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Possible isomers in ligand protected Ag₁₁ cluster ions identified by ion mobility mass spectrometry and fragmented by surface induced dissociation†

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This communication reports the identification of gas phase isomers in monolayer-protected silver clusters. Two different isomers of Ag₁₁(SG)₇⁻ (SG-gulathione thiolate) with different drift times have been detected using combined electrospray ionization (ESI) and ion mobility (IM) mass spectrometry (MS). Surface induced dissociation (SID) of the 3⁻ charge state of such clusters shows charge stripping to give the 1⁻ charged ion with some sodium attachment, in addition to fragmentation. SID and collision induced dissociation (CID) for Ag₁₁(SG)₇⁻ suggest different pathways being accessed with each method. SID was introduced for the first time for the study of monolayer-protected clusters.

Atomically precise monolayer protected clusters (MPCs) of gold and silver belong to a fascinating area of research due to their unique optoelectronic properties and wide range of applications in materials science, electronics, catalysis and biology.^{1–3} Several clusters have been synthesized and many of them have been crystallized including Au₂₅(SR)₁₈,^{4,5} Au₃₀S(SR)₁₈,⁶ Au₃₆(SR)₂₄,⁷ Au₃₈(SR)₂₄,⁸ Au₆₈(SR)₃₂⁹ and Au₁₀₂(SR)₄₄.¹⁰ Some of the silver clusters have also been crystallized including [Ag₁₄(SR)₁₂(PPh₃)₈],¹¹ [Ag₁₆(DPPE)₄(SR)₁₄],¹² [Ag₃₂(DPPE)₅(SCR)₂₄]¹² (DPPE: 1,2-bis-(diphenylphosphino)ethane), Ag₄₄(SR)₃₀^{13,14} and most recently, Ag₂₅(SR)₁₈¹⁵ (SR corresponds to various thiolate ligands). Crystal structures of some of the alloy clusters consisting of Au/Ag^{13,16} and Au/Cu¹⁷ have also been solved. While some of the clusters could be crystallized, there are several others which were identified by optical spectroscopy and mass spectrometry (MS) along with structural insights from theoretical calculations, mainly

density functional theory (DFT).^{18–35} Only a few clusters are known to show well defined mass spectrometric signatures namely, Ag₉(MSA)₇,¹⁸ Ag₁₁(SG)₇,³⁶ Ag₁₅(SG)₁₁,³⁷ Ag₃₁(SG)₁₉,³⁷ Ag₃₂(SG)₁₉,²⁷ Ag₄₄(SR)₃₀,¹⁹ Ag₇₅(SG)₄₀,³⁸ *etc.*, where SG refers to the thiolate form of glutathione. Au₂₅(SR)₁₈ is one of the most widely and systematically studied systems from both experimental and theoretical points of view.^{5,28,34,39–41} The crystal structure reveals the presence of an Au₁₃ core and 6 Au₂(SR)₃ staple motifs.^{4,5} Fragmentation from the core as well as the staple has been identified by an ESI MS/MS study by Angle *et al.*³⁹ In another theoretical study, Liu *et al.* have identified the stepwise fragmentation of the staple motifs as the most favourable fragmentation pathway for Au₂₅(SR)₁₈.⁴² These researchers have shown different isomeric structures of the core which could be responsible for fragmentation and catalytic properties of the clusters.

Due to the core as well as ligand orientation, MPCs can have isomeric forms. However, no isomeric structures have been reported to date for ions in the gas phase. In this context, ion mobility-mass spectrometry (IM-MS), which can separate ions based not only on their mass and charge but also on their size and shape, known as their rotationally averaged collision cross-section (CCS), has great potential. Different conformations can be separated by IM based on differences in their CCS, as is evident from several studies on proteins and other biomolecules.^{43–45} There are a few reports on the use of IM-MS on monolayer protected Au clusters and nanoparticles.^{46–50} For example, Au₂₅(SR)₁₈ cluster fragments were identified by ion mobility.³⁹ Symmetric drift time distribution of these clusters suggested the presence of only one structure or interconverting isomers.³⁹ There is no report on monolayer protected silver clusters which were separated by IM-MS.

