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Ionization and photofragmentation of $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$

Oliver Schalk,^{1,a)} Ida Josefsson,¹ Robert Richter,² Kevin C. Prince,² Michael Odelius,¹ and Melanie Mucke^{3,a)}

¹Department of Chemical Physics, AlbaNova University Centre, Stockholm University, Roslagstullsbacken 21, SE-106 91 Stockholm, Sweden

²Elettra-Sincrotrone Trieste, Area Science Park, I-34149 Basovizza, Trieste, Italy

³Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden

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In this paper, we use a combination of photoelectron spectroscopy, mass spectrometry, and density functional theory calculations to get a detailed understanding of valence single and double ionization and the subsequent dissociation processes. This is exemplified on benchmark systems, trimetallo-dodecacarbonyls $\text{M}_3(\text{CO})_{12}$ with $\text{M} = \text{Ru}, \text{Os}$, where the energy remaining in the molecule after photoionization can be retrieved by measuring the degree of fragmentation of the molecular ion. The intensity of different mass peaks can thus be directly related to ionization cross sections obtained by photoelectron spectroscopy. We find that the $\text{M}-\text{CO}$ dissociation energy rises as the number of CO ligands decreases due to dissociation. Moreover, ionization of the CO ligands has a higher cross section than that of the metal center for both single and double ionization. After advanced fragmentation, a CO bond can break and the carbon atom remains bonded to the metal core. In addition, we found that the valence ionization cross sections of $\text{M}_3(\text{CO})_{12}$ are maximal at about 40 eV photon energy thus showing a more pronounced shape resonance than Ru and Os-complexes with a single metal atom center. Finally, an $np \rightarrow nd$ giant resonance absorption causes a significant increase of the ionization cross section above 50 eV for $\text{Ru}_3(\text{CO})_{12}$. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4933060>]

I. INTRODUCTION

The reaction pathways of molecules upon photoionization can be complex. This complexity increases even more when higher photon energies are used for ionization: New fragmentation channels appear, double or multiple ionizations and intramolecular Coulombic decay can take place,¹ and, at even higher photon energies, core level ionizations and excitations can occur, initiating effects like Auger decay.² Often, these processes are studied by electron spectroscopy and the resulting fragmentation of the parent molecule is not considered. This is so either because the investigated systems have so few atoms that no new information is obtained by studying the fragmentation processes or because the molecule has so many competing dissociation pathways that they cannot profitably be disentangled. However, this is not always the case.

In the present study, we investigated molecules where (i) the fragmentation follows a clear reaction path and which (ii) potentially allow studying several effects that were only investigated in atoms or smaller systems before, such as the appearance energies of double ionization³ or the dynamics triggered by ionization of f electrons.⁴ The investigated molecules are triruthenium and triosmium dodecacarbonyl ($\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$). Below the double ionization threshold there exists only one dissociation channel, namely cleavage of $\text{M}-\text{CO}$ bonds ($\text{M} = \text{Ru}, \text{Os}$). The high number of CO ligands (12)

allows us to follow the excess energy release in these molecules upon ionization by studying the fragmentation pattern using mass spectrometry. Moreover, the ionization process can take place at two different sites of the molecule; either at the central M_3 core with ionization energies between 7.5 and 11 eV⁵ or at the CO ligands with ionization energies between 13.5 and 19 eV.^{6,7} As a consequence, double ionization can occur either exclusively at the M_3 core, where Coulomb repulsion of two positive charges is high³ or at either both the M_3 -core and the CO ligands or the CO ligands only, where the two charges are distributed over the whole molecule. Hence, we are able to identify the influence of the Coulomb repulsion on double ionization. Finally, we can investigate whether the presence of f electrons and the more pronounced relativistic effects in $\text{Os}_3(\text{CO})_{12}$ influence the fragmentation processes.

First fragmentation studies of $\text{Os}_3(\text{CO})_{12}$ using multi-photon ionization experiments were executed by Nakanaga *et al.*,⁸ where the authors looked at ion appearance energies of $\text{Os}_3(\text{CO})_{12}$ as a function of the laser pulse wavelength. They determined the energy required for loss of one, three, and four CO molecules and interpolated the average fragmentation energy to 1.6 eV per CO molecule while their B3LYP/LANL2DZ(Os)/6-311G** (C, O) calculation showed a dissociation energy of 1.16 eV for the first CO. Mizota *et al.* studied ionization properties of $\text{Os}_3(\text{CO})_{12}$ ⁹ and found that a high m/e selectivity could be achieved when applying the right ionization methods and conditions. These results motivated us to study the ionization process and the subsequent fragmentation processes by using a synchrotron radiation

^{a)}Electronic addresses: oliver.schalk@fysik.su.se and melanie.mucke@physics.uu.se

source and applying both photoelectron spectroscopy and mass spectrometry.

II. METHODS

A. Experimental

$\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ were purchased from Sigma-Aldrich with purities of 99% and 98%, respectively, and were used without further purification.

