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The role of radiative de-excitation in the neutralization process of highly charged ions interacting with a single layer of graphene

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Abstract

X-ray emission of slow (< 1 a.u.) highly charged Argon and Xenon ions is measured for transmission through a freestanding single layer of graphene. To discriminate against X-ray emission originating from the graphene's support grid a coincidence technique is used. X-ray emission of 75 keV Ar^{17+} and Ar^{18+} ions with either one or two K-shell vacancies is recorded. Using a windowless Bruker XFlash detector allows us to measure additionally Ar KLL and KLM Auger electrons and determine the branching ratio of radiative vs. non-radiative decay of Ar K-shell holes. Furthermore, X-ray spectra for 100 keV Xe^{22+}-Xe^{35+} ions are compared, showing a broad M-line peak for all cases, where M-shell vacancies are available. All these peaks are accompanied by emission lines at still higher energies indicating the presence of a hollow atom during X-ray decay. We report a linear shift of the main M-line peak to higher energies for increasing incident charge state, i.e. increasing number of M-shell holes.

Keywords: slow highly charged ions, graphene, X-ray emission

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1. Introduction

The interaction of slow ($v << v_0$ … Bohr velocity) highly charged ions (HCI) with solid surfaces leads to charge exchange between the target and the projectile followed by the de-excitation of the ion during and after the interaction process. Already at a distance of several Ångström from the surface the ion starts to capture electrons into highly excited Rydberg states well explained in the classical over-the-barrier model [1]. Thus, an almost neutralized projectile with empty inner shells, a so-called "hollow atom", is formed. Studies of the charge state of slow highly charged ions after the transmission through 5 nm thin carbon films [2] showed exit charge states of the projectiles far away from their equilibrium charge state. By evaluating the mean number of the exit charge state distribution as a function of the projectile velocity the authors of [2] could derive a charge equilibration time of less than 7 fs. A generally excepted model describing the de-excitation processes of hollow atoms exists since more than 20 years [3], although some open questions regarding a too slow de-excitation cascade remained (e.g. [4,5]).

Recently performed experiments using target materials of only 1 nm thickness [6–8] or the ultimate thin target graphene [9] brought up this "bottleneck problem" in the understanding of the observed fast de-excitation of a hollow atom again. By studying the electronic response of a freestanding single layer of graphene (SLG) to the large external field of an approaching HCI an almost complete neutralization of the ion within a few femtoseconds could be concluded [9]. In this short timeframe dozens of electrons are not only transferred from the target to the projectile, but also stabilized in the ground state of the ion, i.e. not lost by auto-ionization. The step by step de-excitation cascades presented in [3] to explain the de-excitation process of the hollow atom would be far too slow. Auger/autoionization rates in the order of 10^{16}-10^{17} s^{-1} would be required to reach the observed neutralization within femtoseconds. Therefore the model had to be refined and the interatomic coulombic decay (ICD) [10] process was proposed [11] as the responsible process for the observed fast de-excitation of a HCI. In the suggested model electrons from high Rydberg states are quenched into low core states of the projectile while the released energy is transferred to electrons of the surrounding target. The ICD process gives rise to the emission of valence electrons into the continuum originating from next neighbouring or even next-nearest neighbouring atoms of the target [11]. However, so far it is

not clear whether the ICD process directly populates the ground state or just low lying excited states, which still have to decay by X-ray or Auger emission.

For inner-shell transitions Auger rates increase to 10^{14}-10^{15} s^{-1} as well as radiative transition rates for K and L-shell filling of up to 10^{14} s^{-1} are possible. As soon as holes in the L, M and N shell are filled, radiative and non-radiative processes become likely to contribute in the very last steps of the neutralization process. In the present work we therefore measure X-ray and Auger electron emission for hydrogen like and bare Ar ions from SLG and estimate the branching ratio of these two competing channels. A slight predominance of emitted Auger electrons is found for both cases. The measured X-ray spectra are compared with atomic structure code calculations [12,13] as well as with experimental data recorded for Argon ions interacting with metal surfaces [14]. To further study the radiative de-excitation channel X-ray emission resulting from the impact of highly charged Xenon ions on the graphene sample are presented.