Here, we report the first observation of the presence of ligand induced isomers of Ag₁₁(SG)₇⁻ by ESIM-MS where two isomers can be distinguished by their different drift times. We also introduce surface induced dissociation (SID) as a method of fragmentation to study such clusters for the first time where charge stripping can generate deprotonated peaks from a higher charged species, in addition to fragmentation. SID is known to result in significantly different fragmentation pathways for

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protein complexes in comparison to CID. We observed different types of fragmentation in SID and CID for $\text{Ag}_{11}(\text{SG})_7\text{Na}_n^{3-}$ suggesting that different pathways are being accessed with each method.^{51,52}

This $\text{Ag}_{11}(\text{SG})_7$ was synthesized by a recently reported method.³⁶ Synthesis and characterization of $\text{Ag}_{11}(\text{SG})_7$ are discussed briefly in ESI.†

An ion mobility study of the clusters using a Waters Synapt G2S instrument capable of measuring drift times and mass spectra simultaneously is presented here. The instrument was in-house modified to incorporate an SID device located before the IM cell.⁵³ Fig. 1A shows a zoom in plot of ion drift time *versus* m/z obtained, highlighting the species of interest, namely $\text{Ag}_{11}(\text{SG})_7\text{Na}_n^{3-}$ (where $n = 3$ and 4). This is the prominent peak observed for the species. About 2–7 Na attached peaks were observed among which 3 and 4 Na additions are the most intense, and are shown in Fig. 1B; the isotope distributions of which match well with the theoretically calculated distribution. For each envelope, there are two species with slightly different structures. This is reflected in the similarity of their drift times, as shown in the plot of ion drift time *versus* m/z (Fig. 1A) as well as in the drift profile (Fig. 1C); in both cases two distributions can be observed.

A sharp peak in the drift time at 4.7 ms is due to the main structural isomer. However, another peak appears around 5.6 ms, which is due to a structural isomer of lower intensity. The relative abundance of the peaks was calculated from the area under each peak. Note that in the previous study of $\text{Au}_{25}(\text{SCH}_2\text{CH}_2\text{Ph})_{18}^-$ a symmetric drift profile was observed indicating the absence of isomers. DFT calculations of the present clusters suggested an Ag_7 core, one $\text{Ag}_2(\text{SG})_3$ staple and two $\text{Ag}(\text{SG})_2$ staples. Six possible structures were reported in the previous work, which are discussed in the ESI.† Considering the energies and HOMO–LUMO gaps along with the observed absorption spectrum, the two structures are of similar energy and stability. Therefore, it is indeed possible that both the structures can co-exist leading to two isomeric forms as seen in IM-MS. The structures are described in the ESI† (see Fig. S7) in detail. Between these two structures, one is more compact compared to the other considering inward and outward projection of the ligands. These structures were calculated

considering SME instead of the whole GSH as the ligand. In the case of isomers, the structures should be calculated with the intact GSH ligand but due to the large number of atoms ($\text{Ag}_{11}\text{C}_{70}\text{H}_{102}\text{N}_{21}\text{O}_{42}\text{S}_7$ for an intact $\text{Ag}_{11}\text{SG}_7$ cluster) it is difficult. Being a tripeptide, GSH has an inherent tendency to make H-bonds with adjacent ligands, which can also lead to isomerism. The two peaks with different drift times may be ascribed to isomers having different structures of the glutathione moieties on identical AgS backbones. The coulombic repulsion between the ligands of multiply charged $\text{Ag}_{11}(\text{SG})_7$ may induce isomerization as in the case of multiply-charged proteins in the gas phase. Considering all these possibilities, the presence of multiple isomers in IM measurements is understandable.

