Fragmentation pathways of tungsten hexacarbonyl clusters upon electron ionization

M. Neustetter,¹ E. Jabbour Al Maalouf,¹ P. Limão-Vieira,^{1,2,a)} and S. Denifl^{1,a)}

¹*Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstrasse 25, A-6020 Innsbruck, Austria*

²*Laboratório de Colisões Atômicas e Moleculares, CEFITEC, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal*

(Received 18 March 2016; accepted 11 July 2016; published online 2 August 2016)

Electron ionization of neat tungsten hexacarbonyl ($\text{W}(\text{CO})_6$) clusters has been investigated in a crossed electron-molecular beam experiment coupled with a mass spectrometer system. The molecule is used for nanofabrication processes through electron beam induced deposition and ion beam induced deposition techniques. Positive ion mass spectra of $\text{W}(\text{CO})_6$ clusters formed by electron ionization at 70 eV contain the ion series of the type $\text{W}(\text{CO})_n^+$ ($0 \leq n \leq 6$) and $\text{W}_2(\text{CO})_n^+$ ($0 \leq n \leq 12$). In addition, a series of peaks are observed and have been assigned to $\text{WC}(\text{CO})_n^+$ ($0 \leq n \leq 3$) and $\text{W}_2\text{C}(\text{CO})_n^+$ ($0 \leq n \leq 10$). A distinct change of relative fragment ion intensity can be observed for clusters compared to the single molecule. The characteristic fragmentation pattern obtained in the mass spectra can be explained by a sequential decay of the ionized organometallic, which is also supported by the study of the clusters when embedded in helium nanodroplets. In addition, appearance energies for the dissociative ionization channels for singly charged ions have been estimated from experimental ion efficiency curves. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4959278>] It may be found at the former link.

This article may be downloaded for personal use only. Any other use requires prior permission of the author and AIP publishing.

I. INTRODUCTION

The present work on electron ionization of tungsten hexacarbonyl, $\text{W}(\text{CO})_6$, clusters is part of a wider research program aimed at understanding the role of metal carbonyl containing complexes for nanostructured surfaces with current demanding applications in Ion Beam Induced Deposition (IBID) and Electron Beam Induced Deposition (EBID) (also referred as FEBIP, Focused Electron Beam Induced Processing) techniques.^{1–4} FEBIP has gained considerable relevance as a new strategy for nanofabrication due to its ability as a precise tool for manipulating and controlling local adsorbed precursor molecules through efficient electron-molecule interactions (e.g., dissociation mechanisms). Under this process, chemically and structurally well-defined deposits are left behind when the tight focused electron beam decomposes transiently adsorbed precursor molecules into non-volatile fragments whereas volatile fragments are pumped away. In these high-energy (tens of keV) electron-driven processes, low-energy secondary electrons (typically below 100 eV) are produced by the interaction of the primary beam with the surface and surface deposits. Low energy electrons can trigger efficient dissociative ionization and electron attachment reactions to deposited organometallic molecules on the surface of a solid substrate. Such secondary electrons escaping from the surface are relevant to determine the nature of deposits formed, i.e., contamination of the deposited structures, as well as dictating their widths imposed by spatial

resolution limitations,^{3,5–9} although currently achieved below 1 nm.¹⁰

Such level of spatial resolution is extremely relevant for the fabrication of functional nanomaterials due to increasing demand for even-smaller structures with properties tailored to specific applications, control over the deposits composition, reduction of broadening, and increase of the deposition rate. The widths have been identified to be a multiple of the incident beam diameter¹¹ determining therefore the deposit size and position of the order of nano- and sub-nanometer scales.¹⁰ Therefore, comprehensive knowledge on the interaction of electrons with molecules as a function of phase and aggregation is important to understand the underlying processes arising from electron-induced chemistry for FEBIP techniques.