2. Experimental Setup

The measurements were performed at the Ion Beam Center of the Helmholtz-Zentrum Dresden-Rossendorf, where highly charged ions are produced in a room-temperature electron beam ion trap (EBIT) [15]. An analyzing magnet is used for charge state separation of the extracted ion beam, which is focused into the target chamber by electrostatic lenses. Inside the experimental chamber an electrostatic analyzer with an energy resolution of $\Delta E/E=1.5*10^{-3}$ and an acceptance angle of 1.6° is mounted for charge state and energy loss measurements of the projectiles after the transmission through thin target samples. After passing the electrostatic analyzer the ions as well as neutral particles are counted in two different channeltrons. Close to the interaction region of the ion beam with the target a windowless Bruker XFlash silicon drift detector is mounted for measuring emitted X-rays as well as Auger electrons with energies above 500 eV. The detector has an energy resolution of ΔE=140 eV at 5.9 keV and is calibrated by using Mn-K_α and Mn-K_β emission lines of a mounted ^{55}Fe source. Figure 1 shows a sketch of the described experimental setup.

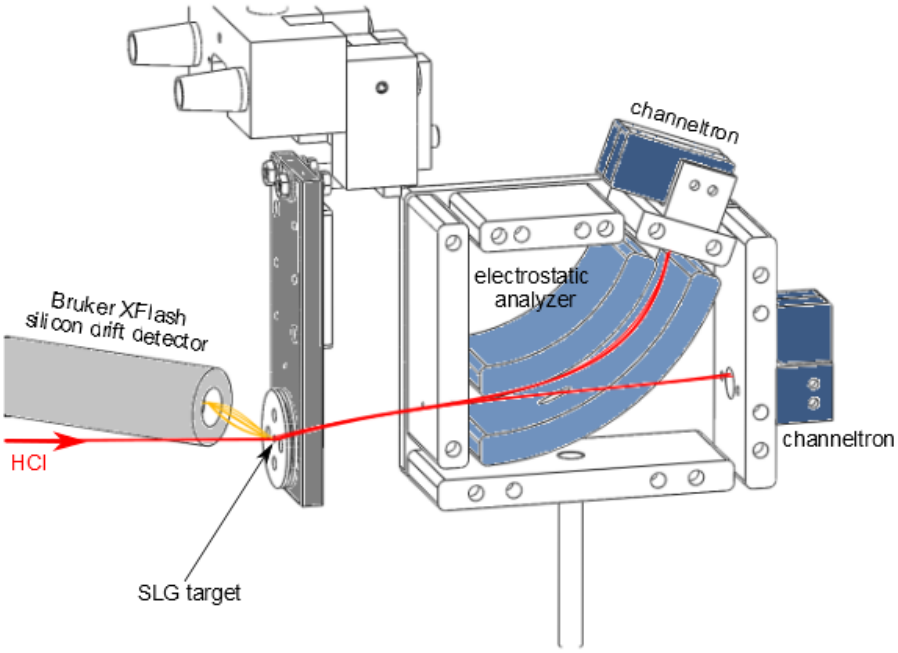

Figure 1: Sketch of the experimental setup. The collimated ion beam is passing the sample, mounted on the rotatable target holder, before it enters the electrostatic analyzer and hits one of the channeltrons.

To discriminate X-rays and electrons emitted from ions interacting with the target support a coincidence technique is used. This ensures that only a signal at the X-ray detector is recorded if there is a corresponding ion signal registered at the channeltron after transmission through the monolayer film.

Freestanding SLG samples of high quality were fabricated at the University of Duisburg-Essen. Commercially available graphene (Graphenea) grown via chemical vapour deposition (CVD) on a copper foil was placed on a transmission electron microscopy (TEM) grid with an additional Quantifoil support on top. The copper foil was removed by etching and remaining contaminations were eliminated by heating the samples at 260 °C in active carbon (for more details see [16]).

3. Results

The SLG sample was irradiated with 75 keV Ar^{17+} and Ar^{18+} projectiles as well as 100 keV Xe^{22+}-Xe^{35+} ions. X-ray emission spectra were recorded in coincidence with projectiles transmitted through the monolayer graphene target.