Experiments were performed at the side branch of the gas phase beamline at the storage ring ELETTRA (Trieste, Italy). The general layout of the beamline and its performance was described earlier.¹⁰ Here, we provide a short overview of the methods used. Photoelectron spectra were recorded with a commercial hemispherical electron energy analyzer (VG 220i) which was placed at the magic angle with respect to the polarization of the incoming synchrotron beam.^{11,12} The analyzer was used with pass energies of 5 eV and 10 eV which provided a resolution of 100 meV for the spectra measured at low photon energies (25–60 eV) and a resolution of 200 meV for the spectra at 120 eV photon energy. For a pass energy of 5 eV, the transmission function was measured using the Auger spectrum of xenon^{13,14} and was flat within $\pm 10\%$ for electrons with kinetic energies between 13 and 35 eV and decreased for lower kinetic energies to 91% of the maximum transmission at 10 eV and 70% of the maximum transmission at 8 eV. The samples were introduced to the interaction region using a resistively heated, anti-inductively wound oven. The temperature was kept at 48 °C for $\text{Ru}_3(\text{CO})_{12}$ and 74 °C for $\text{Os}_3(\text{CO})_{12}$. While $\text{Os}_3(\text{CO})_{12}$ did not decompose at the given temperature, $\text{Ru}_3(\text{CO})_{12}$ showed slight fragmentation and traces of N_2 , H_2O , and CO could be found in both photoelectron and mass spectra of $\text{Ru}_3(\text{CO})_{12}$. Since the metal containing decomposition products had significantly lower vapor pressures than $\text{Ru}_3(\text{CO})_{12}$ itself,¹⁵ we did not expect contributions from these molecules to our data. We added Xe at a constant pressure for relative intensity calibration of the spectra. The first ionization band of Xe appears at 12.12 eV¹⁶ which is well separated from the ionization bands of the dodecacarbonyls; and the photon energy dependent ionization cross sections of this peak are well known.¹⁷

Mass spectra were recorded with a home-made time-of-flight spectrometer and the instrument is described in detail in Ref. 11. The photon energies used were 27 eV, because it allowed using a Mg-filter with an absorption edge of 49.5 eV in order to block higher order radiation, 50 eV as intermediate photon energy still below the giant $np \rightarrow nd$ resonance in $\text{Ru}_3(\text{CO})_{12}$ (see below) and 120 eV which is well above all outer valence resonances.

B. Theoretical methods

The geometries of the $\text{M}_3(\text{CO})_{12}$ and $\text{M}_3(\text{CO})_n^+$ complexes ($\text{M} = \text{Ru}, \text{Os}$) were optimized with the Gaussian 09 code, using density functional theory (DFT) with the mPW1PW91 functional,¹⁸ based on the generalized gradient approximation. The functional has been reported to be a reliable method for predicting structures and vibrational frequencies for second and third row transition metal systems.^{19,20}

To reduce the computational cost, the relativistic LANL2DZ effective core potential plus a basis set of double zeta (DZ) quality^{21–23} was used for the transition metal atoms. The carbon and oxygen atoms were described with an all-electron valence DZ basis set ((9s 5p)/[3s 2p]).²⁴ The adiabatic ionization energy was calculated as the energetic difference between the charged and neutral complexes.

In order to calculate the energy of CO detachment from the clusters, unsaturated $\text{M}_3(\text{CO})_n^+$ ($n = 11, 10, 6, 3-0$) complexes and the single CO molecule were optimized. Zero-point energies were calculated for each species separately and added to the electronic energy. An estimate of the basis set superposition error (BSSE) was obtained through counterpoise correction of the interaction energies between the CO and $\text{M}_3(\text{CO})_{11}^+$ fragments at the $\text{M}_3(\text{CO})_{12}^+$ geometry.

By performing a relaxed scan of the M—C distance in $\text{M}_3(\text{CO})_{12}^+$ and optimizing the geometry to a possible saddle point on the potential energy surface, we investigated if there is a barrier for the M—C dissociation. For this purpose, the PBE functional^{25,26} with Grimme's D3 dispersion correction²⁷ was used.

III. RESULTS

A. Density functional theory calculations

Ion ground state (appearance) energies E_n for $\text{M}_3(\text{CO})_n^+$ ($n = 12-10, 6, 3-0$) are given in Table I while selected structures are shown in Figure 1. The energetic difference between molecules with n CO-groups and molecules with $n - 1$ CO groups increases slightly for smaller n (i.e., increased fragmentation). The appearance energies could be fitted to a parabolic function,

$$E_n (\text{eV}) = a_0 + (12 - n)a_1 + (12 - n)^2 a_2, \quad (1)$$

TABLE I. Dissociation energies $\text{M}_3(\text{CO})_{12}^+ \rightarrow \text{M}_3(\text{CO})_n^+ + (12 - n) \text{CO}$ in eV, including the zero-point energy.

n	Structure	$\text{Ru}_3(\text{CO})_n^+/\text{eV}$	$\text{Os}_3(\text{CO})_n^+/\text{eV}$
12	Bridged ^a	0.00	0.07
12	Twisted ^a	0.06	0.00
11	A ^b	1.59	1.85
11	B ^b	1.59	2.08
10	(4,3,3) ^c	3.20	4.03
10	(4,4,2)	3.24	4.26
6	(3,2,1)	9.73	12.06
6	(2,2,2) (A)	10.39	13.52
6	(2,2,2) (B)	10.62	14.49
3	(1,1,1)	15.59	19.41
2	(1,1,0)	17.36	21.82
2	(2,0,0)	18.41	22.23
1		19.86	24.69
0		21.88	27.59
CP-correction ^d	In-plane	−0.37	−0.34
CP-correction ^d	Out-of-plane	−0.26	−0.31

^aBridged: Two CO-groups are attached to two metal centers, twisted: no bridges are formed, but there is a strong distortion from D_{3h} -symmetry.