Given the need to fully understand such electron-induced mechanisms, gas-phase studies with isolated EBID precursor molecules $\text{W}(\text{CO})_6$, $\text{Co}(\text{CO})_3(\text{NO})$, MeCpPtMe_3 , and $\text{Pt}(\text{PF}_3)_4$ have been reported recently.^{12–16} There the dominant gas phase dissociative electron attachment (DEA) channels of MeCpPtMe_3 and $\text{Pt}(\text{PF}_3)_4$ were in good agreement with the stoichiometry of the initial deposit and thus DEA is suggested to be one of the decomposition processes lending support to bond breaking of the same molecules adsorbed on solid surfaces when exposed to 500 eV electron interactions.¹⁷ However, this is not clearly the case for $\text{W}(\text{CO})_6$ or $\text{Co}(\text{CO})_3(\text{NO})$ as recently reported in Ref. 18. From such DEA experiments with $\text{W}(\text{CO})_6$, incomplete loss of CO ligands was identified to be a mechanism conferring a particular contaminating behavior on the edge of the deposit,¹⁵ which was also recognized in surface experiments yielding partially decarbonylated tungsten

^{a)}Electronic addresses: Stephan.Denifl@uibk.ac.at and plimaovieira@fct.unl.pt

species ($W_x(CO)_y$).¹⁷ Similar incomplete fragmentation was also observed in electron ionization studies with $W(CO)_6$. However, above a threshold (20.87 ± 0.06 eV)¹⁴ W^+ formation with complete CO ligand loss was observable, i.e., conferring therefore a process to yield the deposition of pure metallic structures.

In real EBID environments, single collision conditions provided by earlier experiments are not attainable and electron interactions have to be explored under different stages of aggregation. Recently, we reported the complete ligand loss in electron ionization of the weakly bound organometallic tungsten hexacarbonyl dimer.¹⁹ Such extensive fragmentation process is only possible by fast conversion of the weak van-der-Waals bond into a strong covalent bond between the metal moieties yielding W_2^+ .¹⁹ In the present study, we report the electron ionization mass spectrum up to the $W(CO)_6$ dimer at the electron energy of 70 eV. In addition, the threshold behavior of various ionic species resulting from the electron ionization is reported. The fragmentation pattern is compared with the one for the bare molecule as well as for the cluster present in superfluid helium nanodroplets. The latter provides an ultracold environment with fast cooling of the embedded species to 0.37 K.^{20,21}

In Sec. II, we present a brief discussion of the experimental details. Section III is devoted to the results and discussion, and finally some conclusions that can be drawn from this study are given in Section IV.

II. EXPERIMENTAL SETUP

Electron ionization was performed in a crossed electron-molecular beam experiment equipped with a double focusing mass spectrometer, which has been described in detail before,²² so only a brief review will be given here. A Nier type ion source with a resolution of ~ 1 eV and beam currents of 10 μA were used. Positive ions were extracted by 6 kV potential from the ion source into the double focusing mass spectrometer. The mass selected cations were detected by a channeltron electron multiplier. Tungsten hexacarbonyl cluster measurements were performed at the electron energy of 70 eV when recording mass spectra. For the determination of the threshold behavior of a mass selected species, the ionization energy was scanned in the range below and above the corresponding threshold. The ionization efficiency curves were fitted with a generalized Wannier law²³ to extract the experimental appearance energies (AEs) with improved accuracy. The calibration of the energy scale for the ionization measurements was performed with respect to the formation of Ar^+/Ar at 15.8 eV and Ar^{2+}/Ar at 43.4 eV.²⁴

A neutral beam of $W(CO)_6$ was formed by supersonic expansion through a 50 μm orifice kept at 150 °C to avoid clogging. The $W(CO)_6$ sample was purchased from Sigma Aldrich, Vienna, with a stated purity $\geq 97\%$ and used as delivered. For better clustering conditions, the solid tungsten hexacarbonyl sample was heated up to about 90 °C and argon was used as seeding gas (1.5 bars). Given that the mass spectra (recorded up to the trimer) evidenced a rather small contribution of ion yields above dimer formation ($<0.2\%$ of

the cluster yield between monomer and dimer), we assume that mostly dimers were present in the cluster beam. For non-clustering conditions, the seeding gas was changed to helium with a pressure slightly above 1 bar. The cluster and ionization chambers were separated by a 1 mm skimmer, with working pressures of $\sim 4 \times 10^{-4}$ mbar in the former and 4×10^{-6} mbar in the latter.

