Stabilized Hollow Ions Extracted in Vacuum

S. Ninomiya,[1] Y. Yamazaki,[1] F. Koike,[2] H. Masuda,[3] T. Azuma,[1] K. Komaki,[1] K. Kuroki,[4] and M. Sekiguchi[5,*]

[1]*Institute of Physics, University of Tokyo, Meguro, Tokyo 153, Japan*
[2]*Physics Laboratory, School of Medicine, Kitasato University, Sagamihara, Kanagawa 228, Japan*
[3] *Department of Industrial Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-03, Japan*
[4]*National Research Institute of Police Science, Chiyoda, Tokyo 100, Japan*
[5]*Institute for Nuclear Study, University of Tokyo, Tanashi, Tokyo 18, Japan*

(Received 30 December 1996)

K x rays emitted from 2.1 keV/u N^{6+} ions passed through a thin Ni microcapillary foil were measured in coincidence with the exit charge states. Ions with a *K* hole but with several electrons in outershells, i.e., hollow ions formed above a surface (in the first generation), were successfully extracted in vacuum. It was found that a considerable fraction of extracted hollow ions had extremely long lifetimes of the order of ns. [S0031-9007(97)03372-3]

PACS numbers: 34.50.Dy

The interaction of slow multiply-charged ions (MCIs) with solid surfaces has been intensively studied in recent years [1]. When an MCI approaches a surface, target valence electrons are expected to be resonantly transferred to highly excited states of the MCI. According to the classical over barrier (COB) model, the distance d_c for the resonant charge transfer to start is given by $\sqrt{2q}/W$, where q is the charge of the ion and W is the work function of the solid [2]. Such a multiply excited atom (ion) with many innershell vacancies formed above the surface will be referred to as a hollow atom in the first generation (HA1) hereafter. When the ion further approaches the surface, charge transfer channels to lower excited states open, and some of the electrons already in highly excited states are released in vacuum or returned to empty levels of the target. As the MCI gains some kinetic energy due to its image acceleration, the time interval between the HA1 formation and its arrival at the surface is limited to less than 10^{-14}–10^{-13} sec, which is possibly shorter than its intrinsic lifetime. In other words, an HA1 is in a nonstationary state forming a molecular orbital with the target, which may more suitably be called a "dynamic hollow molecule." At or below the surface, the valence electrons of the target dynamically screen the ion charge, and considerably promote the energy levels, which allows some shallow innershells to be filled via quasiresonant charge transfers or Auger transitions [3]. If the incident ion has holes at levels deeper than these shallow innershells, a hollow atom (ion) can still exist temporarily at or below the surface, which will be referred to as a hollow atom in the second generation (HA2) hereafter. The HA2 eventually decays to its ground state emitting x rays and/or Auger electrons.

Until now, the mainstream of experimental setups to study HA1s has been a combination of slow MCIs and flat surfaces, where MCIs are converted into HA1s near the surface, which are immediately and inevitably reconverted to HA2s at or below the surface. As is evident from this scenario, such an experimental setup has two major difficulties in studying HA1s, i.e., signals from HA2s are often much stronger than those from HA1s as has already been observed by Meyer *et al.* [4], and the survival times of HA1s are possibly too short for their intrinsic and stationary nature to be studied. In order to avoid these difficulties and to preferentially prepare HA1s by suppressing the production of HA2s, thin foils with straight multimicrocapillaries have been employed as targets [5–7], which allows the extraction of HA1s in vacuum and the observation of x rays emitted from them in flight. When MCIs impinge on the target along the capillary axis, they are attracted toward the capillary wall by the image force, and part of them approach the capillary wall with a distance less than d_c at a certain depth from the entrance surface, and are expected to capture electrons resonantly into their excited states, i.e., HA1s are formed as in the case of flat surface targets. If the locations of the HA1 formation are close to the exit of the capillary, they will be extracted in vacuum before they hit the capillary wall. Further, as the cross section of the real capillary varies microscopically along the capillary axis, each capillary has a bottleneck. When HA1s are formed near the bottleneck, part of them are expected to be extracted in vacuum, because the image force is appreciable only near the bottleneck, i.e., the deflection of the ion toward the wall is rather small. Because of a long interaction time, charge transfers through tunneling processes might also play a role. In any case, the ratio of ions which capture finite numbers of electrons to those transmitted is, in the first approximation, geometrically estimated to be $2d_c/r$, where r is the inner radius of the capillary.