^bA: structure with one extended M—M bond B: no extended M—M-bond.

^c(x, y, z) denotes the number of CO attached at each of the metal atoms.

^dThe counterpoise correction in eV for the basis set superposition error calculated for the $\text{M}_3(\text{CO})_{12}^+$ ion.

FIG. 1. Minimum energy structures of selected singly ionized $\text{Os}_3(\text{CO})_n^+$ and $\text{Ru}_3(\text{CO})_n^+$ molecules ($n = 3, 6, 11, 12$), as well as the structures of $\text{Os}_3\text{C}(\text{CO})^+$ and $\text{Ru}_3\text{C}(\text{CO})^+$.

where a_0 , a_1 , and a_2 take values of 7.83 eV, 0.142 eV, and 0.033 eV for $\text{Ru}_3(\text{CO})_{12}$ and 8.23 eV, 0.145 eV, and 0.044 eV for $\text{Os}_3(\text{CO})_{12}$, respectively. It thus gets increasingly harder to split off a CO molecule when less COs are attached to the metal core. The energy differences agree with the experimental findings in Ref. 8 (see Introduction), and also with our experimental results (see below). The retrieved energies depend on several effects which are (i) the position at which fragmentation occurs, i.e., the number of CO ligands which are attached to the different metal atoms, (ii) CO bridging between two metal atoms, and (iii) dissociation barriers. These will be briefly discussed in the following.

- (i) For both molecules, different fragmentation pathways were taken into account, such that, e.g., loss of two CO ligands can occur at the same or two different sites of the molecule. We found that fragmentation from two sites usually led to lower energies. In the case of $\text{Os}_3(\text{CO})_6^+$, the minimum energy was found for an unequal (3, 2, 1) CO distribution. We found no difference for CO detachment in axial or equatorial position implying the molecules are able to rearrange easily.
- (ii) One of the differences between $\text{Ru}_3(\text{CO})_{12}^+$ and $\text{Os}_3(\text{CO})_{12}^+$ is the minimum energy geometry. While $\text{Os}_3(\text{CO})_{12}$ undergoes only small changes upon ionization, $\text{Ru}_3(\text{CO})_{12}$ forms a structure where two C atoms are bridging between two Ru atoms (see Figure 1). However, since the energetic difference between bridged and unbridged species is small for both molecules and the internal energy of the molecules is large after photoionization, there will be a dynamical equilibrium between bridged and unbridged structures for both species. As discussed later, this bridged structure might be the starting point for C=O bond cleavage.

- (iii) We investigated the existence of a dissociation barrier by scanning the potential energy surface upon elongating a M—CO-bond and locating a transition state. However, all attempts failed so we assume barrier-free detachment of CO ligands.

While the main dissociation channel is detachment of whole CO molecules, a break of the C=O bond can be observed if only one or two CO molecules are attached to the metal core (see mass spectra). In case of two attached CO molecules, the C=O bond dissociation energies are 7.03 and 7.07 eV for $\text{Os}_3(\text{CO})_2^+$ and $\text{Ru}_3(\text{CO})_2^+$, respectively, and hence require an additional 5 eV as compared to CO ligand detachment.

The dissociation processes that follow photoionization can also be regarded from a temperature perspective. Using the calculated vibrational frequencies of the cations, it is possible to extract vibrational temperatures of the excited ions. If ionization leaves an additional 1.7 eV of internal energy in the dodecacarbonyl which is a little more than required for dissociation of one CO ligand, it is heated to 500 K (the vibrational temperatures for $\text{Ru}_3(\text{CO})_{12}^+$ and $\text{Os}_3(\text{CO})_{12}^+$ are almost identical).

B. Photoelectron spectra

The photoelectron spectrum of $\text{Os}_3(\text{CO})_{12}$ for ionization energies between 5 and 80 eV recorded at a photon energy of 120 eV is shown in Figure 2. In the high energy region, two dominant peaks appear at 57.7 and 60.4 eV which can be assigned to osmium 4*f* electron ionization ($f_{5/2}$ and $f_{7/2}$ bands). Next to these peaks are two peaks at 52.4 and 64.8 eV which represent ionization from the osmium 5*p*_{3/2} and 5*p*_{1/2} bands. The energies of these bands are in good agreement with those found for $\text{Os}(\text{CO})_4\text{PMe}_3$.²⁸ The low energy part up to ionization energies of 22 eV was recorded for a series of photon energies and is shown in Figures 3 and 4. The origin of the peaks was discussed before^{5,7} and is summarized in Table II: In the energy region between the ionization potential of 7.82 eV

FIG. 2. Photoelectron spectra of $\text{Os}_3(\text{CO})_{12}$ (black) and $\text{Ru}_3(\text{CO})_{12}$ (red) recorded at photon energies of 120 eV and 50 eV, respectively. For the photoelectron spectrum of $\text{Ru}_3(\text{CO})_{12}$, background signal of residual gases, mainly CO, N_2 , and H_2O , has been subtracted.