The helium nanodroplet experiments were performed with a helium droplet source coupled to a hemispherical electron monochromator and a quadrupole mass spectrometer for the mass analysis.²⁵ Helium droplets are formed by supersonic expansion at high pressure (20 bars) with high purity gaseous helium ($>99.9999\%$) and temperatures around 10 K, which is achieved using a closed-cycle cryostat. The expanding flow of helium droplets is skimmed 10 mm downstream of the nozzle and then passes into the monochromator chamber. Before entering the interaction region with the electron beam, the droplet beam passes through a pick-up cell, where the doping with $W(CO)_6$ takes place. Electron ionization mass spectra were recorded at about 70 eV.

Assignment of contributing fragments in the mass spectra was performed from the natural W isotope distribution: ^{182}W 27.7%; ^{183}W 15.1%; ^{184}W 32.3%; ^{186}W 24.9%, fitted to the observed intensities.

III. RESULTS AND DISCUSSION

A. Ionization of bare tungsten hexacarbonyl and its clusters

To our knowledge, no comprehensive mass spectrometric observation of cations formed upon electron ionization to van-der-Waals bonded $W(CO)_6$ clusters has been reported yet. However, we have recently reported on the complete ligand loss in electron ionization of the weakly bound organometallic tungsten hexacarbonyl dimer, leading to bare W_2^+ metal cation formation.¹⁹

Figure 1 shows the electron ionization mass spectrum above 180 u (the weight of W^+ is ~ 184 u) up to the monomer for two different expansion conditions. The upper panel (a) shows the mass spectrum, when the neutral beam consisted of monomers only (obtained by using a low amount of helium as seeding gas), while the lower panel was recorded with conditions mentioned in Section II which led to clustering. Spectrum (a) can directly be compared with the mass spectrum for the single molecule shown on the NIST homepage²⁶ as well as the most recent 100 eV electron ionization mass spectrum published by Wnorowski *et al.*¹⁴ In general, good agreement can be observed. The mass spectrum shown in Ref. 14 shows less abundance of all ions above ~ 250 u which may be ascribed to the higher electron energy used (100 eV vs. 70 eV used presently) or mass transmission effects by the quadrupole mass spectrometer used.

Electron ionization on tungsten hexacarbonyl clusters also leads to the formation of observable doubly charged species. Figure 2 shows the formation of doubly charged ions in the mass range from W^{2+} (~ 92 u) up to $W(CO)_6^{2+}$ (~ 176 u)

FIG. 1. Electron ionization mass spectrum between 180 u and 360 u for two different neutral beam expansion conditions. In panel (a) the neutral beam consisted of W(CO)_6 monomers only (obtained by using low amount of helium as seeding gas), while panel (b) was recorded at neutral beam source conditions, where W(CO)_6 clusters were formed (seeding gas argon with 1.5 bars). Both spectra were recorded at an electron energy of 70 eV and normalized to the most abundant fragment.

in case of the molecular beam (upper panel) and in case of the cluster beam (lower panel), respectively. The mass spectra for the single molecule shown in Figures 1 and 2 demonstrate a rich fragmentation pattern upon single and double ionization of the molecule. However, for both charge states, the distinct formation of a parent ion can be observed too. About 39% of W(CO)_6^+ relative to the most intense ion signal for W(CO)_3^+ is observed (see Fig. 1(a)). The same calculation amounts 22% for the doubly charged species (see Fig. 2(a)) where W(CO)_2^{2+} is the most abundant fragment ion. For comparison, Ref. 14 reported ~18% of W(CO)_6^+ relative to the most intense ion signal for W(CO)_3^+ . The latter fragment ion is formed upon the loss of 3 CO ligands from the monomer. The loss of CO ligands is the dominating fragmentation channel upon single and double ionization of

FIG. 2. Electron ionization mass spectrum between 90 u and 180 u for two different neutral beam expansion conditions. In panel (a) the neutral beam consisted of W(CO)_6 monomers only (obtained by using low amount of helium as seeding gas), while panel (b) was recorded at neutral beam source conditions, where W(CO)_6 clusters were formed (seeding gas argon with 1.5 bars). Both spectra were recorded at an electron energy of 70 eV and normalized to the most abundant fragment.