These clusters show good mass spectral signatures, which allowed us to proceed further to see the fragmentation pattern from a specific charge state. The instrument is capable of dissociating any of these ions in both SID and CID modes. In the CID mode, we observed the usual fragments of $\text{Ag}_{11}(\text{SG})_7\text{Na}_n^{3-}$ (which is actually $[\text{Ag}_{11}(\text{SG})_7 - n\text{H} + n\text{Na}]^{3-}$). AgSG^- loss was apparent as the main fragmentation pathway to give $\text{Ag}_{10}(\text{SG})_6\text{Na}_n^{2-}$ at the lowest collision energy (Fig. 2A). The fragment AgSG^- is detected at the lower mass range. With increasing collision energy, lower mass fragments were observed. Mostly the fragmentation occurs *via* AgSG^- loss.

The smallest fragment observed was AgSG^- at the highest collision energy (Fig. 2A, additional details are in Fig. S2–S5, ESI†) at the mass range studied. However, at the lower mass range (< 500 Da), AgSG^- is seen as a major peak along with SG^- and its fragments from SG^- . A corresponding change is also observable from the drift time profile where shorter drift times imply smaller, more compact fragments (Fig. 2B and C). Interestingly, one ligand loss from the parent ion gives $\text{Ag}_{10}(\text{SG})_6\text{Na}_n^{2-}$ with a drift time of 8.2 ms, causing a loss of the isomeric structure (only one peak in the drift profile) which implies that the isomerism is ligand induced in this case. Detecting only one isomeric structure for the fragment could also be due to annealing of the ion as a result of CID. Another ligand loss at slightly higher energy resulted in $\text{Ag}_{10}(\text{SG})_5\text{Na}_n^{2-}$ (a drift time of 7.0 ms) where no isomeric structure has been observed.

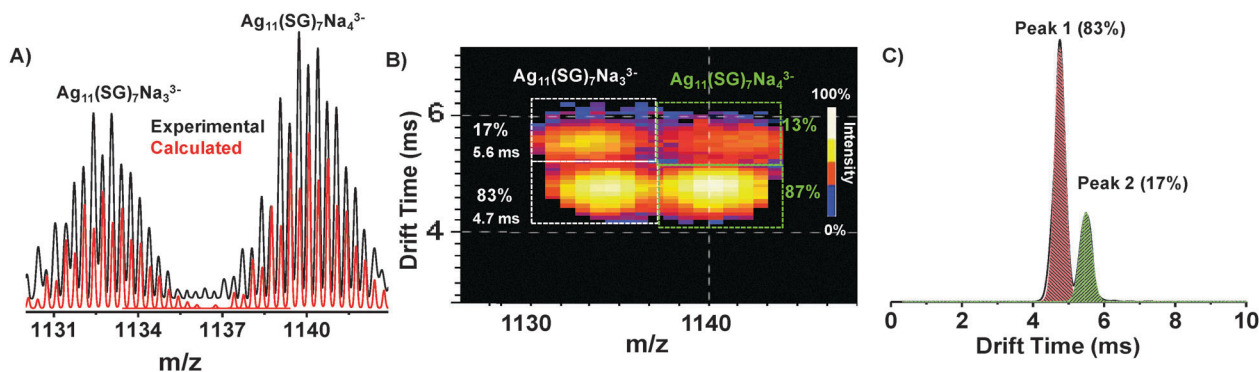


Fig. 1 (A) Zoom in view of the ESI MS of $\text{Ag}_{11}(\text{SG})_7$ showing 3-charged ion with three and four Na attachments. The peaks match exactly with the theoretically calculated pattern. (B) Plot of ion mobility drift time *versus* m/z of $\text{Ag}_{11}(\text{SG})_7\text{Na}_3^{3-}$ and $\text{Ag}_{11}(\text{SG})_7\text{Na}_4^{3-}$ is showing the presence of two isomeric species. Relative abundances of the isomers found from the drift profiles are labelled. Drift profile of $\text{Ag}_{11}(\text{SG})_7\text{Na}_3^{3-}$ is shown in (C) where two clear peaks indicate the presence of two isomeric structures. Relative abundances of the isomers were found by calculating the area under each peak.

