On the highly charged ion transmission spectroscopy applied to 2D materials

Richard A. Wilhelm
TU Wien, Institute of Applied Physics, Wiedner Hauptstr. 8-10/E134, 1040 Wien, Austria, EU
E-mail: wilhelm@iap.tuwien.ac.at

Abstract. The interaction of ions with solid materials may lead to charge exchange. Previous results show that charge exchange is confined to the uppermost surface layers of a solid or to the thickness of a freestanding 2D material, even when initially highly charged ions are used. Several processes are active during charge exchange and a clear distance or impact parameter dependence is observed. Here I show, that highly charged ion transmission can be used to determine the material structure of 2D materials especially when atomically resolved electron microscopy cannot be applied. The method is based on measurement of energy-, charge-, and angle-resolved ion transmission spectra in coincidence and a comparison with a local model for a time-dependent change in the projectile's electron occupation and consequently the scattering potential. Also necessary experimental procedures are discussed.

1. Introduction
The elastic and inelastic scattering of photons and charged particles is used in many different techniques for surface and bulk material characterizations [1, 2]. In angle-resolved photoelectron spectroscopy the absorption of photons leads to the emission of electrons and their angle-vs-energy spectrum reveals the material band structure [3]. Electron illumination of surfaces leads to electron emission used in secondary electron microscopy for image generation and the emission of characteristic electron energies due to an inner-shell Auger transition is used for elemental mapping in scanning Auger spectroscopy [4, 5]. Many more variations of electron and photon scattering techniques are used for a plethora of analytical purposes.

Elastic and inelastic ion scattering are also used in quantitative material analysis, i.e. low and medium energy ion scattering, Rutherford backscattering spectrometry, elastic recoil detection, particle induced x-ray and gamma ray emission and many more. However, in all established methods only the particle's energy, mass and/or angle of incidence (or angle of emission) is used for analysis. Heavy ions posses another degree of freedom: their charge state. Here I show, that the ion charge state and charge exchange is not just an obstacle when stopping forces are to be evaluated, but can in fact be used for sub-nm porosity determination in ultrathin materials. The recently emerged collection of organic and inorganic 2D materials contains different possible crystallographic phases, grain sizes and orientation, lateral and vertical heterostructures, and defect structures. Especially intrinsic defects in transition metal dichalcogenides (TMDs) demand atomic resolution in electron microscopy to be seen and density inhomogeneities in short-range ordered molecular nanosheets (SROMN) [6] stay hidden with current methods at hand. When materials become as thin as a single atom (graphene) or a few atoms (TMDs,
SROMN), single atomic defects, defect clusters and atomic scale variations in their homogeneity have a big impact on their properties. Hence, to control these defects one must detect them. As it turns out, charge exchange spectroscopy of ions is well suited for the task, especially in cases where atomic resolution in microscopy cannot be obtained. The reason lies in a strong interatomic distance dependence of charge exchange, which confines the important parts of the interaction process to the Å-length scale. From a spectroscopic analysis of the transmitted ions in comparison with a model simulation, detailed knowledge about the atomic scale structure of a material can be gained.

2. Charge exchange of highly charged ions

Studies on the interaction of highly charged ions revealed many interesting features. The formation of hollow atoms in front of the surface [7, 8], the emission of characteristic x-rays [9, 10], the emission of a large number of low energy electrons and a small number of high energy Auger electrons [11, 12, 13], the formation of nanostructures on susceptible materials and many more [14, 15]. One peculiarity emerged from the fact that ions scattered under grazing incidence from HOPG or transmitted through few nm carbon foils were found mainly in their neutral charge state [16, 17]. This pointed towards an extremely efficient charge exchange process, where several candidates were discussed in literature [18]. Some dispute arose around the sample preparation and vacuum conditions, where contaminations could severely affect the charge exchange. Experiments with C60 clusters in the gas phase, however, were very much in line with the previous findings on surfaces showing the same fast neutralization [19, 20]. Here, ‘contaminations’ can be ruled out.