W(CO)_6 . This leads to the most intense series of fragment ion peaks of the type W(CO)_n^+ ($0 \leq n \leq 6$) and W(CO)_n^{2+} ($0 \leq n \leq 6$). In addition, a series of closely spaced peaks can be assigned to WC(CO)_n^+ ($0 \leq n \leq 3$). In Figure 2, the doubly charged ions WC(CO)_n^{2+} ($0 \leq n \leq 4$) are also discernible. These fragment ions are formed by the cleavage of a CO ligand and can be observed albeit with lower intensity than the loss of intact CO units.

If we compare now the ion yields for the single molecule (see Figs. 1(a) and 2(a)) with the cluster ion yields up to the monomer (see Figs. 1(b) and 2(b)), obviously less fragmentation can be observed. The parent ion W(CO)_6^+ increases to a similar abundance as the still dominant fragment ion W(CO)_3^+ . More precisely, the ions W(CO)_6^+ , W(CO)_5^+ , and W(CO)_4^+ increase by a factor ~1.8 relative to the fragment ion series W(CO)_n^+ ($0 \leq n \leq 3$). The same behavior is recognizable in the case of the doubly charged species (Fig. 2) for W(CO)_4^{2+} and W(CO)_6^{2+} , whereat the main abundant fragment changed from W(CO)_3^+ (in the singly charged case) to W(CO)_2^{2+} .

Figure 3 shows the positive ion mass spectrum of W(CO)_6 clusters formed by electron ionization at 70 eV where the scan range extends from 345 u up to 715 u. The peaks observed correspond to cluster ions containing up to two tungsten hexacarbonyl units. Like for the mass range below the monomer, also here the most intense peaks are associated with the loss of CO ligands. A series of peaks are ions of the type $\text{W}_2(\text{CO})_n^+$ ($0 \leq n \leq 12$). In addition, a series of closely spaced peaks are observed and are assigned to $\text{W}_2\text{C(CO)}_n^+$ ($0 \leq n \leq 10$). While the $\text{W}_2(\text{CO})_n^+$ ($1 \leq n \leq 9$) ion series show a monotonic increase with increasing number of carbonyl ligands (from 1 to 9), $\text{W}_2(\text{CO})_{10}^+$ and $\text{W}_2(\text{CO})_{11}^+$ are particularly weak compared to the loss of 3 and more CO ligands from the dimer. Comparing the fragmentation pattern of the monomer (where the loss of only one CO ligand is unfavorable compared to the loss of two CO ligands; see Fig. 1(a)), we may assume that $\text{W}_2(\text{CO})_{10}^+$ is formed by one ligand loss from each moiety rather than the loss of two units from one moiety. This is in contrast with the most abundant fragment $\text{W}_2(\text{CO})_9^+$ which corresponds to the loss of 3 COs and thus covers with the most abundant fragment formed by the electron ionization of W(CO)_6 .

FIG. 3. Electron ionization mass spectrum between 345 u and 715 u for W(CO)_6 clusters. Argon was used as seeding gas with 1.5 bars and the electron energy was 70 eV.

The ligand loss can be observed up to the bare W_2^+ . The formation of this ion was discussed in detail in the work of Neustetter *et al.*¹⁹ We therefore do not repeat the detail of those arguments presented there, rather we reiterate very briefly the following rationale. Such formation was proposed by fast conversion of the weak van-der-Waals bond into a strong covalent bond between the metal moieties,¹⁹ which significantly lowers the threshold for the production of bare deposits suggested in previous studies with single molecules.¹⁴