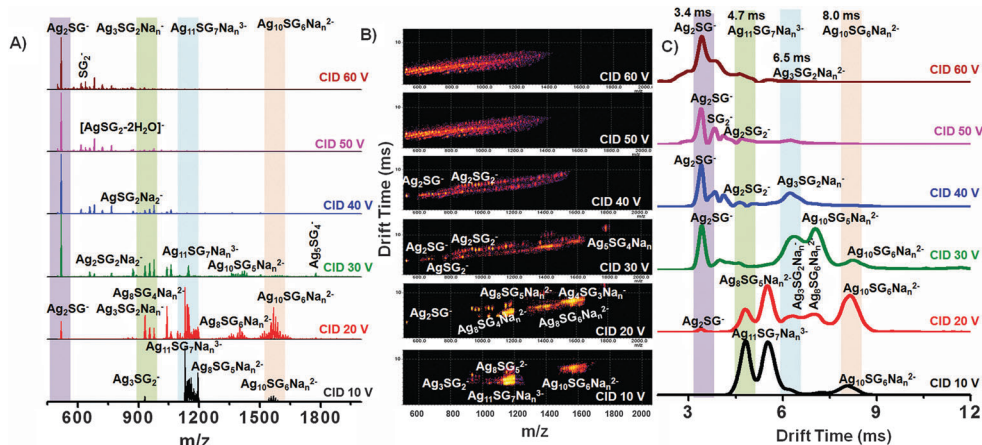


Fig. 2 (A) CID of $\text{Ag}_{11}(\text{SG})_7\text{Na}_n^{3-}$ with major products labeled. Corresponding drift time plots of ion mobility drift time versus m/z are shown in (B) and the respective peaks are labeled. Corresponding drift time profiles are shown in (C). Each of these plot of ion drift time versus m/z and the mass spectra are shown separately in Fig. S2–S5 (ESI †). Major fragments are marked with highlight.

This fragmentation is due to the loss of one $\text{Ag}(\text{SG})_2$ staple which might be responsible for the disappearance of the isomeric structure. Each of these staples is directly linked to two Ag atoms of the core. Therefore, loss of one staple will directly affect the core conformation and hence the isomeric structure. Other smaller fragments observed in CID also do not exhibit any isomers. A probable fragmentation pathway is shown in Scheme 1 along with the drift time of the resulting fragments. The peaks are assigned to respective ions in Fig. 2B. The plot of ion mobility drift time versus m/z shown in Fig. 2B for each CE is expanded in the ESI † (Fig. S2–S5). Note that all the data presented for the plot of ion drift time versus m/z are as obtained from Driftscope V2.8 software and are presented without any change. SID of the same species on a fluorocarbon self-assembled monolayer (SAM) grown on a gold-coated surface showed completely different types of fragmentation. SID differs from CID in the sense that fragmentation results from a single collision with the surface, as opposed to multiple collisions as in the case of CID. Details of the instrumental parameters are listed in the ESI † . In SID at the lowest energy used here, one AgSG loss was observed for $\text{Ag}_{11}(\text{SG})_7\text{Na}_n^{3-}$ as seen for CID (see Fig. 3). We have observed two isomeric species of $\text{Ag}_{10}(\text{SG})_6\text{Na}_n^{3-}$, with a drift time of 8.2 ms as the major component and a smaller peak at 8.6 ms as the minor one, which was absent in CID. This may be explained in terms of different types of fragmentation channels of

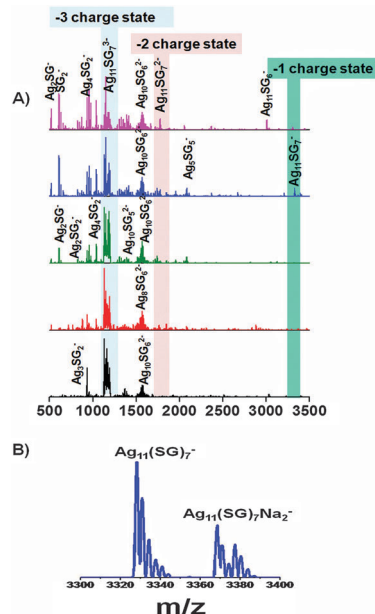
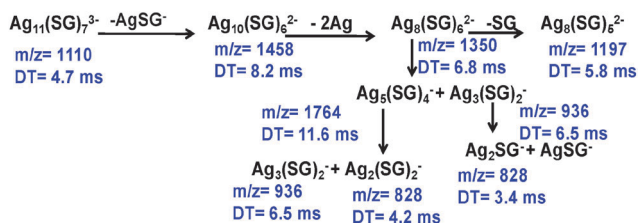