In the present Letter, we show, for the first time, that a considerable fraction of extracted ions with a *K*-shell hole are extremely stabilized, though keeping as many as 4 electrons in outershells. We have suggested that spin-aligned states with less than half-filled shells are the

minimum requirements of the stabilization [6]. As any empty innershells are immediately filled by electrons from higher lying states irrespective of the spin alignment, no innershells of stabilized atoms (ions) can be completely empty. At the same time, if some outershells are more than half-filled, part of the electrons have spins in the opposite direction to the major spin direction, which immediately relax to innershells, i.e., all the active shells should be less than half-filled.

A 2.1 keV/u N^{6+} beam was extracted from a Hyper-ECR ion source at the Institute for Nuclear Study, University of Tokyo. The beam was collimated using a four-jaw slit and transported into a vacuum chamber which was evacuated down to $\sim 10^{-9}$ Torr [8]. A Ni microcapillary target was installed onto a manipulator, the thickness and the hole diameter of which were ~ 1.5 μm and ~ 250 nm, respectively, i.e., the interaction time of the ion with the capillary could be as long as $\sim 10^{-12}$ sec. The geometrical opening ratio of the target and the observed transmission ratio were $\sim 50\%$ and $\sim 15\%$, respectively. The difference between the observed and geometrical transmission ratio might be partly attributed to the image acceleration towards the capillary wall, finite beam divergence, nonuniform capillary diameter, etc. An electrostatic charge state selector was installed ~ 50 cm downstream from the target. X rays were measured with a Si(Li) x-ray detector without a window. A movable shield was inserted between the target and the detector, which varied the detection region to determine the lifetimes of N K hole in flight. Further details of the experimental setup are given in Ref. [6].

It was found that $\sim 1\%$ of the ions transmitted through the capillary captured at least one electron, which is in accord with the expected ratio $2d_c/r \sim 1.4\%$. Figure 1 shows an example of the charge state distribution $f(q_f)$ of the transmitted nitrogen ions as a function of the final charge state q_f. As the exit charge state q_f decreases, the corresponding ion fraction gradually decreases, which is quite different from that observed for specularly reflected ions [9,10,11] and foil transmitted ions [12] in a similar energy range. For example, in the case of glancing scattering of 3.75 keV/u O^{8+} at an Au(110) surface [9], $\sim 90\%$ of the reflected particles are neutralized, and $f(q_f)$ decreases drastically as q_f increases for $q_f \geq 0$. The time necessary to neutralize MCIs at less than ~ 2Å from the surface is evaluated to be ~ 30 fs [13], which indicated that the major part of the charge transferred ions observed in the present study suffered only distant collisions with the target surface. It is then known that the capillary foil is an effective and unique material supplying some limited number of electrons keeping the charge state distribution away from its equilibrium. Since the transmitted ions reach the charge state analyzer $\sim 10^{-6}$ sec after they interact with the target, the ions in the analyzer are expected to have relaxed to their ground states via emission of Auger electrons and/or x rays, i.e., the charge state of the ion at the moment of the charge transfer is equal to or lower than the observed one. In the case of a gaseous C_{60} target, electron removal cross sections $\sigma(q_f)$ are found to show a similar weak dependence on q_f, which could be another way to limit the number of electrons transferred [14,15]. In the case of C_{60}, however, ions capturing multiple electrons via a distant collision (COB-like process) eventually hold only a few electrons, which is compared with the present observation, where ions holding several electrons were effectively produced via distant collisions as discussed above. Such a distinct difference is probably due to the large difference of the interaction time between the capillary target and C_{60} target ($\sim 10^{-15}$ sec). In the latter case, charge changing Auger relaxations take place after the termination of the interaction, while in the former case, the relaxations proceeded in parallel with the interaction, where additional electrons are supplied when necessary.