FIG. 3. Photoelectron spectra of $\text{Os}_3(\text{CO})_{12}$ between 7 and 11.5 eV recorded at different photon energies. The spectra are normalized with respect to simultaneously measured Xe. See text for details.

and 11 eV, peaks result from ionization of the $5d$ orbitals of the Os_3 center while the bands between 13 and 17 eV stem from the $5\sigma + 1\pi$ orbitals of the CO ligands and the bands between 17 and 21 eV originate from the 4σ orbitals of the CO ligands. For comparison, the 5σ , 1π , and 4σ -molecular orbitals of free CO have vertical ionization potentials of 14.01 eV, 16.91 eV (with a 1.5 eV progression), and 19.72 eV, respectively.²⁹ The larger width of the peaks labeled C2 and D2 in Figure 3 suggests that these are composed of two peaks which are not well separated. A more detailed analysis is given in Section IV.

When investigating the photon energy dependence of the photoelectron spectra of $\text{Os}_3(\text{CO})_{12}$ in the region between 25 and 60 eV, we found that the total cross sections for d -electron ionization and CO ionization as well as the isolated peaks were maximal at (41 ± 3) eV photon energy (see Figure 5(a)). When looking at the ratio between the ionization cross section of the d electrons and the ionization of the CO molecules, we saw a minimum value of 0.19 at (43 ± 3) eV photon energy (Figure 5(b)) meaning that most electrons are emitted from CO ligands. However, at a photon energy of 120 eV we observed an

FIG. 4. Photoelectron spectra of $\text{Os}_3(\text{CO})_{12}$ between 12 and 22 eV recorded at different photon energies. The spectra are normalized with respect to simultaneously measured Xe. See text for details.

TABLE II. Ionization potentials for $\text{Os}_3(\text{CO})_n$ and $\text{Ru}_3(\text{CO})_n$. The labels A-D are according to the nomenclature used in Figure 3 and Ref. 5.

Peak label	A	B1	B2	C1	C2	D1	D2
Symmetry	$2a_1'$	$2e'$	$2e'', 1e'$	$2a_1''$	$1e''$	$1a_1'$	a_2''
$\text{Os}_3(\text{CO})_{12}$	7.82	8.26	8.54	9.10	9.65	10.27	10.63
$\text{Ru}_3(\text{CO})_{12}$	7.72	7.90	8.25	8.94	9.41	~ 9.8	10.19

even lower value of 0.12. The cross-section of the $5d$ electrons falls rapidly with increasing photon energy due to the Cooper minimum, which occurs at about 200 eV.³⁰

The spectra for $\text{Ru}_3(\text{CO})_{12}$ are shown in Figure 6. They are similar to the spectra of $\text{Os}_3(\text{CO})_{12}$ and the ionization potential of 7.72 eV is just 0.1 eV below that of $\text{Os}_3(\text{CO})_{12}$. However, the $\text{Ru}_3(\text{CO})_{12}$ spectra are less well resolved which might be due to relativistic contributions in the heavier osmium molecule.^{5,6,31} The $\text{Ru}_3(\text{CO})_{12}$ spectra taken at 30 and 60 eV photon energy are clearly distinct from the other spectra. At 60 eV, we observe an intensity increase of the $2a_1'$ and the $1e''$ bands (A and C2 in Figure 6, compare labeling with Table II). The same bands

show a higher relative oscillator strength at 30 eV, however, now they also seem to be spectrally narrower. Between 35 and 50 eV, the cross section for d -electrons ionization was maximal at (42 ± 3) eV, close to the value for $\text{Os}_3(\text{CO})_{12}$.

C. Mass spectra

Mass spectra of $\text{Os}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ measured at photon energies of 27, 50, and 120 eV together with assignments of the fragments are shown in Figures 7 and 8. The peak widths are predominantly caused by the isotope distributions of Ru and Os. The main fragmentation channel is the loss of CO groups. At an excitation energy of 27 eV, fragmentation down to $n = 2$ can be observed for the singly ionized fragments of $\text{Ru}_3(\text{CO})_{12}$, i.e., $\text{Ru}_3(\text{CO})_n^+$, where n is the number of remaining CO molecules. For $\text{Os}_3(\text{CO})_{12}$, the smallest number of remaining CO-molecules is $n = 3$. This degree of detachment is in excellent agreement with the energetic results from our DFT calculations as well as Equation (1). In Section IV B, we show how the intensity distribution of the mass peaks correlates with the photoelectron spectrum. In addition, for doubly ionized $\text{Os}_3(\text{CO})_{12}$, we observe fragmentation down to $n = 9$.