We now turn our discussion to the observation that single CO ligand loss is much less favorable than multiple ligand loss and below the monomer the yield of $W(CO)_5^+$ is increased in case of clusters (see Fig. 1). The loss of one and two carbonyl ligands from tungsten hexacarbonyl dimer may be related to a possible particular intermediate transition state in the dissociation process. Such assumption seems rather plausible since previous two-colour multiphoton dissociation experiments on $W(CO)_6$, by measuring photofragment velocity distributions after electron ionization of the neutral products, have revealed fast loss of a CO ligand through non-statistical dissociation to form electronically excited $W(CO)_5$.²⁷ After internal conversion, a vibrationally hot fragment in the electronic ground state decays further to yield $W(CO)_4$ via a statistical decay. Another interesting aspect has been reported by Gutmann *et al.*²⁸ where they have explored the photodissociation dynamics of $Cr(CO)_6$ through two dynamical channels for decarbonylation via a short lived transient state, $Cr(CO)_5$, which undergoes in the femtosecond time scale fragmentation into a lower coordinated carbonyl, $Cr(CO)_4$. Given the geometrical similarities between both set of compounds, $W(CO)_6$ and $Cr(CO)_6$, and although we were not able to probe the fast dynamical processes as in the experiments of Gutmann *et al.*²⁹ in $Cr(CO)_6$ clusters, we may assume that ultrafast dynamics must proceed also in the case of tungsten hexacarbonyl since metal-metal bond formation has been recognized as a major driving force straight after CO dissociation from a van-der-Waals bound unit.²⁹ As so, such bond formation may provide additional excess energy which can be disposed of by CO ligand loss and $Cr(CO)_6$ evaporation.²⁹ This mechanism may be prevalent even in the strong fragmentation process typical for electron ionization in tungsten hexacarbonyl clusters.

B. Appearance energies

We determined the ion efficiency curves close to the ionization threshold for several ions resulting from ionization of the clusters.

Figure 4 shows two examples ($W(CO)_6^+$ and $W(CO)_3^+$) of typical threshold curves. Table I lists all appearance energies determined by the fitting procedure introduced in Sec. II. Thresholds of fragment ions below the monomer are compared with the previous data of Wnorowski *et al.*¹⁴

In the case of electron ionization of single $W(CO)_6$, the experimental threshold for the formation of $W(CO)_3^+$ was 13.91 eV,¹⁴ i.e., about 0.6 eV lower than the present case but taking into account the error still comparable. An intact monomer of tungsten hexacarbonyl is obtained as the second most intense ion with an appearance energy of 8.9 eV slightly

FIG. 4. Near threshold $W(CO)_6^+$ ion yield (a) and $W(CO)_3^+$ ion yield (b) as a function of the initial electron energy. The experimental data are shown as solid lines, while the fits based on the Wannier threshold law are shown in dashed lines.

higher with the value reported in Ref. 14 (see Table I). While monomer fragmentation is abundant, W^+ is also discernible at an appreciable intensity. This fragment is formed by the cleavage of the six carbonyl ligands and the intermolecular bond. Taking the mean bond dissociation energy of a carbonyl ligand, ~ 2 eV,¹⁴ the expected threshold value for W^+ is ~ 12 eV higher than that for $W(CO)_6^+$ (see Table I).

Electron ionization of tungsten hexacarbonyl dimer resulting in $W_2(CO)_9^+$ and $W_2(CO)_{12}^+$ formation shows experimental threshold values of 15.2 eV and 9.6 eV, respectively (Table I), the latter 5.6 eV lower than the former. If we take the mean bond dissociation energy of a carbonyl ligand as ~ 2 eV, the expected threshold value for $W_2(CO)_{12}^+$

TABLE I. Appearance energies (AEs) for positive ions formed in electron ionization of $W(CO)_6$ clusters. The differences in the errors of $W_2(CO)_{12}^+$, $W_2(CO)_9^+$, and W^+ compared to the others are due to their lower intensities and statistics.

Assignment	m/z	AE (eV)		
		This work	Reference 14	Reference 19
$W_2(CO)_{12}^+$	704	9.6 ± 1	...	...
$W_2(CO)_9^+$	620	15.2 ± 0.8	...	...
$(W(CO)_6 \cdot Ar)^+$	392	9.0 ± 0.6	...	...
W_2C^+	380	...	...	32.9 ± 0.6
W_2^+	368	...	...	29.3 ± 0.6
$W(CO)_6^+$	352	8.9 ± 0.6	8.47 ± 0.06	...
$W(CO)_3^+$	268	14.5 ± 0.6	13.91 ± 0.06	...
W^+	184	20.9 ± 1	20.87 ± 0.06	...

would be ~ 6 eV lower than that for $W_2(CO)_9^+$, which fits very well with our measurements. The appearance energy of $W(CO)_3^+$ is also about 5.6 eV higher than the appearance energy of $W(CO)_6^+$ which covers, like expectable, with the energy necessary to remove 3 CO ligands from $W_2(CO)_{12}^+$.