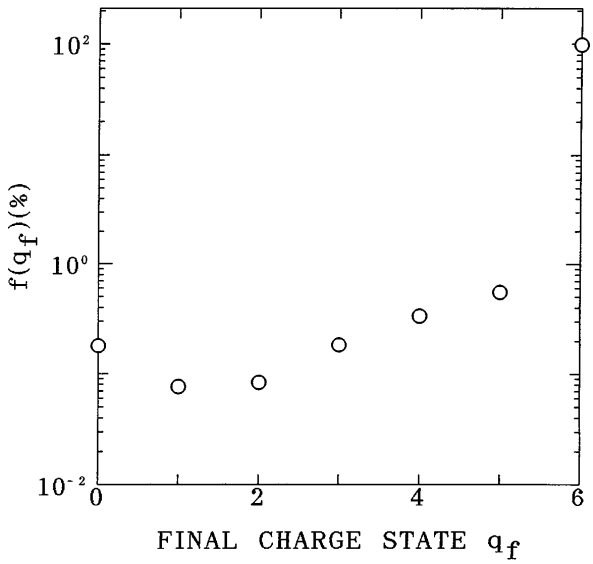

FIG. 1. The charge state distribution $f(q_f)$ of 2.1 keV/u N^{6+} ions transmitted through the Ni capillary. The fractions are not compensated for q_f-dependent angular distributions, i.e., lower charge fractions which showed wider angular distributions may be slightly higher than plotted.

K x rays of N ions were measured in coincidence with the final charge state q_f of the transmitted ions. The lifetimes of the K-shell hole of transmitted ions were determined with measurements of "integrated delayed x-ray yield," the intensity of which is given by $\eta(t_d, q_f) = \eta(x/v, q_f) = \int_{x/v}^{\infty} \zeta(x'/v, q_f) d(x'/v)$, where $\zeta(x'/v, q_f)$ is the differential x-ray intensity correlated with q_f at x' from the target along the ion path and v the projectile velocity [6]. It is noted again that the charge state measured is equal to or higher than that at the moment of the x-ray emission. The triangles ($\triangle$), circles ($\bigcirc$), squares ($\square$), and diamonds ($\diamond$) in Fig. 2 show integrated delayed x-ray yields $\eta(t_d, q_f)$ normalized per

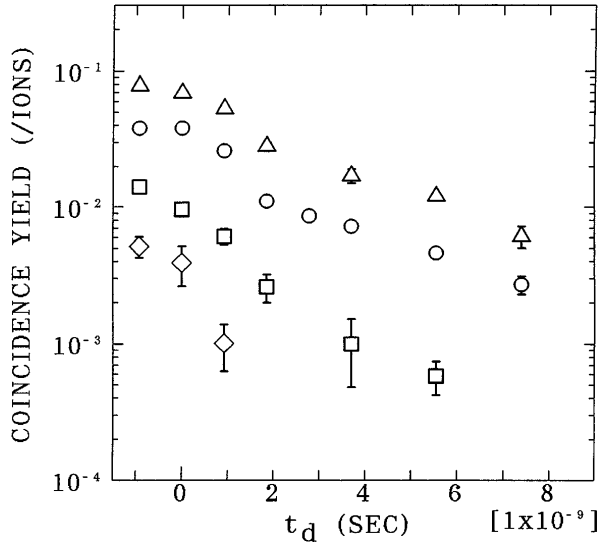

FIG. 2. The integrated delayed x-ray yields, $\eta(t_d, q_f)$ normalized per one N^{q_f+} ion; $q_f = 5$ (△), 4 (○), 3 (□), and 2 (◇).