A comprehensive explanation of the fast neutralization of HCI could recently be given by taking a multi-electron interatomic de-excitation channel into account: Interatomic Coulombic Decay (ICD) [21]. ICD is a process by which a donor (hollow atom) transfers its excitation energy to a neighbouring atom (or several of them). Electrons from the neighbouring sites are then ionized or excited. It turns out that ICD has an interatomic distance dependent rate, which agrees well with the observed de-excitation time scales. Currently, intensive work is dedicated to ab-initio calculation of the distance dependent ICD rate for extended systems [22, 23], well in agreement with results obtained from HCI transmission through 1 nm thick amorphous carbon nanomembranes (CNMs), single-, bi- and tri-layer graphene, single layer hBN, and single layer MoS2 [24, 25]. The link between the ICD rate and HCI transmission spectroscopy results is discussed below.

3. Experimental procedures

Ion scattering from surfaces or molecules in the gas phase are typically performed in a standard ion beam setup using electrostatic [26], time-of-flight (TOF) [27] or magnetic spectrometers [28, 29] to determine the ion energy after interaction with the target. Especially, when it comes to charge exchange determination, additional demands must be met. The detector must be charge state sensitive, which is fulfilled by all the three concepts above, when ions are post accelerated by a DC voltage in the TOF measurement. However, also neutrals must be detected efficiently, which typically is challenging with electrostatic and magnetic spectrometers. When separate neutral counting in forward direction is performed, then special care must be taken to maintain the same solid angle for the neutral and the ion detector. Important for all concepts is the fact that detector efficiencies may depend on the ion charge state, when heavy ions at 10-100 keV energies are used, because here the electronic stopping contribution in the detector material is small and secondary electrons may be emitted with different probabilities depending on the charge state upon impact on the detector. Fig. 1 shows the pulse height distributions from a channeltron for different impinging Xe charge states after post amplification using a standard shaping amplifier. Even though the kinetic energy is not fixed here, one can still see a
Figure 1. (color online) Post amplified pulse height distributions from a channeltron operated at 1900 V bias voltage for different incident Xe charge states and kinetic energies of $4.4 \text{kV} \times q$, i.e. $E_{\text{kin}} = 22 - 176 \text{keV}$.

charge state dependence, and especially low charge states and low kinetic energies may not be detected with $\sim 100\%$ efficiency. As a consequence, the detector efficiency must be calibrated for low ion charge states and for the correct kinetic energy range.

Recently it was shown that charge exchange depends strongly on the ion impact parameter, and consequently charge exchange observation depends on the observation (scattering) angle \cite{30}. Therefore, it is highly advantageous to perform angle-resolved measurements with an angular resolution of $\sim 0.5^\circ$ or better. One option is to use small apertures in electrostatic and magnetic spectrometers and perform subsequent measurements for different observation angles, i.e. move the detector stepwise. One crucial issue then is ion induced beam damage, which can be important especially for 2D materials and when highly charged ions are used \cite{31, 32}. As sequential measurements of energy and angle increase the necessary exposure of the sample significantly, special care must be taken to collect enough statistics before the sample deteriorates too strongly.

One way to circumvent most of the issues here is to use a TOF based setup, which provides a high duty cycle, detects all charge states simultaneously, and uses a position sensitive ion detector providing angle resolution as well \cite{33}. Using secondary electrons emitted from the interaction process with the target material as a start signal for the TOF measurement allows a duty cycle of 100% if the ion current is in the range of $10^5 \text{ions/s}$. Even for somewhat higher intensities, measurements can be performed, when multi-start and multi-stop analysis is performed \cite{34}. Electrostatic beam choppers, commonly used in TOF setups, provide a duty cycle of about $\sim 10^{-3}$ (chopper opening time ($\sim \text{ns}$) over TOF ($\sim \mu\text{s}$)). This may not be an issue if the ion source provides enough beam current. When sources for highly charged ions, i.e. typically electron beam ion traps (EBITs) \cite{35, 36}, are used, ion intensities of $10^3 - 10^5 \text{ions/s}$ can be expected for the highest charge states ($q \gtrsim 30$) without chopping. A position sensitive multi-channel plate (MCP) with high timing resolution, e.g. a MCP with delay line anode \cite{37}, is favourable as a stop detector. Using a set of slits and a parallel plate deflector the impact positions on the MCP can be directly related to the charge state and the scattering angle. The timing information provides the stop trigger for the TOF measurement.