In the case of $\text{Os}_3(\text{CO})_{12}$, at photon energies of 50 and 120 eV, full abstraction of CO molecules is observed for the singly as well as for the doubly ionized molecule. In addition, $\text{Os}_2(\text{CO})_n^{2+}$ fragments are observed ($n = 1-6$). No singly charged $\text{Os}(\text{CO})_n$ -ions are found in the mass spectrum, implying that all charge is localized at the $\text{Os}_2(\text{CO})_n^{2+}$ unit in the case of a metal-metal bond cleavage. In addition, no series of singly charged $\text{Os}_2(\text{CO})_n^+$ fragments was detected. Moreover, there is no markedly high probability for complete CO abstraction at the investigated photon energies, i.e., a single ionization event does not provide much more internal energy than needed for complete CO loss, otherwise we would expect to detect more Os^{3+} ions.

The spectrum taken at 120 eV shows an increased background at masses between 300 and 320 amu. In this region, we see unexpected fragments of $\text{Os}_3\text{C}(\text{CO})^{2+}$ and $\text{Os}_3\text{C}(\text{CO})_2^{2+}$ peaking at energies of 306 and 320 amu. The $\text{Os}_3\text{C}(\text{CO})_n^{2+}$ fragments result from CO bond cleavage. This cleavage is accessible because the bridging structure of CO molecules between two Os atoms strengthens the metal-carbon bond and weakens the CO bond as discussed in the theory section. The DFT-optimized geometry of $\text{Os}_3\text{C}(\text{CO})^+$ is shown in Figure 1. The appearance of this fragmentation is most prominent upon excitation at 120 eV when more internal energy is potentially available, but also visible when using 50 eV photons. A weak peak indicating a CO bond cleavage can also be observed for the singly charged complexes at a mass

FIG. 5. (a) Peak intensities corresponding to relative ionization cross sections of the d electrons with ionization energies between 7 and 11 eV and the ligand electrons with energies between 13 and 21 eV for $\text{Os}_3(\text{CO})_{12}$ at different photon energies. Labels of the bands are according to Figure 3 and Table II. E and F denote ionization from 4σ - and $5\sigma+1\pi$ orbitals of the ligands, respectively. (b) Ratio between ionization from the Os_3 core and the ligands. Added is a cubic spline fit to the data.

FIG. 6. Photoelectron spectra of $\text{Ru}_3(\text{CO})_{12}$ between 7 and 11.5 eV recorded at different photon energies. The spectra are normalized with respect to simultaneously measured Xe. See text for details.

of ~ 585 amu, indicating Os_3C^+ . The ion formation ratios of $\text{Os}_3(\text{CO})_n^+$: $\text{Os}_3(\text{CO})_n^{2+}$: $\text{Os}_2(\text{CO})_n^{2+}$ are listed in Table III.

The mass spectrum of $\text{Ru}_3(\text{CO})_{12}$ is similar to the spectrum of $\text{Os}_3(\text{CO})_{12}$ in many respects. Both molecules show the same fragmentation pattern, i.e., complete CO split-off, no singly

ionized $\text{Ru}_2(\text{CO})_n^+$, a low intensity of the $\text{Ru}_3(\text{CO})_{10}^+$ peak, carbide peaks of $\text{Ru}_3\text{C}(\text{CO})^+$ and $\text{Ru}_3\text{C}(\text{CO})_2^+$ etc. However, there are some notable differences: (i) The fragmentation pattern of $\text{Ru}_3(\text{CO})_n^{2+}$ has holes, i.e., peaks with $n = 9$ and

FIG. 7. Mass spectra of the fragments upon ionization of $\text{Os}_3(\text{CO})_{12}$ with 27 (black), 50 (green), and 120 eV (red).

FIG. 8. Mass spectra of the fragments upon ionization of $\text{Ru}_3(\text{CO})_{12}$ with 27 (black), 50 (green), and 120 eV (red).

TABLE III. Ionization and fragmentation channels of $\text{Os}_3(\text{CO})_n$ and $\text{Ru}_3(\text{CO})_n$ upon excitation with different photon energies.

Photon energy (eV)	$\text{Os}_3(\text{CO})_n^+$ (%)	$\text{Os}_3(\text{CO})_n^{2+}$ (%)	$\text{Os}_2(\text{CO})_n^{2+}$ (%)	$\text{Ru}_3(\text{CO})_n^+$ (%)	$\text{Ru}_3(\text{CO})_n^{2+}$ (%)	$\text{Ru}_2(\text{CO})_n^{2+}$ (%)
27	99	1	...	100	...	...
50	79	20	1	70	28	2
120	43	38	19	58	30	12

$n = 7$ are missing. (ii) CO-cleavage of the singly ionized species continues to $n = 2$ instead of $n = 3$, signifying a lower binding energy of CO molecules to the metal core. (iii) In contrast to $\text{Os}_3(\text{CO})_{12}$, $\text{Ru}_3(\text{CO})_{12}$ shows an increased probability of complete CO loss upon single ionization, which might indicate either a smaller CO binding energy or a larger metal-metal bond strength. (iv) The double ionization cross sections of $\text{Os}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ must be clearly different: While double ionization is slightly preferred in $\text{Ru}_3(\text{CO})_n$ at 50 eV, it is more prominent for $\text{Os}_3(\text{CO})_{12}$ at 120 eV. We speculate that this might be influenced by the additional f electron ionization channel in $\text{Os}_3(\text{CO})_n$.