N^{q_f+} ion with $q_f = 5$, 4, 3, and 2, respectively, assuming isotropic x-ray distributions. The time resolution of this measurement was ~1 ns. As has already been reported for Ne^{9+} ions [6], a considerable fraction of the transferred ions with a K-shell hole are in extremely stabilized states. The yields of the delayed K x rays for $q_f = 5$, 4, 3, and 2 were ~8%, ~4%, ~1%, and ~0.5%, respectively. On the other hand, conincidences were barely visible for $q_f = 1$ and 0 within the experimental accuracies, e.g., the yield for $q_f = 0$ at $t_d = 0$ was $(5.5 \pm 3.5) \times 10^{-4}$. The $q_f = 0$ component was measured setting a channeltron at 0°, deflecting all charged components by the analyzer. It can be seen that (i) the x-ray emission from the stabilized states was observed not only from a few electron systems but also from multielectron systems [e.g., a 5-electron system ($q_f = 2$)], and (ii) the decay curves of the N K-shell hole depended only weakly on the final charge state, and consisted of at least two components for $q_f = 5$, 4, and 3. The lifetimes of the longer components were ~4, ~4, and ~2.5 ns for $q_f = 5$, 4, and 3, respectively, which are several orders of magnitude longer than typical lifetimes of a N K hole with filled L shell. It is known that the ions with a K-shell hole observed here are strongly correlated with HA1s produced via COB-like processes above the surface (distant collisions).

Figure 3(a) shows the K x-ray spectrum for 2.1 keV/u N^{6+} interacting with a flat A1 target with its surface normal at ~20° to the beam. The peak energy is observed at ~390 eV, which is consistent with the tabulated value of 392 eV, which corresponds to the transitions from a filled L shell. The energy spectra, $d\eta(t_d, q_f)/dE$ at $t_d = 0$ ns for $q_f = 5$, 4, and 3 are shown in Fig. 3(b). The spectral shapes and peak energy positions are similar to each other. Figure 3(c) shows