Since charge exchange spectroscopy is particularly powerful for 2D materials or the outermost surface layers of a bulk material, surface science methods for sample preparation and/or cleaning are necessary. Therefore, UHV conditions must be met as well as sample heating to $\gtrsim 400^\circ\text{C}$ should be possible.
The following results are produced using an EBIT. HCI charge states are selected with a Wien filter. Ions are extracted from the source by a constant electrostatic field and decelerated in front of the target by a retarding field to adjust their final kinetic energy. Samples are kept at UHV conditions, i.e. below $5 \times 10^{-9}$ mbar. Samples are prepared typically by chemical vapour deposition on suitable substrates and transferred onto standard TEM grids equipped with a Quantifoil support film without the use of a sacrificial polymer layer where-ever possible. Carbon Nanomembranes (CNM) are produced by cross-linking a self-assembled monolayer of nitro-biphenylthiol (NBPT) on a Au(111) surface. CNMs are subsequently transferred on a TEM grid. Some samples were treated with a specialized cleaning procedure to obtain large contamination free areas [38]. Electrons emitted from the ion interaction with the target are collected by a biased grid ($+200-500$ V) and accelerated to 30 keV to be measured in a surface barrier detector [39]. Ions are detected by a Roentdek delay line detector $\sim 1.1 \text{m}$ behind the sample.

4. Ion transmission through 2D materials

Ion transmission through 2D materials reveals interesting details about the interaction of ions with solids. Before concrete conclusions can be drawn, a few things need to be considered. First, 2D materials can exist as freestanding membranes, but they can span over areas of a few $\mu$m in diameter at most. Therefore, support grid structures are typically used, e.g. holey or lacy carbon, or Quantifoil. Ion beams are typically focused to 0.1-1 mm in diameter if no focussed ion beams are used. Consequently, the ion beam probes large areas of the sample, i.e. the result may be influenced by inhomogeneities in the sample over the mm scale. Especially influences of a support film need to be considered as well as multilayer and contaminated areas. One way to deal with these effects is the use of the coincidence technique. Here, ions are measured with respect to their energy (loss) and charge state in a way, that either charge state spectra can be filtered by the TOF or vice versa. Fig. 2 shows the charge state spectrum of 177 keV Xe$^{40+}$ ions transmitted through a single layer of graphene together with the corresponding TOF spectrum. The sample already shows large coverage and homogeneity, which is not always the case for 2D materials.
Figure 3. (color online) (a) and (d): Charge state patterns before and after exposure of a NBPT-CN to 324 keV Xe$^{36+}$, respectively, obtained using 180 keV Xe$^{20+}$ ions. (b) and (c): Charge state patterns of the same sample measured while exposure to 324 keV Xe$^{36+}$. 

Materials. However, the as-measured charge state spectrum shows a peak at $q = 0$, 12, and at 40. At the same time the TOF spectrum shows a background noise of about 10 counts per bin (bin size 0.3 ns), a peak at 2200 ns and slightly higher background at larger TOFs. Filtering the charge state spectrum for TOFs between 2100-2300 ns in Fig. 2(a) yields the red spectrum. The peak at $q = 40$ almost vanished and can be associated with ions passing through large uncovered areas in the sample. Those ions do not produce a start signal, because no electron emission takes place. Therefore, no TOF is measured for these ions and they are effectively filtered. Note, that the residual intensity at $q = 40$ is the result of random coincidences, i.e. electrons emitted from ion impinging on the TEM grid material itself (typically Cu or Au) and ions passing through uncovered areas. The number of ions impinging on the TEM grid and the number of ions transmitted through cracks are both large and therefore the probability of random coincidences is non-vanishing. In fact, the overall background signal in the TOF spectrum is the direct result of this.