Fig. 3 (A) SID of $\text{Ag}_{11}(\text{SG})_7\text{Na}_n^{3-}$ at increased voltage shows multiple fragmentations at all the energies, unlike in CID. At higher voltages, charge stripping was observed to give a -2 charged species and finally at SID 40, -1 ion peak was observed. Two Na attached peaks were also observed as expanded in (B).

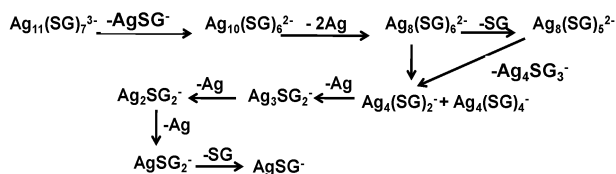
Probable Fragmentation Pathways in Collision Induced Dissociation (CID)



Scheme 1 Probable fragmentation pathways in CID.

the isomeric $\text{Ag}_{11}(\text{SG})_7\text{Na}_n^{3-}$ precursor upon different amounts of internal energy transfer. As we increase the energy, more and more fragmentations to smaller thiolates were observed. Unlike CID, at similar energy (ΔV) in SID, a wide range of fragment ions were observed including the main precursor ion. SID at 30 V, we observed charge stripping of the ion from -3 to -2 . Upon SID at 40 V, the -1 peak was also observed. Charge stripping from a higher charged species to a lower charge was not observed before for any other cluster (both Au and Ag) although this is commonly seen for proteins. Fragments and probable fragmentation pathways observed are shown in Scheme 2.

Probable Fragmentation Pathways in Surface Induced Dissociation (SID)



Scheme 2 Probable fragmentation pathways in SID.

Ligand induced isomerism was confirmed from the proposed structures as well as CID. SID showed the presence of two structural isomers, which might be due to the different types of configurations of the cluster, which fragment differently upon colliding with the surface. At higher voltages (in SID), charge stripping of -3 charged ions resulted in the formation of deprotonated ions, which has not been observed in any cluster system. Similar studies may be used to identify the presence of isomeric clusters, which will expand the science of noble metal clusters.