IV. DISCUSSION

A. Photon energy dependence of the electron spectra

The total ionization cross sections are maximum at a photon energy between 40 and 45 eV both for the metal core $5d$ electrons and the ligand bands of $\text{Os}_3(\text{CO})_{12}$. While the cross sections for s - and p -electrons in atoms or small molecules are typically maximal directly at the ionization threshold,³² there exists a centrifugal barrier for d and f electrons that causes the maximum ionization cross section to be at higher energies.^{33,34} These so called shape resonances can also occur in smaller molecules if the continuum wavefunction of the outgoing electron has components with a high l value, e.g., for the Σ states in CO.^{35,36} The highest lying resonance in CO can be found at photon energies of 32 eV for the $\text{B}^2\Sigma^+$ state.

For elementary osmium, the maximum of the ionization cross section lies around 25 eV³⁰ (the ionization potential of Os is 8.7 eV³⁰) and decreases with increasing photon energy. In complexes with a single osmium atom, shape resonances are prevalent. For example, in $\text{Os}(\eta\text{-C}_5\text{H}_5)_2$,³⁷ two weak maxima at photon energies of 50 and 65 eV can be seen. For OsO_4 , the cross sections of different ionization bands have their maxima at 53 and 66 eV, close to those of $\text{Os}(\eta\text{-C}_5\text{H}_5)_2$.³⁸ As a general trend for all bands, however, one observes that the cross sections start to decay at about 35 eV³⁷ and that the superimposed resonances are typically weak. In contrast, for $\text{Os}_3(\text{CO})_{12}$, we see a maximum of the total cross section at (41 ± 3) eV for the $5d$ electrons and the $5\sigma + 1\pi$ ligand electrons while the maximum from the 4σ ligand electrons occurs at (44 ± 3) eV. We did not find any sign of sharp shape resonances. We conclude that the more complex structure of the d orbitals in $\text{Os}_3(\text{CO})_{12}$ as compared to molecules with a single metal center leads to an increased centrifugal barrier causing the maximum of the ionization cross section to appear at higher photon energies.

For $\text{Ru}_3(\text{CO})_{12}$, the photon energy dependence of the spectra is more complicated. Between 35 and 50 eV, the ionization cross section is maximal at 40 eV which is in agreement with the data of $\text{Os}_3(\text{CO})_{12}$. However, at a photon energy of 60 eV, we observe an increased ionization cross section for the $2a_1'$ and the $1e''$ band (A and C2 in Figure 6). This behavior is well known for ruthenocene and was assigned to an $np \rightarrow nd$ giant absorption resonance followed by a super Koster-Kronig decay which is caused by the close proximity of the np and the $e_1''^*$ orbitals.³⁷ The same effect seems to take place here and shows a close connection between the Ru_3 metal core and a single Ru atom in a complex. Furthermore, we observe different band shapes at a photon energy of 30 eV. Here, the $2a_1'$ and the $1e''$ bands are spectrally narrower as compared to the spectra at higher photon energies. This effect was not observed in ruthenocene and might be specific for carbonyl ligands. Earlier publications have shown that shape resonances can lead to a strong modulation of the ionization cross sections depending on intranuclear distances and hence the vibrational distributions; see, e.g., Ref. 39. These modulations were seen in states that could couple to ionic states with high l values.³⁶ We speculate that the same mechanism holds for the $2a_1'$ and the $1e''$ bands in $\text{Ru}_3(\text{CO})_{12}$ at 30 eV, where continuum coupling could play a role analogous to what was observed in CO before.⁴⁰ However, more theoretical effort is needed to validate this hypothesis.

So far, we considered the shape resonances from the metal perspective, but they have also been observed for CO adsorbed on metal surfaces, where they show a maximum ionization cross section at energies around 35 eV for ionization from both 5σ and 4σ orbitals for various types of surfaces (see Ref. 41 for an overview). This maximum is clearly shifted for our samples, which shows that the wavefunction of the total system has to be considered and that a metallic surface has a different influence on the adsorbed species than the metal trimer in our dodecacarbonyls.

B. Reconstruction of the fragmentation pattern

A formula for the calculated appearance energies for the various fragments of $\text{Os}_3(\text{CO})_{12}$ and $\text{Ru}_3(\text{CO})_{12}$ is given by Equation (1) and can be used to compare the experimental mass spectra and photoelectron spectra shown in Figures 3-5, 7, and 8 in the following way: In Figure 9, we show integrated photoelectron spectra of $\text{Os}_3(\text{CO})_{12}$ for different photon energies (solid lines, the integration is executed from 0 eV up to the ionization energy value indicated on the x-axis). They are normalized at an ionization energy of 12 eV, which includes the osmium $5d$ band but is below that of ionization of the CO ligands. In a next step, we determined the integrated areas of individual peaks from the mass spectra. We assumed that