The emission spectrum of slow hydrogen like Ar^{17+} ions interacting with a graphene sheet is presented in figure 2. The filling of one K-shell vacancy results in peaks in the X-ray spectrum between 2800 eV and 4000 eV. Assuming a Gaussian shaped detector function with a full width of half maximum (FWHM) of 140 eV (energy resolution of the Bruker XFlash detector) the observed spectrum can be very well reproduced by atomic structure code calculations performed by Bhalla [12]. For various electronic configurations of the Ar ion (i.e. population of excited states in the L, M and higher shells) shifts in the K_α and K_β emission energies have been calculated as well as the relative intensities of these lines. Comparison with our experimental data indicates that the filling of the K-shell occurs while some vacancies in the L- and M-shell of the Ar ion are still present. X-ray emission for the interaction of Ar^{17+} with a Be sample has previously been measured by Schenkel et al. [14] using a calorimeter detector. The comparison of these results with the presented data shows almost no differences in whether a 3D solid or only a monolayer thick target is used, apart from a small broadening of the K_α peak towards lower energies in case of the SLG target. Our data indicate that the radiative de-excitation of the initially highly charged Ar ion occurs before the filling of the L-shell is complete. According to [12] the main peak of the spectrum at 3006 eV would correspond to about 3 L-shell holes present during the 2p → 1s transition.

Since a windowless silicon drift detector is used for the X-ray measurements also electrons with energies above 500 eV can be registered, which otherwise would be unable to pass a Be window at the entrance of the detector. Emitted Ar KLL and KLM Auger electrons due to the de-excitation process of the HCI can be seen in figure 2 as a broad distribution above the noise level and below 2800 eV. The KLL and KLM Auger electron emission results in a multiple peak structure with energies between 2506 eV and 2926 eV [17], which can no longer be resolved as sharp lines due to energy loss and straggling of electrons in the dead layer of the detector.

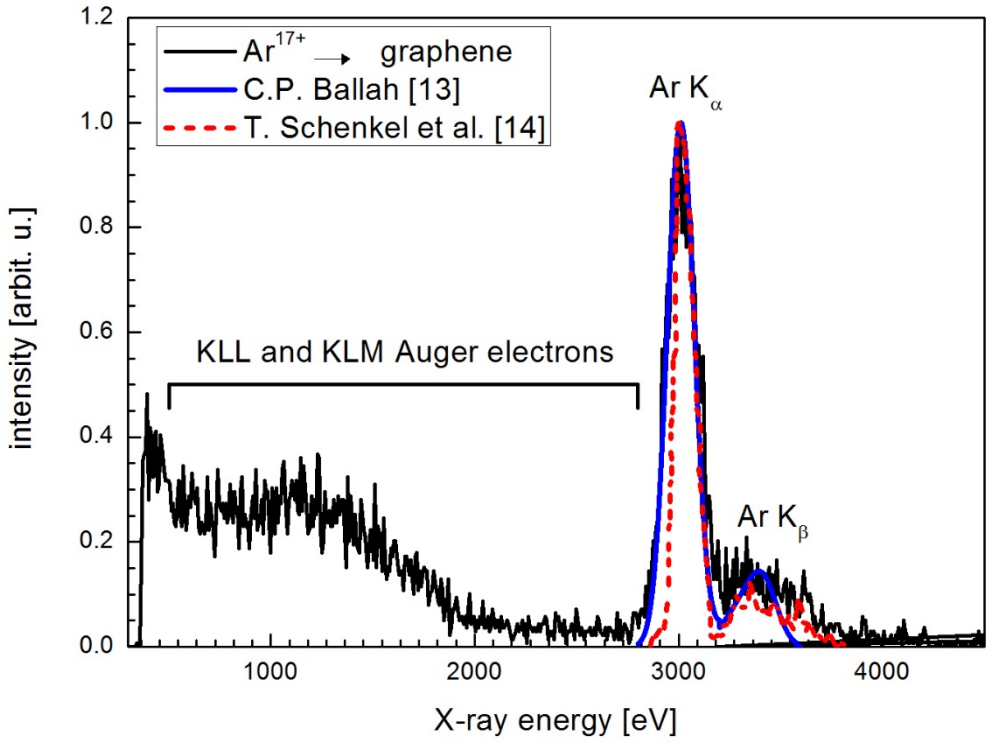

Figure 2: X-ray, KLL and KLM Auger electron emission spectrum following slow H-like Ar^{17+} ions traversing a SLG. The measured X-ray spectrum (black solid curve) is compared with atomic structure code calculations [12] (blue curve) and with recorded X-ray emission resulting from slow Ar^{17+} ion impact on a Be target [14] (red broken curve).