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References

- 1 A. Mathew and T. Pradeep, *Part. Part. Syst. Charact.*, 2014, **3**, 1017.
- 2 T. Udayabhaskararao and T. Pradeep, *J. Phys. Chem. Lett.*, 2013, **4**, 1553.
- 3 R. Jin, *Nanoscale*, 2010, **2**, 343.
- 4 M. W. Heaven, A. Dass, P. S. White, K. M. Holt and R. W. Murray, *J. Am. Chem. Soc.*, 2008, **130**, 3754.
- 5 M. Zhu, C. M. Aikens, F. J. Hollander, G. C. Schatz and R. Jin, *J. Am. Chem. Soc.*, 2008, **130**, 5883.
- 6 D. Crasto, S. Malola, G. Brosofsky, A. Dass and H. Hakkinen, *J. Am. Chem. Soc.*, 2014, **136**, 5000.
- 7 C. Zeng, H. Qian, T. Li, G. Li, N. L. Rosi, B. Yoon, R. N. Barnett, R. L. Whetten, U. Landman and R. Jin, *Angew. Chem., Int. Ed.*, 2012, **51**, 13114.
- 8 H. Qian, W. T. Eckenhoff, Y. Zhu, T. Pintauer and R. Jin, *J. Am. Chem. Soc.*, 2010, **132**, 8280.
- 9 M. Azubel, J. Koivisto, S. Malola, D. Bushnell, G. L. Hura, A. L. Koh, H. Tsunoyama, T. Tsukuda, M. Pettersson, H. Haekkinen and R. D. Kornberg, *Science*, 2014, **345**, 909.
- 10 P. D. Jadzinsky, G. Calero, C. J. Ackerson, D. A. Bushnell and R. D. Kornberg, *Science*, 2007, **318**, 430.
- 11 H. Yang, J. Lei, B. Wu, Y. Wang, M. Zhou, A. Xia, L. Zheng and N. Zheng, *Chem. Commun.*, 2013, **49**, 300.
- 12 H. Yang, Y. Wang and N. Zheng, *Nanoscale*, 2013, **5**, 2674.
- 13 H. Yang, Y. Wang, H. Huang, L. Gell, L. Lehtovaara, S. Malola, H. Hakkinen and N. Zheng, *Nat. Commun.*, 2013, **4**, 2422.
- 14 A. Desireddy, B. E. Conn, J. Guo, B. Yoon, R. N. Barnett, B. M. Monahan, K. Kirschbaum, W. P. Griffith, R. L. Whetten, U. Landman and T. P. Bigioni, *Nature*, 2013, **501**, 399.
- 15 C. P. Joshi, M. S. Bootharaju, M. J. Alhilaly and O. M. Bakr, *J. Am. Chem. Soc.*, 2015, **137**, 11578.
- 16 S. Wang, X. Meng, A. Das, T. Li, Y. Song, T. Cao, X. Zhu, M. Zhu and R. Jin, *Angew. Chem., Int. Ed.*, 2014, **53**, 2376.
- 17 H. Yang, Y. Wang, J. Yan, X. Chen, X. Zhang, H. Hakkinen and N. Zheng, *J. Am. Chem. Soc.*, 2014, **136**, 7197.
- 18 T. U. B. Rao, B. Nataraju and T. Pradeep, *J. Am. Chem. Soc.*, 2010, **132**, 16304.
- 19 K. M. Harkness, Y. Tang, A. Dass, J. Pan, N. Kothalawala, V. J. Reddy, D. E. Cliffler, B. Demeler, F. Stellacci, O. M. Bakr and J. A. McLean, *Nanoscale*, 2012, **4**, 4269.
- 20 M. S. Bootharaju and T. Pradeep, *Langmuir*, 2013, **29**, 8125.
- 21 Y. Negishi, K. Nobusada and T. Tsukuda, *J. Am. Chem. Soc.*, 2005, **127**, 5261.
- 22 S. Kumar, M. D. Bolan and T. P. Bigioni, *J. Am. Chem. Soc.*, 2010, **132**, 13141.
- 23 Z. Wu, E. Lanni, W. Chen, M. E. Bier, D. Ly and R. Jin, *J. Am. Chem. Soc.*, 2009, **131**, 16672.
- 24 Y. Negishi, R. Arai, Y. Niihori and T. Tsukuda, *Chem. Commun.*, 2011, **47**, 5693.
- 25 S. Knoppe, A. C. Dharmaratne, E. Schreiner, A. Dass and T. Burgi, *J. Am. Chem. Soc.*, 2010, **132**, 16783.
- 26 T. Udaya Bhaskara Rao and T. Pradeep, *Angew. Chem., Int. Ed.*, 2010, **49**, 3925.
- 27 J. Guo, S. Kumar, M. Bolan, A. Desireddy, T. P. Bigioni and W. P. Griffith, *Anal. Chem.*, 2012, **84**, 5304.