FIG. 9. Solid lines: Areas of the $\text{Os}_3(\text{CO})_{12}$ photoelectron spectra integrated over the region from 0 eV up to the respective ionization energies on the x-axis. Areas are normalized to a value of 1 at 12 eV, which corresponds to the plateau between d-electron ionization and CO-ligand ionization. Added are integrated mass spectra, normalized also at 12 eV (filled symbols). Ionization energies are calculated by Equation (1) using the experimental ionization potential of $a_0 = 7.83$ eV. Numbers above the symbols are indicating the remaining number of CO molecules attached to the metal core. Open triangles represent a best fit of the data in the case of 120 eV photon energy. See text for details on the construction of the graph.

events where less energy than E_{11} remains in a molecule after ionization lead to no fragmentation ($n = 12$), i.e., we observe the parent ion in the mass spectrum; events where an internal energy between E_{10} and E_{11} is left in a molecule lead to loss of one CO ligand ($n = 11$), etc. These energies represent the abscissa values. The y-axis is the sum of the mass peak areas up to the respective fragmentation. The sums of the integrated mass peaks are also normalized at 12 eV and added to Figure 9 as filled symbols. As an alternative normalization, we performed least squares fits of the mass peaks to the photoelectron spectra to get optimal conversion factors between the mass and photoelectron spectra. One of these fits is shown exemplarily for a photon energy of 120 eV (open triangles). Using the comparison between mass and photoelectron spectra, the following features can be observed.

- The good agreement between mass and photoelectron spectra provides an explanation for the intensity distribution of the mass spectrum and corroborates the basic assumption of the analysis that the energy deposited in the molecule during the ionization event is channeled into detachment of CO molecules. For example, the small peak for $\text{Os}_3(\text{CO})_{10}^+$ is caused by the small ionization cross section of the molecule between E_9 and E_{10} , because the energy window lies between ionization from the osmium 5d bands and ionization from the CO ligands. Similarly, the dominating peaks of $\text{Os}_3(\text{CO})_8^+$ and $\text{Os}_3(\text{CO})_7^+$ are caused by the strong CO ionization cross section. In addition, this analysis shows that the CO binding energy must be smaller in $\text{Ru}_3(\text{CO})_{12}$, because the mass spectrum seems to be shifted toward increased fragmentation which is emphasized by the more intense peak at $n = 7$ as compared to the corresponding peak in the $\text{Os}_3(\text{CO})_{12}$ mass spectrum. Finally, the mass-peak

which represents the highest degree of fragmentation at a photon energy of 27 eV is $n = 3$ which is nicely recovered by Equation (1) and in disagreement with Ref. 8 whose proposed dissociation energy of 1.6 eV per CO molecule would lead to fragmentation down to $n = 1$ in the experiment.

- The normalization of the photoelectron spectrum at 12 eV leads to deviation of the curves at higher ionization energies. While the mass spectra at photon energies of 50 and 120 eV show less intensity at higher masses than the photoelectron spectrum, the mass spectrum at 27 eV shows too much. The low intensity in the 50 and 120 eV spectra might originate from the double ionization channel which provides additional photoelectrons but the corresponding fragments show up at different masses in the mass spectrum. This is not the case for 27 eV photons because of the reduced double ionization cross section close to the threshold.⁴²
- The intensity of the low fragmentation peaks ($n = 10$ –12) and especially the parent peak is too high when compared to the photoelectron spectrum (see Figure 9). In principle, this could be caused by a dissociation barrier. Another possibility is that energy redistribution might take too long for ionization just above the fragmentation threshold to initiate dissociation before the masses are recorded (metastable ions). Since our calculations rule out a dissociation barrier, the most probable reason for the extra intensity is the slow energy redistribution. However, careful dynamical simulations would be required to reach a detailed insight into the dissociation of the parent compound.

Despite some minor discrepancies, the data show good overall agreement between mass and photoelectron spectra which is an indication for the internal charge flow between ligands and metal core being fast. As a consequence, we detected only small amounts of CO^+ molecules because after ionization the positive charge is transferred to the metal core before dissociation can take place. Moreover, a $\text{C}=\text{O}$ vibrational mode has an energy of about 0.25 eV.^{43–46} which would cause an extra loss in potential energy in the remaining metal complex if the dissociated CO molecule were to be vibrationally excited. Such a loss is not observed in our data. The cleavage of vibrationally unexcited CO can be explained by the weak coupling of the CO-vibrational mode with the other vibrations of the molecule. For $\text{Os}_3(\text{CO})_{12}^+$, for example, we calculated the CO modes to lie between 2000 and 2145 cm^{-1} while the coupling modes between CO and the Os_3 core lie between 606 and 18.5 cm^{-1} . Similar results were found for $\text{Ru}_3(\text{CO})_{12}^+$, where the lowest CO frequencies were the ones from the bridging CO molecules at 1878 and 1912 cm^{-1} . A small translational energy can be inferred from the fact that dissociation is a statistical ground state process where not much excess energy is stored in the vibrational mode leading to dissociation. Even for the excited state dissociation of $\text{Ru}_3(\text{CO})_{12}$ with 400 and 267 nm photons, time constants on the order of 100 ps were measured by Glascoe *et al.*⁴⁵ in the liquid phase, which does not point toward a direct dissociation channel and hence is in agreement with our study.