If we assume a Moyal distribution for the energy loss of these electrons, which is the analytic approximation for the Landau distribution describing energy loss of particles traversing thin targets [18,19], we can at least estimate the integral number of Auger electrons from a fit to the electron energy distribution. The ratio between radiative and non-radiative filling of one K-shell hole can subsequently be determined. In case of the presented data in figure 2 the branching ratio between these two competitive de-excitation processes is found to be $\partial = \frac{\gamma_{KLL/KLM}}{\gamma_{X-ray}} \approx 1.65$, if we assume an equal detection efficiency for X-rays and electrons with $\gamma_{KLL/KLM}$ and γ_{X-ray} as the KLL+KLM-Auger and K_α+K_β yields, respectively. Comparing our result with the data provided by [12] we determine an electronic configuration of about 5 electrons in the L-

shell during the radiative transition. This is well in agreement with X-ray emission from 3D solid targets reported so far [14,20,21] with a K_α mean energy of about 3006 eV.

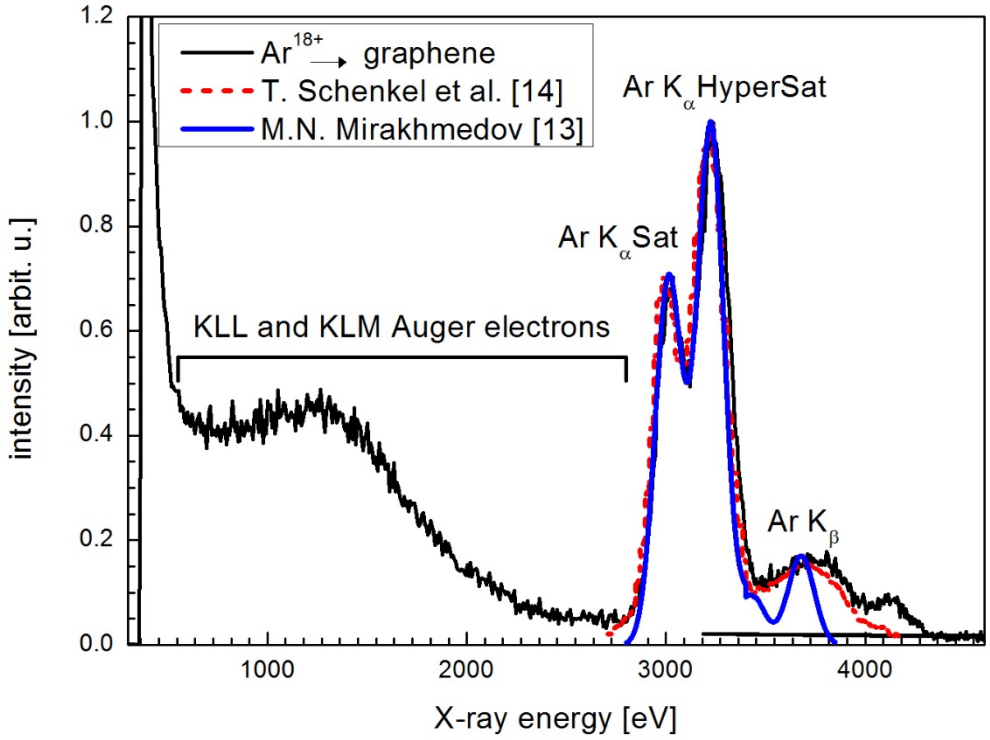

Figure 3: X-ray, KLL and KLM Auger electron emission recorded for bare Ar^{18+} ion impact on SLG. The measured X-ray spectrum (black solid line) is compared with tabulated radiative transition amplitudes for Ar^{18+} impact on metal surfaces [13] (blue curve) and measured data for Ar^{18+} impact on Be [14] (red broken curve).