Furthermore, the intensity of the peak at $q = 0$ in Fig. 2(a) is reduced as well, because these ions are transmitted through the Quantifoil support film. Since the film is 10-20 nm thick, ions are mainly in their neutral state. These ions have TOFs mostly larger than 2300 ns and contribute to the enhanced background at larger TOFs in Fig. 2(b). Finally, the distribution at $q = 12$ is the result of ions transmitted through the SLG itself and have a TOF in the region of 2100-2300 ns. The inset in Fig. 2(a) also shows how the noise level can be significantly reduced by TOF filtering.

The procedure can also be reversed and the TOF spectrum is filtered by the 2D angle-charge map in (a). Now the background in (b) is reduced almost to 0, i.e. the signal-to-noise ratio is large in order to determine energy losses precisely.

Data filtering by the means described above is helpful and even necessary when samples show low coverage or materials deteriorate quickly under the ion beam. In both cases only small statistics can be acquired in reasonable measurement time (also considering dark noise of the detector) or before the sample is destroyed.

TOF and charge state determination in a coincidence method enables also unambiguous identification of particular ion trajectories (e.g. through the support material), which would not be possible if both quantities are measured separately.

Ion transmission spectroscopy also allows to follow material damage in time. Fig. 3 shows different charge state patterns obtained from HCI transmission through a 1 nm thick NBPT-
CNM [40]. In (a) a spectrum is shown using 180 keV Xe$^{20+}$ ions, where it was previously reported that this charge state is below a threshold for material perforation [41]. After the initial spectrum was measured, the sample was exposed to 324 keV Xe$^{36+}$ ions and the charge state pattern is monitored continuously (c.f. Fig. 3(b)-(c)). While the charge state distribution at lower charge states below $q = 10$ remains constant, an upper charge state distribution develops between $q = 34 - 20$. As previously shown and also evident from the small angular range of these transmitted ions, the upper charge state distribution is a result of large impact parameter scattering. In fact, the impact parameter is above $\sim 2\,\text{Å}$ in order to maintain the high charge states for the ions (see discussion in the section below) [42]. It was also shown, that at the high charge state of $q = 36$ pores can be introduced efficiently into the material with diameters of up to 15 nm [41]. Ion transmission through previously damaged, i.e. perforated areas, will then lead to small charge exchange only. After the irradiation with $q = 36$, the sample was investigated with $q = 20$ again (c.f. Fig. 3(d)) and a significant change in the charge pattern can be observed. A pronounced distribution at higher exit charge states is visible, again in agreement with pore formation due to the high charge state irradiation.

5. Charge exchange mechanism in solids

In order to quantify charge exchange patterns from ion transmission and extract material porosity (c.f. Fig 3) a model calculation needs to be applied. Charge exchange of highly charged ions can be distinguished by two subsequent phases. The first phase is characterized by over-barrier charge transport from the surface to the ion. The classical-over-barrier (COB) model [43] describes quantitatively the distance of first electron transport and serves therefore as an input for the following full charge exchange model. One should notice that the COB model can only describe subsequent single electron transfers. At normal incidence conditions and with ion velocities in the range of $10^5\,\text{m/s}$ or above, multi-electron transport must be considered. However, most quantities are determined by the critical distance for first electron transport, which can be reliably calculated.

The COB phase is followed by a quenching of the neutralized, but highly excited atom (hollow atom). The second phase consists of a competition of several de-excitation processes. Radiative de-excitation is charge conserving, but appears with lifetimes in the ns-$\mu$s range especially for the Rydberg-like states occupied in a hollow atom. Non-radiative de-excitation appears intra- and inter-atomic, whereas only the latter is charge conserving. The former leads to an efficient recharging of the hollow atom due to ionization of the Auger electrons in contrast to the latter, where the Auger electron is emitted from the target atom. It is important to consider, that inter-atomic Auger-type de-excitation has a distance dependent lifetime, which approaches about 1 fs for interatomic distances $R < 1\,\text{Å}$ and drops rapidly for larger $R$. In short, non-radiative de-excitation typically dominates and within this channel charge conserving inter-atomic Auger-type decay dominates for close collisions and recharging intra-atomic Auger-type decay dominates at distant collisions.

