spectrum, from 1.5–2.5 keV, comes from the $n = 4$ to $n = 3$ transitions. We see, for the highest ℓ calculated, only one peak at about 2 keV which is from the $4f$-$3d$ transitions. There is some intensity for the $5f$-$3d$ transitions at 2.7 keV, but, due to selection rules, nothing for the

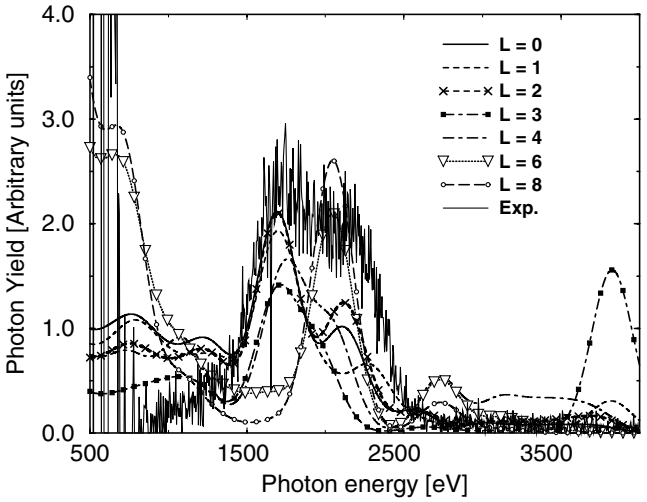

FIG. 2. The x-ray spectrum for Ta^{46+} (single initial M vacancy) after single-electron capture from He in comparison with cascade calculations for different initial angular momentum, ℓ, in $n = 17$.

17ℓ-$3d$ transition at about 3.8 keV. It is most striking that $5p$ or $5f$ to $3d$, $6p$ or $6f$ to $3d$, etc., and 17ℓ-$3d$, as well as 5ℓ-$4\ell'$, transitions are very weak in the measured spectra. The fact that $4p$ to $3d$ and $4f$ to $3d$ account for almost all of the intensity indicates a balance between two cascade branches [one branch along the states with highest angular momentum (yrast line) and one along states with low angular momentum]. This is only possible for a well-selected initial ℓ. In fact, the calculated spectrum for $\ell = 2$ seems to agree best with the measured spectrum. Some intensity at the high energy side of the main peak ($\sim$2.3 keV) is missing and we will come back to this point later.

In an attempt to understand the x-ray spectra for the case where no M vacancy is initially present in the ion, e.g., Ta^{43+} ($3d^{10}4s^2$), a similar cascade calculation was performed. The results are shown in Fig. 3 (solid dots for an equal population of all ℓ up to $\ell = 8$ of $n = 16$) and show no resemblance with the data. The weak predicted peak at 1.6 keV is from the direct $n = 16$ to $n = 4$ transition and cannot be expected to be that strong, since it is not seen for Ta^{46+} (Fig. 2). Also, starting from levels higher than predicted by the OBM will not change the spectrum considerably, as the primary contribution is from the last step of the cascade.

Apparently, an alternative, and hitherto not considered, capture-deexcitation path is responsible for the observed very high and energetic x-ray intensity at $\sim$2 keV. Such a possibility was investigated by calculations. In addition to the singly excited Rydberg configurations used in the cascade calculation, we have also considered doubly excited configurations of the type $3d^9 4s^2 4\ell 4\ell'$ (one M hole). Because of electron correlation, the true states will be a mixture of both types of configurations. The energy levels and the degree of mixing can be obtained by diagonalization of the Hamiltonian. The doubly excited levels are distributed from ~ -400 eV below the ionization

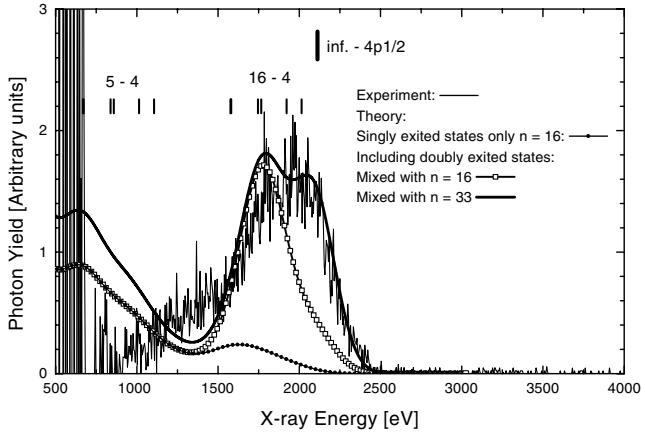

FIG. 3. The x-ray spectrum for Ta^{43+} (no initial M vacancies) after single-electron capture from He in comparison with theory (averaged over $\ell = 0-8$). For details of the inclusion of bound doubly excited states, see text.