Figure 3 shows our measured X-ray, KLL and KLM Auger electron spectrum recorded for the interaction of 75 keV bare Ar^{18+} ions with a single layer graphene. The stepwise filling of the two present K-shell vacancies can clearly be seen in the K_α hypersatellite spectrum with pronounced peaks at 3236 eV and 3018 eV, corresponding to configurations with two K-shell and about 5 L-shell holes (3236 eV) and one K-shell and about 3 L-shell holes (3018 eV) [13]. The third dominant peak at an energy of 3730 eV can be attributed to the filling of the K-hole with electrons from the M-shell at the presence of an empty L-shell [13]. The presented data is

compared with data from Schenkel et al. [14] for bare Ar^{18+} ions interacting with a Be target. Convoluting the radiative transition amplitudes tabulated by Mirakhmedov [13] with Gaussian detector functions (FWHM of 140 eV) and summing all received Gaussians up shows a good agreement between our results and the tabulated values (blue line).

Besides the three most intensive groups of satellites corresponding to two K_α transitions in configurations with either one or two K-shell holes and K_β transition in an ion configuration with two K-shell vacancies, an additional pronounced peak at higher energies has been recorded. This peak at an energy of 4130 eV was neither reported by [14] nor calculated in [13] for ion interaction with metal surfaces. Zhao et al. [22] compares X-ray emission following from the interaction of slow bare Ar ions with residual gas atoms with the one resulting from the interaction with a beryllium surface. While interacting with gas atoms only a few electrons are transferred to the projectile, which leads to higher transition energies due to less screening of less present spectator electrons in the L, M and N shell during the transition. For this case the authors report $K_{\gamma,\sigma}$ energies above 4100 eV, which they cannot find in the spectrum following from the interaction with the metal surface [22]. A possible explanation for the observed peak at 4130 eV in our measurements could be that also the two-dimensional target presents a limited electron supply for the incoming ions similar to the interaction with gas atoms. Less screening electrons lead to transitions at higher energies resulting in the observed X-ray emission at 4130 eV in our spectrum. Graphene therefore seems to be an intermediate case between a 3D solid and a gas target.

The branching ratio between all radiative and the non-radiative de-excitation (E< 2800 eV) for bare Ar ions interacting with a SLG target was found to be $\partial = \frac{\gamma_{KLL/KLM}}{\gamma_{x-ray}} \approx 1.82$. Again, a Moyal distribution for receiving the fraction of emitted K-Auger electrons was assumed [19].

In order to study the influence of the incident charge state of the projectile X-ray emission resulting from the filling of M-shell vacancies in Xe^{q+} ions was measured for different numbers of M-shell vacancies. The kinetic energy of the ions was kept at a constant value of 100 keV to avoid a change in the interaction time of the projectiles with the SLG target. In figure 4 X-ray spectra for Xe projectiles with 0, 1, 4, 7 and 9 M-shell vacancies impinging on a monolayer

graphene target can be seen. An energy shift of the main peak, which can be assigned to transitions of N-shell electrons into M-shell vacancies, with increasing incident charge state towards higher energies can be observed. The broad distribution of these M X-ray lines originates from the multitude of electronic configurations being present at the moment the transition occurs [23]. The main peak centred at 780 eV in the case of Xe^{27+} can be attributed to 4f → 3d transitions. The less likely transitions 4p → 3d result in a shoulder on the low energy side of the main peak, becoming more and more visible (but also shifting) with increasing incident charge state.