We also note that under specific expansion conditions (lower evaporation temperature of $W(CO)_6$), mixed clusters with argon can be observed. However, the ion $(W(CO)_6 \cdot Ar)^+$ has an appearance energy of 9.0 eV with a threshold value similar to $W(CO)_6^+$ (see Table I). Such is only possible if in $(W(CO)_6 \cdot Ar)^+$, the electron was removed from the $W(CO)_6$, since the ionization energy of $W(CO)_6$ (8.9 eV) is much lower than that for Ar^+ (~ 15.76 eV).²⁴

C. Ionization in helium droplets

Figure 5 shows the ionization mass spectra between 360 u and 720 u obtained by electron ionization of helium nanodroplets doped with tungsten hexacarbonyl at the electron energy of 70 eV and two different helium expansion conditions. Pick-up conditions were chosen so that preferentially dimers of $W(CO)_6$ were formed, i.e., no signals from larger clusters were observed within the detection limit of the apparatus.

Figure 5(a) shows the spectrum recorded at the helium source temperature of 10 K which corresponds to a helium droplet size of about 50 000 He atoms.³⁰ In contrast, a temperature of 11.5 K was chosen for the spectrum in Figure 5(b) which corresponds to a droplet size of about 2000 He atoms. Compared to the bare clusters, a remarkable

FIG. 5. Electron ionization mass spectrum between 360 u and 720 u for $W(CO)_6$ clusters embedded in helium nanodroplets. For panel (a), the helium droplet source temperature was 10 K, i.e., the neutral He droplet size was about 50 000. For panel (b), the helium droplet source temperature was 11.5 K, i.e., the neutral He droplet size was about 2000. Both spectra are normalized on the peak of $W_2(CO)_{11}^+$ and for better visibility, the region around the dimer is zoomed with a factor of 10.

difference can be observed, when the clusters embedded in helium droplets are ionized: the formation of the intact dimer ion is very weak and the mass spectrum is dominated by fragment ions. We note that in Figure 5(b), this ion is not discernibly from helium containing ions covering the whole mass range. We can ascribe this result to the different ionization mechanism operative for the bare clusters and the clusters embedded in the helium matrix. While in the former case direct electron ionization occurs and the electron may also deposit a low fraction of excess energy in the cluster (without electronic excitation), the ionization process in the helium droplet occurs upon charge transfer from an ionized helium atom, which deposits substantial excess energy in the cluster (difference between ionization energy of the helium atom and of the dimer, i.e., around 15 eV). It is known that for clusters deeply buried in a helium droplet, the electron ionization of the doped droplet initially creates an ionized helium atom before few resonant charge transfer processes between He atom lead to migration of the hole to the dopant.^{31,32} This explanation also is in line with the fragmentation mechanism discussed above where an electronically excited state of the cluster ion formed in the ionization drives the fragmentation process. The low amount of the dimer ion observed in Figure 5(a) may be ascribed to fragmentation from larger clusters, since the distribution of the neutral $W(CO)_6$ molecules deposited in the droplet is not uni-sized.

Due to the substantial excess energy deposited by the charge transfer, we suggest that the ionized dimer is in an electronically excited state, which quickly decays by the loss of a CO ligand from one or both $W(CO)_6$ moieties. As discussed above, such non-ergodic dissociation occurs via a repulsive reaction coordinate and cannot be quenched by the surrounding helium matrix as shown in the previous case for anions.^{33,34} However, the subsequent decay of the vibrationally hot $W_2(CO)_{10}^+$ and $W_2(CO)_{11}^+$ ions via further loss of CO ligands may be (at least partially) quenched by the surrounding helium matrix, which provides an efficient heat bath. Indeed, the $W_2(CO)_{10}^+$ and $W_2(CO)_{11}^+$ ions, which are barely visible for the neat clusters (see Fig. 2), become substantially enhanced, when embedded in the helium matrix. Moreover, though the quenching seems incomplete, the loss of more than 5 CO ligands is considerably reduced compared to the bare clusters. However, the resulting fragmentation pattern depends on the size of the surrounding helium droplet (see Figs. 5(a) and 5(b)), indicating an incomplete cooling process of a statistical decay of vibrationally hot ions.