A quantitative formulation of the discussion above yields three rate equations for different electron occupations in the projectile

\[ \frac{dN_{\text{core}}}{dt} = 0, \]  

\[ \frac{dN_{\text{cap}}(t)}{dt} = \lambda(t) (Z - N_{\text{core}} - N_{\text{cap}}(t) - N_{\text{stab}}(t)) - \gamma(t)N_{\text{cap}}(t), \]  

\[ \frac{dN_{\text{stab}}(t)}{dt} = \gamma(t)N_{\text{cap}}(t). \]  

Here $N_{\text{core}}$ is the number of frozen core electrons, $N_{\text{cap}}(t)$ the number of electrons captured from the surface and bound in highly excited Rydberg-like states, and $N_{\text{stab}}(t)$ the number of electrons
Figure 4. (color online) (a): Charge state patterns from 180 keV Xe\(^{20+}\) ions from a TDPot calculation and from experiment. (b): Respective simulated material structure. The simulation cell is indicated as well as the region in which impact parameters are chosen. The latter is selected to be smaller than the simulation cell to avoid edge effects (i.e. finite size effects). (c): Same as (a), but for the material after exposure to a Xe\(^{36+}\) beam, i.e. with ion induced pores. (d): Respective simulated material structure with a 25 Å pore.

quenched into lowly excited states such that they cannot undergo autoionization anymore. The rates \(\lambda(t)\) and \(\gamma(t)\) are the classical-over-barrier transport rate and the hollow atom quenching rate, respectively. An elaborated discussion about the determination of these rates can be found in [42]. In short, \(\lambda\) is assumed to be 0 for \(R > R_c\), where \(R_c\) is the critical capture distance from the COB model, and 1 a.u. for \(R \leq R_c\). The value of \(\gamma = \gamma(R[t])\) is taken from the \(R\)-dependence of the Interatomic Coulombic Decay (ICD) process [21]. The occupation number of core, lowly excited and highly excited levels in the projectile modifies the screening of the interaction potential between ion and target atoms. In fact, the potential

\[
V(R,t) = \frac{(N_{core} + N_{stab}(t))Z_2}{a_1((N_{core} + N_{stab}(t)),Z_2)} + \frac{N_{cap}(t)Z_2}{a_2(Z_2)} \phi_{hollow} (R, r_0) + \frac{(Z_1 - N_{core} - N_{stab}(t) - N_{cap}(t))Z_2}{R} \phi \left( \frac{R}{a_2(Z_2)} \right),
\]

becomes explicitly time-dependent. The screening functions \(\phi\) and \(\phi_{hollow}^{cap}\) as well as the corresponding screening lengths \(a_1\) and \(a_2\) are described within the framework of the TDPot model [42]. With the help of Eqs. (1)-(4) the final charge state of the projectile as well as the nuclear and electronic energy losses can be calculated for every individual impact parameter. The electronic energy loss follows from the fact that for scattering in a time-dependent potential the center-of-mass (cms) kinetic energy is not conserved, whereas the momentum conservation still holds. The difference in cms kinetic energy before and after scattering is spent in the rearrangement of the electron configuration (alteration of the potential) and is here termed ‘electronic energy loss’. Note, that the scattering is always inelastic when charge exchange occurs, i.e. nuclear energy loss can only be defined by the energy transfer to target nuclei, but not as the ‘elastic’ contribution. It is obvious that in case of charge exchange, nuclear and electronic energy loss are closely coupled and can not be treated as independent contributions to the stopping force anymore.