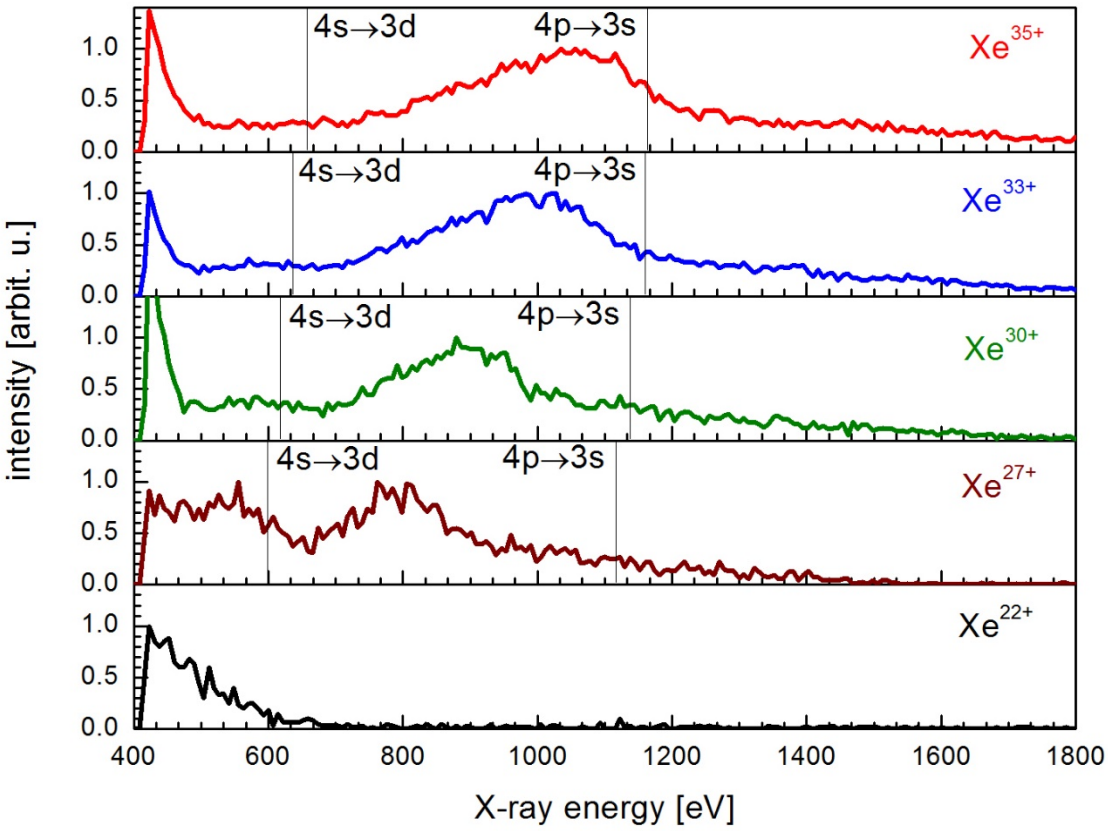

Figure 4: X-ray emission resulting from filling of M-shell vacancies (main peak) and high energy tail of N-shell filling (above noise and below 700 eV) for Xe ions at 100 keV with 0, 1 ,4 ,7 and 9 M-shell holes. High energy tail of main peak due to electron transitions from $n > 4$ levels into M-shell vacancies.

The X-ray spectrum recorded for Co-like Xe^{27+} ion impact on SLG shows a second dominant peak at an energy of 510 eV. Considering a lack in the detection efficiency for energies below 500 eV the assumption of this peak being the high energy tail of the broad N-shell X-ray lines seems reasonable. This tail is also present in the recorded X-ray spectrum of Xe^{22+} ion where no M-shell lines are visible. These transitions may also occur in the case of higher incident charge states but are compared to the M-shell filling less pronounced. A broad high energy tail of the main peak in the spectra can also be seen in figure 4 as a monotonically decrease from 0.9 keV to 1.5 keV and from 1.2 keV to 2.2 keV for Xe^{27+} and Xe^{35+} ions, respectively. These M-shell lines with their high energy tail have already been reported for the interaction of slow Xe ions with Ge and Si targets [24], indicating the presence of a hollow atom during the X-ray transition. Since in all spectra with initial M-shell vacancies in figure 4 transitions at higher energies than the 4p → 3s transition (shifting of energy levels with increasing charge state) are still present, high *n* shell transitions (e.g. 30f → 3d) have to be taken into account. With this strong evidence the presence of a hollow atom during the X-ray transition cannot be neglected but the observed monotonically decrease and the dominance of 4f → 3d transitions indicates that the main fraction of the radiative de-excitation of the ion happens after a large amount of inner shell vacancies are already filled.

A shift of the main peak towards higher energies with increasing charge states (increasing number of M-shell vacancies) can be clearly seen in figure 4 and is further remarked in figure 5. A linear increase of 30 eV per additional M-shell vacancy is found. This shift to higher energies indicates that the average number of spectator electrons at the time of the transition decreases with the increase of M-shell vacancies.