- 28 Y. Niihori, W. Kurashige, M. Matsuzaki and Y. Negishi, *Nanoscale*, 2013, **5**, 508.
- 29 Y. Yu, X. Chen, Q. Yao, Y. Yu, N. Yan and J. Xie, *Chem. Mater.*, 2013, **25**, 946.
- 30 L. G. Abdul Halim, S. Ashraf, K. Katsiev, A. R. Kirmani, N. Kothalawala, D. H. Anjum, S. Abbas, A. Amassian, F. Stellacci, A. Dass, I. Hussain and O. M. Bakr, *J. Mater. Chem. A*, 2013, **1**, 10148.
- 31 Y. Niihori, M. Matsuzaki, T. Pradeep and Y. Negishi, *J. Am. Chem. Soc.*, 2013, **135**, 4946.
- 32 O. M. Bakr, V. Amendola, C. M. Aikens, W. Wenseleers, R. Li, L. Dal Negro, G. C. Schatz and F. Stellacci, *Angew. Chem., Int. Ed.*, 2009, **121**, 6035.
- 33 I. Chakraborty, A. Govindarajan, J. Erusappan, A. Ghosh, T. Pradeep, B. Yoon, R. L. Whetten and U. Landman, *Nano Lett.*, 2012, **12**, 5861.
- 34 A. Mathew, G. Natarajan, L. Lehtovaara, H. Hakkinen, R. M. Kumar, V. Subramanian, A. Jaleel and T. Pradeep, *ACS Nano*, 2014, **8**, 139.
- 35 T. Udayabhaskararao, M. S. Bootharaju and T. Pradeep, *Nanoscale*, 2013, **5**, 9404.
- 36 A. Baksi, M. S. Bootharaju, X. Chen, H. Hakkinen and T. Pradeep, *J. Phys. Chem. C*, 2014, **118**, 21722.
- 37 F. Bertorelle, R. Hamouda, D. Rayane, M. Broyer, R. Antoine, P. Dugourd, L. Gell, A. Kulesza, R. Mitric and V. Bonacic-Koutecky, *Nanoscale*, 2013, **5**, 5637.
- 38 I. Chakraborty, T. Udayabhaskararao and T. Pradeep, *Chem. Commun.*, 2012, **48**, 6788.
- 39 L. A. Angel, L. T. Majors, A. C. Dharmaratne and A. Dass, *ACS Nano*, 2010, **4**, 4691.
- 40 J. F. Parker, C. A. Fields-Zinna and R. W. Murray, *Acc. Chem. Res.*, 2010, **43**, 1289.
- 41 M. Walter, J. Akola, O. Lopez-Acevedo, P. D. Jadzinsky, G. Calero, C. J. Ackerson, R. L. Whetten, H. Gronbeck and H. Hakkinen, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 9157.
- 42 C. Liu, S. Lin, Y. Pei and X. C. Zeng, *J. Am. Chem. Soc.*, 2013, **135**, 18067.
- 43 K. B. Shelimov, D. E. Clemmer, R. R. Hudgins and M. F. Jarrold, *J. Am. Chem. Soc.*, 1997, **119**, 2240.
- 44 T. Wyttenbach, G. von Helden and M. T. Bowers, *J. Am. Chem. Soc.*, 1996, **118**, 8355.
- 45 B. T. Ruotolo, J. L. P. Benesch, A. M. Sandercock, S.-J. Hyung and C. V. Robinson, *Nat. Protoc.*, 2008, **3**, 1139.
- 46 K. M. Harkness, A. Balinski, J. A. McLean and D. E. Cliffler, *Angew. Chem., Int. Ed.*, 2011, **50**, 10554.
- 47 K. M. Harkness, D. E. Cliffler and J. A. McLean, *Analyst*, 2010, **135**, 868.
- 48 K. M. Harkness, D. E. Cliffler and J. A. McLean, *Analyst*, 2010, **135**, 868.
- 49 K. M. Harkness, L. S. Fenn, D. E. Cliffler and J. A. McLean, *Anal. Chem.*, 2011, **82**, 3061.
- 50 K. M. Harkness, B. C. Hixson, L. S. Fenn, B. N. Turner, A. C. Rape, C. A. Simpson, B. J. Huffman, T. C. Okoli, J. A. McLean and D. E. Cliffler, *Anal. Chem.*, 2010, **82**, 9268.
- 51 M. Zhou, S. Dagan and V. H. Wysocki, *Angew. Chem., Int. Ed.*, 2012, **51**, 4336.
- 52 M. Zhou and V. H. Wysocki, *Acc. Chem. Res.*, 2014, **47**, 1010.
- 53 M. Zhou, C. Huang and V. H. Wysocki, *Anal. Chem.*, 2012, **84**, 6016.