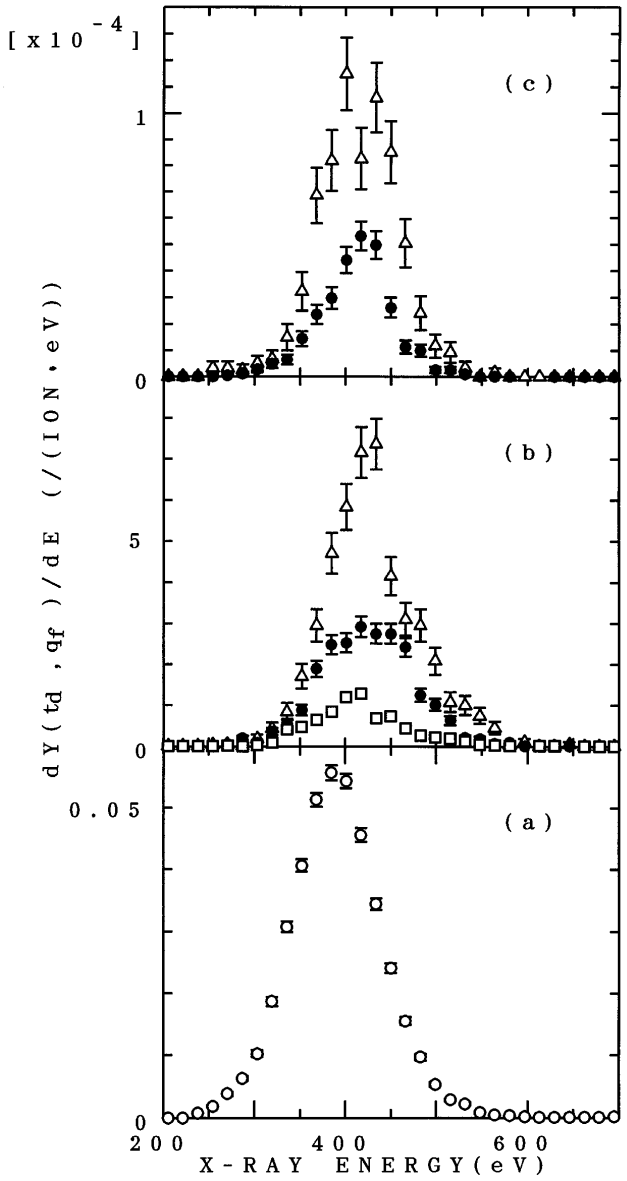

FIG. 3. Energy spectra of N x rays (a) interacting with a flat A1 target with its surface normal at ~20° to the beam, (b) interacting with a Ni microcapillary $d\eta(t_d, q_f)/dE$ at $t_d \sim 0$ ns for $q_f = 5$ (△), 4 (●), and 3 (□), and (c) $d\eta(t_d, q_f)/dE$ at $t_d \sim 6$ ns for $q_f = 5$ (△), 4 (●).

$d\eta(t_d, q_f)/dE$ for $q_f = 5$ and 4 at $t_d \sim 6$ ns , i.e., the x-ray energy spectra belonging to the transitions of the longer lifetime components. The peak energy of $d\eta(t_d, q_f)/dE$ is ~420 eV for all t_d and q_f studied, which is ~30 eV higher than that for the flat A1 target, i.e., the number of L-shell electrons is very small, independent of t_d and q_f. It is noted that the higher energy tails (≥500 eV) which correspond to transitions from higher excited states ($n \geq 3$) are visible in Fig. 3(b) but not in Fig. 3(c), i.e., such transitions have relatively short lifetimes.

Decay curves of the x rays observed here strongly indicate that the configurations of the excited states are in spin-aligned metastable states. Once the spin-aligned states are formed with some electrons in each shell, both radiative and Auger transitions are induced only via spin-flip processes, which are larger for lower excited states with a finite orbital angular momentum. It is then reasonable that the relative x-ray intensities from $n \geq 3$ in Fig. 3(c) are much weaker than those in Fig. 3(b). In a very simple argument that the spins of captured electrons have random directions, the probability of having the highest spin multiplicities, i.e., the probability of getting stabilized hollow atoms (ions), is proportional to 2^{-n}, where n is the total number of electrons captured. The q_f dependences of $\eta(t_d, q_f)$ shown in Fig. 2 are more or less consistent with this expectation. For further discussion, one should know the fluorescence yield for each stabilized state.

Theoretical predictions on transition energies and their lifetimes indicate that the long lifetime component for $q_f = 5$ is $1s2p\,^3P_1$, which decays to $1s^2\,^1S_0$ emitting a 424 eV x ray with a lifetime of 4.4 ns. In the case of $q_f = 4$, the most probable candidate of the stabilized state is $1s2s2p\,^4P_{3/2}$, which decays to $1s^22s\,^2S_{1/2}$ emitting a 413 eV x ray [16] with a lifetime of 5.4 ns [17]. These identifications are the same as those for Ne^{9+} on an Al_2O_3 capillary discussed in Ref. [6]. Possible candidates for the short lifetime component for $q_f = 4$ are $1s2p^2\,^4P_{1/2,3/2}$, which have lifetimes of $\sim$2 ns emitting 414 eV x rays [18]. Although we do not have theoretical predictions at hand for $q_f \leq 3$, observed transition energies and lifetimes strongly suggest that (1) the number of L-shell electrons are similar to those for $q_f \leq 4$, and (2) the rest of the electrons are in highly excited states which have little influence on the lifetimes of the stabilized L-shell electrons.

In summary, stabilized hollow ions with lifetimes of the order of ns were extracted in vacuum, employing a combination of a microcapillary foil and slow multiply-charged ions. The final charge state distribution of the capillary-transmitted ions shows that the capillary foil is a unique material supplying some limited but finite number of electrons. Comparisons of the lifetimes and transition energies with theoretical evaluations reveal that the stabilized states are attributed to spin-aligned less than half-filled states. The present technique could be a powerful new tool for spectroscopy of metastable states with deep innershell holes, which may be referred to as beam capillary spectroscopy.