With a quantitative description of the charge exchange dynamics in a way that allows the determination of the final ion charge, energy, and angle, a material structure can be simulated
and the result compared to experiment. In Fig. 4(a) the charge pattern of 180 keV Xe\textsuperscript{20+} transmitted through a 1 nm thick amorphous CNM is shown (same as Fig. 3(a)), both as a result of a TDPot calculation (left) and the experiment (right). Fig. 4(b) shows the material structure as used for TDPot. A carbon layer was simulated, where the atom positions are chosen randomly within a cell of 100 Å in diameter and thickness of 10 Å. The atom areal density in TDPot is \(5.54 \times 10^{15} \text{at} \times \text{cm}^{-2}\), which matches an estimated value from the production process of CNMs, i.e. the areal density of carbon atoms in the self-assembled monolayer of NBPT molecules on a Au(111) surface, which serves as a precursor for CNMs. The agreement between TDPot and experiment is good, i.e. the charge state distribution at \(q < 5\) is well reproduced. TDPot shows additionally higher transmitted charge states \((5 < q < 12)\) at small angles. A separated, somewhat higher charge state distribution was previously observed for CNMs also in experiment [30], but not for this particular sample here. A reason could be the presence of additional contaminations at the sample, which block the forward transmission of high charge states. Detailed analysis of the TDPot results show, that these higher transmitted charge states pass regions in the CNMs where the atom-atom distances are larger, i.e. low density regions in the membrane. This is in agreement with the small deflection angles both in TDPot (c.f. Fig. 4(a) < 0.1°) and previous experiments. If severe contaminations are present then they increase the areal density of the material, thus the probability to pass a low density area (channel) in the material decreases and higher transmitted charge states in the pristine case are absent.

Fig. 4(c) and (d) show the TDPot and experimental charge pattern as well as simulated structure for the same sample after it was exposed to a 324 keV Xe\textsuperscript{36+} beam. In both, TDPot and experiment a pronounced high charge state distribution at small deflection angles is observed. TDPot was simulated with a 25 Å pore in the center of the simulation cell. Pore formation for ions with \(q > 20\) was observed previously utilizing transmission electron microscopy [31]. As expected, ions transmitted through the pore remain in high charge states and only ions passing the rim of the pore within the COB critical capture distance of \(\sim 10\) Å undergo charge exchange but almost no ICD. Afterwards intra-atomic Auger decay takes place, i.e. the projectile recharges. Additionally, TDPot uses a finite simulation cell (100 Å diameter) and impact parameters are selected within a square of 37.5 Å/√2 edge length to avoid finite size effects in the simulation. Thus, the ratio between lower and higher charge state distribution is a direct measure for the average pore density in the membrane, i.e. 1 pore/700 nm\(^2\) = \(1.4 \times 10^{11}\) pores/cm\(^2\). This is in fair agreement with the fluencies typically applied for ion transmission measurements until severe material degradation (perforation) occurs. However, for a more detailed quantitative analysis further measurements and microscopy analysis are needed.

6. Outlook

Highly charged ion transmission spectroscopy is powerful not only for basic research in charge exchange of ions with solids, but also for material structure determination. As shown above, the methodology can be applied to materials, where the structure is not known and cannot be determined by transmission electron microscopy as it is the case for amorphous materials. Porosity can be determined on the sub-nm length scale, especially interesting for molecular sieving and desalination applications of these organic membranes. To further boost the quantitative comparison of experiments with simulations, material quality must be improved, i.e. cleaning procedures to reduce contaminations must be applied. Further, the ion transmission spectroscopy must be gauged against known structures, i.e. using crystalline 2D materials with different structures where the atomic positions are well known. This allows the determination of input parameters necessary for a simulation, such that the simulation can then be applied to unknown samples. A critical parameter is the distance dependent ICD rate, which is not known from ab-initio calculations at the moment for small atom separations. Currently, the hollow atom quenching rate (ICD rate) is estimated from an extrapolation of literature values at larger
separations. Either adjusting the rate in the simulation to fit experimental results for various known sample structures or an approach to determine the rate at small separations from first principles must be done. In the not so far future, HCI based ion transmission spectroscopy may become a powerful addition for material structure determination for amorphous or short-ranged ordered molecular nanosheets.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft (WI 4691/1-1, project no. 322051344), the Austrian FWF (project no. Y 1174-N36), and the TU Wien (Innovative Projects) is gratefully acknowledged. I want to express my gratitude to F. Aumayr, S. Creutzburg, J. Schwestka, A. Niggas, and P.L. Grande for support of this work. I thank my collaborators M. Schleberger, L. Madauß, J. Kotakoski, H. Inani, A. Turchanin, and A. George for sample preparation and characterization. Parts of this research were carried out at IBC at the Helmholtz-Zentrum Dresden - Rossendorf e. V., a member of the Helmholtz Association. I would like to thank S. Faesko and R. Heller for assistance.