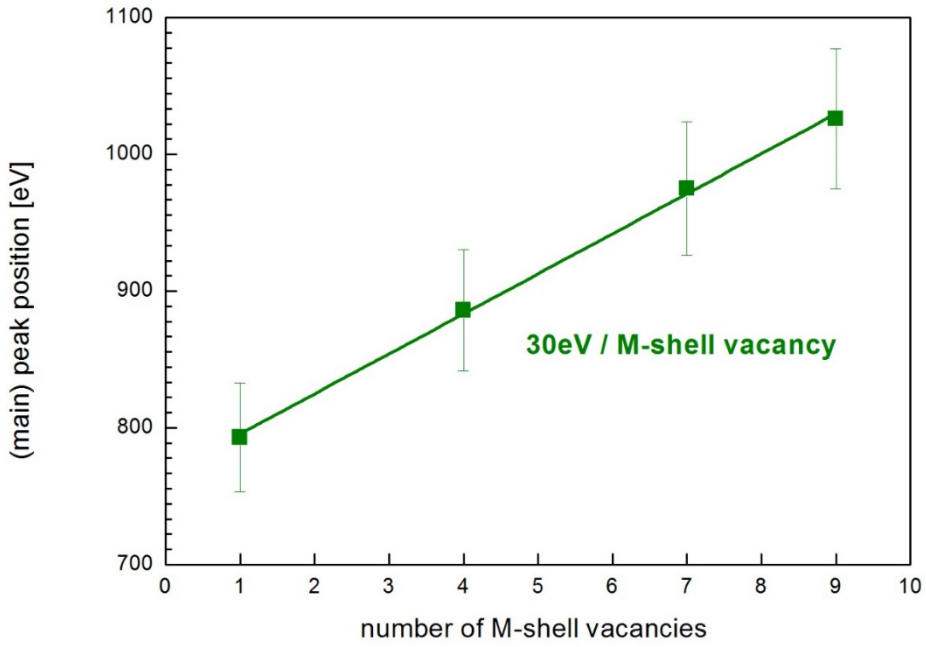

Figure 5: Linear increase of M-shell X-ray emission energy for increasing incident Xe^{q+} charge state. The main peak (4f → 3d) energy shifts about 30 eV towards higher energies for every additional M-shell vacancy.

4. Discussion and Conclusion

X-ray emission as a possible de-excitation channel for slow highly charged Ar^{q+} and Xe^{q+} interaction with only a single layer of carbon atoms was studied. The observed X-ray emission energies and intensities are well in agreement with emitted X-rays following ion impact on metal solid surfaces. The observed data for Ar X-ray emission are very well reproduced by atomic structure code calculations found in literature, estimating electronic defect configurations of the projectile with specific intensities at the moment of the X-ray emission. However, for Ar^{18+} impacting on a freestanding graphene target additional transitions from higher shells into K-shell vacancies could be found. X-ray emission at these energies were not reported for interaction with beryllium surfaces but for the interaction with gas atoms. Hence, the monolayer of single carbon atoms seems to represent the expected connecting link between 3D solid targets and isolated atoms in a binary collision picture. Measured transitions

of electrons from highly excited states into M-shell vacancies inside a Xe ion projectile indicates the presence of a hollow atom during the X-ray emission. Therefore, the radiative decay constitutes also in the interaction with only a monolayer target a possible de-excitation channel for a slow highly charged ion. Even though transitions of electrons captured into highly excited Rydberg states and directly de-excited into inner shell vacancies do exist, the radiative decay cannot be considered as the main contribution in the de-excitation process of a HCI. It has to be emphasized that the majority of X-ray transitions occur in a late state of the de-excitation process in which many inner shell vacancies are already filled. The proposed ICD process in [11] leads to the de-excitation of a large amount of electrons from highly excited states into core holes of the projectile in less than 10 fs . Such a fast process is not 100% efficient and a few inner shell vacancies may be left unfilled. These holes may then be filled by either a short Auger electron emission cascade or via radiative decay resulting in the here presented emission spectra.

Acknowledgments

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