IV. CONCLUSIONS

Positive ion mass spectra of $W(CO)_6$ clusters formed by electron ionization at 70 eV have been investigated in a crossed electron-molecular beam experiment coupled to a mass spectrometer system. Here we find that electron ionization processes are highly efficient in breaking multiple W–CO intramolecular bonds. The present results for bare clusters are in agreement with a previous suggestion of the dissociation process of ionized $W(CO)_6$, where the ion decays due to electronic excitation quickly by the loss of a CO ligand before further loss of CO ligands from this vibrationally

excited fragment occurs in a statistical decay. Mass spectra recorded for $\text{W}(\text{CO})_6$ embedded in helium droplets support this assumption.

Concerning implications of the present results for the nanofabrication processes through beam induced deposition techniques, we note that the present reaction environment bridges the simple gas-phase and condensed phase studies. We obtain strong fragmentation of the organometallic molecule, which is desired in beam induced deposition in order to produce pure metallic deposits. However, the (single) electron collision process accompanied by dissociative ionization leads to only the partial removal of CO ligands which is also preserved for clusters. Compared to other electron induced decomposition processes like dissociative electron attachment, we note that also the choice of the substrate will influence the secondary electron energy distribution and thus the relative importance of ionization and attachment processes as discussed previously.¹⁸

ACKNOWLEDGMENTS

This work has been supported by FWF, Wien, Austria (Grant Nos. P24443 and I1015). PLV acknowledges funding from the Portuguese Foundation for Science and Technology (FCT) through research Grant Nos. PTDC/FIS-ATO/1832/2012 and UID/FIS/00068/2013. Some of this work forms part of the EU/ESF COST Action CELINA—CM1301.

- ¹I. J. Luxmore, I. M. Ross, A. G. Cullis, P. W. Fry, J. Orr, and P. D. Buckle, *Thin Solid Films* **515**, 6791 (2007).
- ²M. Song and K. Furuya, *Sci. Technol. Adv. Mater.* **9**, 023002 (2008).
- ³F. Porriati, R. Sachser, and M. Huth, *Nanotechnology* **20**, 195301 (2009).
- ⁴I. Sychugov, Y. Nakayama, and K. Mitsuishi, *J. Phys. Chem. C* **113**, 21516 (2009).
- ⁵H. W. P. Koops, R. Weiel, D. P. Kern, and T. H. Baum, *J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.* **6**, 477 (1988).
- ⁶P. D. Rack, S. Randolph, Y. Deng, J. Fowlkes, Y. Choi, and D. C. Joy, *Appl. Phys. Lett.* **82**, 2326 (2003).
- ⁷J. J. L. Mulders, L. M. Belova, and A. Riazanova, *Nanotechnology* **22**, 055302 (2011).
- ⁸I. Utke, P. Hoffmann, and J. Melngailis, *J. Vac. Sci. Technol., B: Microelectron. Nanometer Struct.* **26**, 1197 (2008).
- ⁹W. F. van Dorp and C. W. Hagen, *J. Appl. Phys.* **104**, 081301 (2008).