[1] Chang C C 1971 Surf. Sci. 25 53–79
[2] Ferraioli L, Wang M, Pucker G, Navarro-Urrios D, Daldosso N, Kompocholis C and Pavesi L 2007 J. Nanomater. 2007 1–5
[3] Damascelli A 2004 Phys. Scr. T109 61
[4] Seiler H 1983 J. Appl. Phys. 54 R1–R18
[5] Hembree G and Venables J 1992 Ultramicroscopy 47 109–120
[6] Müller V, Hinaut A, Moradi M, Baljozovic M, Jung T A, Shahgaldian P, Möhwald H, Hofer G, Kröger M, King T B, Meyer E, Glätzel T and Schlüter A D 2018 Angew. Chemie Int. Ed. 57 10584–10588
[7] Limburg J, Schippers S, Hoekstra R, Morgenstern R, Kurz H, Aumayr F and Winter H 1995 Phys. Rev. Lett. 75 217–219
[8] Briand J P, de Billy L, Charles P, Essaba S, Briand P, Geller R, Desclaux J P, Bliiman S and Ristori C 1990 Phys. Rev. Lett. 65 159–162
[9] Briand J P, de Billy L, Charles P, Essaba S, Briand P, Geller R, Desclaux J P, Bliiman S and Ristori C 1991 Phys. Rev. A 43 565–567
[10] Schwestka J, Wilhelm R, Gruber E, Heller R, Kozubek R, Schleberger M, Faesko S and Aumayr F 2018 Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms 422 63–67
[11] Aumayr F and Winter H 2007 Slow Heavy-Particle Induc. Electron Emiss. from Solid Surfaces (Springer Tracts in Modern Physics vol 225) ed Winter H P and Burgdörfer J (Berlin, Heidelberg: Springer Berlin Heidelberg) chap 3, pp 79–112 ISBN 978-3-540-70788-2
[12] Köhrbrück R, Sommer K, Biersack J P, Bleck-Neuhaus J, Schippers S, Roncin P, Lecler D, Fremont F and Stolterfoth N 1992 Phys. Rev. A 45 4653–4660
[13] Kost D, Faesko S, Möller W, Hellhammer R and Stolterfoth N 2007 Phys. Rev. Lett. 98 225503
[14] Faesko S, Meissl W, Heller R, Wilhelm R, El-Said A S, Kowarik G, Ritter R and Aumayr F 2009 J. Phys. Conf. Ser. 194 012060
[15] Heller R, Faesko S, Wilhelm R A and Möller W 2008 Phys. Rev. Lett. 101 096102
[16] Winecki S, Cocke C L, Fry D and Stöckli M P 1996 Phys. Rev. A 53 4228–4237
[17] Hattass M, Schenk T, Hamza A V, Barnes A V, Newman M W, McDonald J W, Niedermayr T R, Machico G A, and Schneider D H 1999 Phys. Rev. Lett. 82 4795–4798
[18] Arnau A, Aumayr F, Echenique P, Grether M, Heiland W, Limburg J, Morgenstern R, Roncin P, Schippers S, Schuch R, Stolterfoth N, Varga P, Zouros T and Winter H 1997 Surf. Sci. Rep. 27 113–239
[19] Martin S, Brédy R, Bernard J, Désesquelles J and Chen L 2002 Phys. Rev. Lett. 89 183401
[20] Wilhelm R A, Gruber E, Schwestka J, Kozubek R, Madeira T I, Marques J P, Kobus J, Krasheninnikov A V, Schleberger M and Aumayr F 2017 Phys. Rev. Lett. 119 103401
[21] Cederbaum L S, Zobeley J and Tarantelli F 1997 Phys. Rev. Lett. 79 4778–4781
[22] Hemmerich J L, Bennett R and Buhmann S Y 2018 Nat. Commun. 9 2934
[23] Bennett R, Votavová P, Kolorenc P, Miteva T, Sisourat N and Buhmann S Y 2019 Phys. Rev. Lett. 122 153401