threshold to $\sim$600 eV above threshold. Levels of singly and doubly excited states are plotted for a selected energy range in Fig. 4. The dashed line indicates the energy level which could be populated by capture according to the OBM. From the energy levels of the singly excited states ($3d^{10}4s^2 n\ell$) and the density of doubly excited states ($3d^9 4s^2 4\ell' 4\ell''$) in Ta^{42+}, it is apparent that within a few cascading steps, or even during the collision, a $3d^{10}4s^2 n\ell$ state could be nearly degenerate with $3d^9 4s^2 4\ell 4\ell'$ states. With the existence of such an energy degeneracy, the intermediate doubly excited state with an M-shell vacancy can be populated through the electron-electron interaction (configuration mixing) and will then decay with high probability by x-ray emission. The calculation gives, however, a small mixing coefficient for these rather spatially separated configurations. We assumed that during the collision, when the singly excited states are tuned over $\sim$1 eV due to molecular effects, mixing will be strongly enhanced.

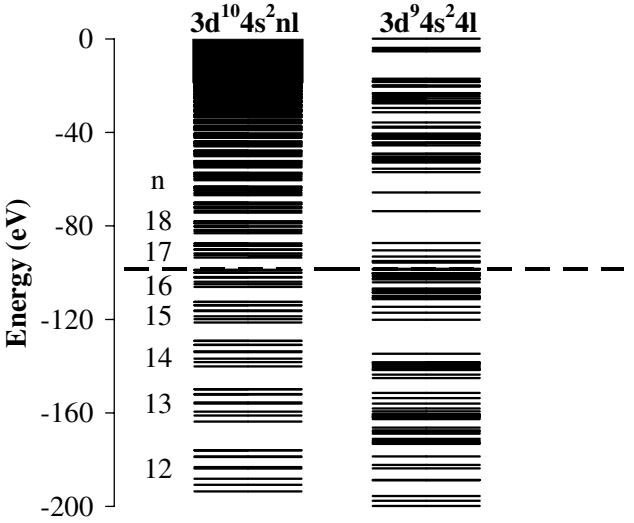

FIG. 4. Energy levels of $3d^{10}4s^2 n\ell$ singly excited and $3d^9 4s^2 4\ell' 4\ell''$ doubly excited states in Ta^{42+}.

Starting from a population of the 16ℓ states (as predicted by the OBM) and assuming a 20% relative probability to populate the doubly excited states, we have obtained the results shown in Fig. 3 (open squares). An equal population of all $\ell \leq 8$ is assumed as well.

The appearance of a strong x-ray intensity at about 1.8 keV (Fig. 3) verifies the mixing of the Rydberg state with the bound doubly excited state. Still, a large intensity at higher x-ray energies of 2 keV and above remains to be explained. The ground state of Ta^{42+}, $3d^{10}4s^24p_{1/2}$, has an ionization energy of 2.11 keV and only initial states lying just below the ionization threshold can give x-ray photons above 2 keV. The OBM predicts the initial capture state to be $n = 16$. Even if direct transitions from $n = 16$ to the ground state would occur with high probability, the large x-ray intensity at energies above 2 keV, as seen in Fig. 3, could not be explained. We thus conclude that capture must also occur to states of much higher n than predicted by the OBM. If one includes Rydberg states up to $n = 33$, as well as bound doubly excited states in the same energy range, one indeed finds bound doubly excited states where the main decay channel leads to $\sim$2.1 keV photons. If, in addition, we assume that these states are populated with high probability (a factor of 4 higher than bound doubly excited states in the energy range comparable to $n = 16$), one gets the intensity represented by the full line and this explains quite well the measured spectrum. The explanation of the high energy side of the x-ray peak requires, without a doubt, a deviation from the OBM, since the responsible x-ray line has to have its peak intensity close to 2.1 keV. The binding energy difference between the $n = 33$ and $n = 16$ state is approximately 75 eV. The present data is sensitive to such shifts. A reason for the missing intensity at the high energy side of the peak in Fig. 2 could be a contribution of bound doubly excited states also existing in Ta^{46+}. A good calculation of the energy levels in the case of open shells ($3d^9nl$ and $3d^84l4l$) is, however, more demanding and will be the subject of future studies.