- ¹⁰W. F. van Dorp, B. van Someren, C. W. Hagen, P. Kruit, and P. A. Crozier, *Nano Lett.* **5**, 1303 (2005).
- ¹¹N. Silvis-Cividjian, C. W. Hagen, and P. Kruit, *J. Appl. Phys.* **98**, 084905 (2005).
- ¹²S. Engmann, M. Stano, Š. Matejčík, and O. Ingólfsson, *Phys. Chem. Chem. Phys.* **14**, 14611 (2012).
- ¹³S. Engmann, M. Stano, Š. Matejčík, and O. Ingólfsson, *Angew. Chem., Int. Ed.* **50**, 9475 (2011).
- ¹⁴K. Wnorowski, M. Stano, W. Barszczewska, A. Jówko, and Š. Matejčík, *Int. J. Mass Spectrom.* **314**, 42 (2012).
- ¹⁵K. Wnorowski, M. Stano, C. Matias, S. Denifl, W. Barszczewska, and Š. Matejčík, *Rapid Commun. Mass Spectrom.* **26**, 2093 (2012).
- ¹⁶O. May, D. Kubala, and M. Allan, *Phys. Chem. Chem. Phys.* **14**, 2979 (2012).
- ¹⁷S. G. Rosenberg, M. Barclay, and D. H. Fairbrother, *Phys. Chem. Chem. Phys.* **15**, 4002 (2013).
- ¹⁸R. M. Thorman, T. P. Ragesh Kumar, D. H. Fairbrother, and O. Ingólfsson, *Beilstein J. Nanotechnol.* **6**, 1904–1926 (2015).
- ¹⁹M. Neustetter, A. Mauracher, P. Limão-Vieira, and S. Denifl, *Phys. Chem. Chem. Phys.* **18**, 9893–9896 (2016).
- ²⁰S. Denifl, *Eur. Phys. J.: Spec. Top.* **222**, 2017–2033 (2013).
- ²¹O. Echt, T. D. Märk, and P. Scheier, *Handbook of Nanophysics Clusters and Fullerenes* (CRC Press, 2010), Vol. 7.
- ²²D. Almeida, D. Kinzel, F. F. da Silva, B. Puschnigg, D. Gschliesser, P. Scheier, S. Denifl, G. García, L. González, and P. Limão-Vieira, *Phys. Chem. Chem. Phys.* **15**, 11431 (2013).
- ²³G. H. Wannier, *Phys. Rev.* **90**, 817 (1953).
- ²⁴B. Gstir, S. Denifl, G. Hanel, M. Rümmele, T. Fiegele, P. Cicman, M. Stano, S. Matejčík, P. Scheier, K. Becker, A. Stamatovic, and T. D. Märk, *J. Phys. B: At., Mol. Opt. Phys.* **35**, 2993 (2002).
- ²⁵S. Denifl, V. Vizcaino, T. D. Märk, E. Illenberger, and P. Scheier, *Phys. Chem. Chem. Phys.* **12**, 5219 (2010).
- ²⁶See www.nist.gov for an electron ionization mass spectrum of single tungsten hexacarbonyl.
- ²⁷B. Venkataraman, H. Hou, Z. Zang, S. Chen, G. Bandukwalla, and M. Vernon, *J. Chem. Phys.* **92**, 5338 (1990).
- ²⁸M. Gutmann, J. M. Janello, M. S. Dickebohm, M. Grosseckhöfer, and J. Lindener-Roenneke, *J. Phys. Chem. A* **102**, 4138 (1998).
- ²⁹M. Gutmann, M. S. Dickebohm, and J. M. Janello, *J. Phys. Chem. A* **103**, 2580 (1999).
- ³⁰L. F. Gomez, E. Loginov, R. Sliter, and A. F. Vilesov, *J. Chem. Phys.* **135**, 154201 (2011).
- ³¹A. M. Ellis and S. Yang, *Phys. Rev. A* **76**, 032714 (2007).
- ³²F. Ferreira da Silva, S. Jaksch, G. Martins, H. M. Dang, M. Damp, S. Denifl, T. D. Märk, P. Limão-Vieira, J. Liu, S. Yang, A. M. Ellis, and P. Scheier, *Phys. Chem. Chem. Phys.* **11**, 11631 (2009).
- ³³S. Denifl, F. Zappa, A. Mauracher, F. Ferreira da Silva, A. Bacher, O. Echt, T. D. Märk, D. K. Böhme, and P. Scheier, *ChemPhysChem* **9**, 1387–1389 (2008).
- ³⁴S. Denifl, F. Zappa, I. Mähr, A. Mauracher, M. Probst, T. D. Märk, and P. Scheier, *J. Am. Chem. Soc.* **130**, 5065–5071 (2008).