[24] Gruber E, Wilhelm R A, Pétuya R, Snejkal V, Kozubek R, Hierzenberger A, Bayer B C, Aldazabal I, Kazansky A K, Líbisch F, Krasheninnikov A V, Schleberger M, Faesko S, Borisov A G, Arnau A and Aumayr F 2016 Nat. Commun. 7 13948
[25] Wilhelm R, Gruber E, Schwestka J, Heller R, Faesko S and Aumayr F 2018 Appl. Sci. 8 1050
[26] Markin S, Primetzhofer D and Bauer P 2009 Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms 267 634–637
[27] Klingner N, Heller R, Hlawacek G, von Borany J, Notte J, Huang J and Facsko S 2016 Ultramicroscopy 162 91–97
[28] Vieluf M, Munnik F, Neelmeijer C, Kosmata M and Teichert S 2012 Thin Solid Films 520 5900–5905
[29] Kosmata M, Munnik F, Hanf D, Grötzschel R, Crocoll S and Möller W 2014 Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms 337 27–33
[30] Wilhelm R A, Gruber E, Ritter R, Heller R, Facsko S and Aumayr F 2014 Phys. Rev. Lett. 112 153201
[31] Ritter R, Wilhelm R A, Stöger-Pollach M, Heller R, Mücklich A, Werner U, Vieker H, Beyer A, Facsko S, Göllzhäuser A and Aumayr F 2013 Appl. Phys. Lett. 102 063112
[32] Kozubek R, Tripathi M, Ghorbani-Asl M, Kretschmer S, Madauß L, Pollmann E, O’Brien M, McEvoy N, Ludacka U, Susi T, Duesberg G S, Wilhelm R A, Krasheninnikov A V, Kotakoski J and Schleberger M 2019 J. Phys. Chem. Lett. 10 904–910
[33] Schwestka J, Melinc D, Heller R, Niggas A, Leonhartsberger L, Winter H, Facsko S, Aumayr F and Wilhelm R A 2018 Rev. Sci. Instrum. 89 085101
[34] Jagutzki O, Cerezo A, Czasch A, Dorner R, Hattas M, Min Huang, Mergel V, Spillmann U, Ullmann-Pfleger K, Weber T, Schmidt-Bocking H and Smith G 2002 IEEE Trans. Nucl. Sci. 49 2477–2483
[35] Schmidt M, Peng H, Zschornack G and Sykora S 2009 Rev. Sci. Instrum. 80 063301
[36] Micke P, Kühn S, Buchauer L, Harries J R, Bücking T M, Blaum K, Cieluch A, Egl A, Hollain D, Kraemer S, Pfeifer T, Schmidt P O, Schüssler R X, Schweiger C, Stöhlker T, Sturm S, Wolf R N, Bernitt S and Crespo López-Urrutia J R 2018 Rev. Sci. Instrum. 89 063109
[37] Czasch A, Milhes J, Hay N, Wicking W and Jagutzki O 2007 Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip. 580 1066–1070
[38] Algara-Siller G, Lehtinen O, Turchanin A and Kaiser U 2014 Appl. Phys. Lett. 104 153115
[39] Lakits G, Aumayr F and Winter H 1989 Rev. Sci. Instrum. 60 3151–3159
[40] Turchanin A and Göllzhäuser A 2016 Adv. Mater. 28 6075–6103
[41] Wilhelm R A, Gruber E, Ritter R, Heller R, Beyer A, Turchanin A, Klingner N, Hübner R, Stöger-Pollach M, Vieker H, Hlawacek G, Göllzhäuser A, Facsko S and Aumayr F 2015 2D Mater. 2 035009
[42] Wilhelm R and Grande P 2019 Commun. Phys. 2 89
[43] Burgdörfer J, Lerner P and Meyer F W 1991 Phys. Rev. A 44 5674–5685