We thank Ann Currell for her careful reading of and making suggestions about the manuscript. The research is supported by a Grant-in-Aid for Scientific Research on Priority Area, Atomic Physics of Multiple Charged Ions (05238103) and by a Grant-in-Aid for Developmental Scientific Research (07555006) from the Ministry of Education, Science and Culture.

*Present address: Center for Nuclear Study, School of Science, University of Tokyo, Tanashi, Tokyo 188, Japan.

[1] J.-P. Briand *et al.*, Phys. Rev. Lett. **65**, 159 (1990); H. Winter, Europhys. Lett. **18**, 207 (1992); H. Kurz *et al.*, Phys. Rev. Lett. **69**, 1140 (1992); J. Das and R. Morgenstern, Phys. Rev. A **47**, R755 (1993); F. W. Meyer *et al.*, Phys. Rev. A **48**, 4479 (1993); M. Grether *et al.*, Phys. Rev. A **52**, 426 (1995).

[2] J. Burgdörfer, P. Lerner, and F. W. Meyer, Phys. Rev. A **44**, 5674 (1991).

[3] J. Burgdörfer, C. Reinhold, and F. Meyer, Nucl. Instrum. Methods Phys. Res., Sect. B **98**, 415 (1995); J. Limburg *et al.*, Phys. Rev. A **51**, 3873 (1995); A. Arnau *et al.*, Phys. Rev. A **51**, R3399 (1995); M. Grether *et al.*, Phys. Rev. A **52**, 426 (1995); R. Díez Nuiño *et al.*, Phys. Rev. Lett. **76**, 4636 (1996).

[4] F. W. Meyer *et al.*, Phys. Rev. Lett. **67**, 723 (1991); F. W. Meyer, C. C. Havener, and P. A. Zeijlmans van Emmichoven, Phys. Rev. A **48**, 4476 (1993).

[5] H. Masuda and K. Fukuda, Science **268**, 1466 (1995); H. Masuda and M. Satoh, Jpn. J. Appl. Phys. **35**, L126 (1996).

[6] Y. Yamazaki *et al.*, J. Phys. Soc. Jpn. **65**, 1199 (1996).

[7] S. Ninomiya *et al.*, Phys. Scr. (to be published); Y. Yamazaki, Phys. Scr. (to be published).

[8] S. Ninomiya *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. B **115**, 177 (1996).

[9] F. W. Meyer, L. Folkert, and S. Schippers, Nucl. Instrum. Methods Phys. Res., Sect. B **100**, 366 (1995).

[10] N. Hatke *et al.*, Nucl. Instrum. Methods Phys. Res., Sect. B **115**, 165 (1996).

[11] S. T. de Zwart *et al.*, J. Phys. B **18**, L623 (1985).

[12] D. Wickholm and W. S. Bickel, J. Opt. Soc. Am. **66**, 502 (1976).

[13] L. Folkert *et al.*, Phys. Rev. Lett. **74**, 2204 (1995).

[14] B. Walch *et al.*, Phys. Rev. Lett. **72**, 1439 (1994); B. Walch *et al.*, in VIth International Conference on The Physics of Highly Charged Ions, edited by P. Richard, M. Stoeckli, C. L. Cocke, and C. D. Lin, AIP Conf. Proc. 274 (AIP, New York, 1993).

[15] J.-P. Briand *et al.*, Phys. Rev. A **53**, R2925 (1996).

[16] M. H. Chen, B. Crasemann, and H. Mark, Phys. Rev. A **27**, 544 (1983).

[17] B. F. Davis and K. T. Chung, Phys. Rev. A **39**, 3942 (1989).

[18] M. H. Chen, B. Crasemann, and H. Mark, Phys. Rev. A **26**, 1441 (1982).