The energies for $4\ell5\ell'$ have also been calculated. It was found that the energies for these states are in the continuum and thus cannot contribute to the spectrum. This explains why the measured spectrum for Ta^{43+} shows only $n = 4$ to $n = 3$ (M_α) transitions, and the $n = 5$ to $n = 3$ (M_β) transitions are missing. It becomes clear from this comparison and discussion that the observed x-ray intensity produced by the bound doubly excited state is very sensitive to the n state populated in the capture. This is contrary to photoemission which results from the cascade of a singly excited state, where one is rather sensitive to the initial ℓ, as shown above.

A striking result is the high probability with which this mixing between Rydberg- and core-excited states occurs. This gives a huge cross section for inner-shell vacancy production. The probability for obtaining bound doubly excited states can be estimated from the data by neglecting contributions from these states for ions with initial M vacancies. The M x-ray intensity of the main peak, normalized per single capture event, provides the x-ray detection efficiency. We find, in fact, that this value compares well with the geometrical solid angle of the Si(Li) detector. We estimate that the probability for the formation of bound doubly excited states in single-electron capture of Ta^{43+} from He to be on the order of 0.3. From this probability, one obtains an M x-ray cross section of $\sigma_M = 6 \times 10^{-15}$ cm^2 by using the OBM cross section for single capture [16] of $\sigma = 2 \times 10^{-14}$ cm^2. A huge cross section for inner-shell vacancy production is thus obtained. This σ_M should not vary much with the ion energy (as σ does not), but should decrease with decreasing charge state as expected from a decreasing number of bound doubly excited states near the ionization limit. This was also observed in the experiment by changing q from 39 to 44.

In conclusion, we have observed, for the first time, an x-ray cascade after single-electron capture by very highly charged slow ions. We have found a large M x-ray intensity for incident ions that do not have an initial M vacancy. The theoretical interpretation suggests that the Rydberg electron excites, by a correlation effect, the strongly bound core, i.e., an M-shell electron into a bound doubly excited state. From energy resonance conditions, one derives an n, which the electron is captured into, that is higher than predicted by the classical overbarrier model. The probability for this process was found to be quite large, accounting for surprisingly high x-ray emission, for ions without inner-shell vacancies, and a very large cross section for inner-shell vacancy production.

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[1] See, e.g., *The Physics of Electronic and Atomic Collisions,* edited by Y. Itikawa *et al.,* AIP Conf. Proc. No. 500 (AIP, New York, 2000).
[2] Th. Weber *et al.,* Nature (London) **405**, 658 (2000).
[3] K. Dennerl *et al.,* Science **277**, 1625 (1997).
[4] N. Stolterfoht, Phys. Scr. **T46**, 22 (1993).
[5] P. Roncin *et al.,* J. Phys. B **26**, 4181 (1993).
[6] F. Fremont *et al.,* Phys. Rev. A **54**, R4609 (1996).
[7] M. A. Abdallah *et al.,* Phys. Rev. A **58**, 2911 (1998).
[8] A. Burgess, Astrophys. J. **141**, 1588 (1965).
[9] R. Schuch *et al.,* Phys. Rev. Lett. **70**, 1073 (1993).
[10] L. Kocbach *et al.,* Phys. Scr. **T73**, 311 (1997).
[11] E. D. Donets, Nucl. Instrum. Methods Phys. Res., Sect. B **9**, 522 (1983).
[12] J. P. Briand *et al.,* Phys. Rev. Lett. **65**, 159 (1990).
[13] M. Clark *et al.,* Phys. Rev. A **47**, 3983 (1993).
[14] U. Fano and W. Lichten, Phys. Rev. Lett **14**, 627 (1965).
[15] A. Niehaus, J. Phys. B **19**, 2925 (1986).
[16] N. Selberg *et al.,* Phys. Rev. A **54**, 4127 (1996).