C. Double ionization

Besides single ionization, double ionization is a significant part of the radiation induced dynamics of the investigated complexes. At $h\nu = 27$ eV, we observe fragmentation to $\text{Os}_3(\text{CO})_n^{2+}$, $n = 9-12$. With a dipole moment of 0.122 D, CO is not a polar molecule wherefore we expect no major influence of the changes on the dissociation behavior of the molecule. Thus, we assume only slightly larger dissociation energies for singly than for doubly charged molecules which sets the threshold to double ionization between 22.4 eV and 20.8 eV ($27 \text{ eV} + a_0 - E_3$ and $27 \text{ eV} + a_0 - E_4$, where E_3 and E_4 are defined by Equation (1)). These energies agree well with the empirical formula for the double ionization energy $E_{\text{DI},1 \text{ site}}$ from Molloy *et al.*,³

$$E_{\text{DI},1 \text{ site}} = 2.20 E_I + 11.5 \text{ eV}/r_{12}, \quad (2)$$

where E_I is the ionization potential in eV and r_{12} the distance of the electron vacancies in Å. If we assume ionization at two metal atoms ($r_{12} = 2.84$ Å), we expect an $E_{\text{DI},1 \text{ site}}$ of 21.3 eV. In fact, it was found that for delocalized systems, r_{12} is often smaller than the distance of the atoms that are the furthest away from each other³ which would result in a slightly higher E_{DI} .

A similar $E_{\text{DI},1 \text{ site}}$ value is expected for $\text{Ru}_3(\text{CO})_{12}$, however, no doubly charged ions are observed in the 27 eV mass spectrum. In that case, the double ionization cross section may be too low to produce a signal. Unfortunately, we do not know how large the signal contribution from higher photon energies is because the mass peaks for $\text{Ru}_2(\text{CO})_n^{2+}$ ($n = 11, 12$) overlap with those of $\text{Ru}_3(\text{CO})_n^+$ ($n = 0, 1$) which prohibits any judgment about the double ionization cross section.

Similarly to the singly charged ions, we find a reduced amount of $\text{Os}_3(\text{CO})_n^{2+}$ ions for $10 \leq n$ in the mass spectra taken with 50 and 120 eV photons. For single ionization, we explained this effect by the energy gap of 5.7 eV between ionization of the $5d$ orbitals which have a low oscillator strength, and ionization of the CO ligands, which have a higher cross-section (see above). For double ionization, where one electron stems from the metal and one from the ligands, we expect an ionization threshold of

$$E_{\text{DI},2 \text{ sites}} = 1.10(E_{I,\text{metal}} + E_{I,\text{CO}}) + 11.5 \text{ eV}/r_{12}. \quad (3)$$

The distance between the center of the Os—Os bond and the center of the CO-group furthest away is 4.9 Å which results in a two site double ionization energy of $E_{\text{DI},2 \text{ sites}} = 25.8$ eV, which is 4.5 eV above the single site $E_{\text{DI},1 \text{ site}}$. This is close to the energy that is needed to dissociate 3 CO molecules from the ion and in agreement with the experimental observation.

The double ionization spectrum of $\text{Os}_3(\text{CO})_n$ shows about the same intensities for all mass peaks with $2 \leq n \leq 9$, signifying an uniform energy distribution for the outgoing electrons and hence also for the energy that remains in the molecules. The main reason is likely the high density of states of the large complexes.

Finally, we briefly want to address the break-up of the M_3 -core after double ionization. Whenever we observe fragmentation into an $\text{M}_2(\text{CO})_n$ and an $\text{M}(\text{CO})_m$ species, $n + m \leq 12$, we find both charges localized at the $\text{M}_2(\text{CO})_n$. When comparing the energies of the optimized structures of $\text{Ru}(\text{CO})_4$

and $\text{Ru}_2(\text{CO})_8^{2+}$ with the energies of $\text{Ru}(\text{CO})_4^+$ and $\text{Ru}_2(\text{CO})_8^+$, we found that the case of distributed charges is more stable by 3.7 eV. Hence, the Coulomb repulsion is higher than the potential gain in ligand field stabilization energy which can be expected due to singlet products instead of doublets. One possible explanation of the experimental observation of $\text{M}_2(\text{CO})_n^{2+}$ might be dynamical effects (barriers etc.). Due to the size of the systems, we did not investigate this in more detail.

V. CONCLUSION

In conclusion, we studied the photoelectron spectra and the fragmentation patterns of $\text{Ru}_3(\text{CO})_{12}$ and $\text{Os}_3(\text{CO})_{12}$ as a function of the photon energy used for ionization, and compared our experimental observations with results from DFT calculations. For $\text{Os}_3(\text{CO})_{12}$, we found a maximum of the ionization cross section of d and ligand electrons at (41 ± 3) eV which we assigned to a larger rotational barrier than that for complexes with a single metal center. For $\text{Ru}_3(\text{CO})_{12}$, the cross section also peaked around 40 eV and rose again at 60 eV due to a giant $np \rightarrow nd$ resonance.

Further, we have seen that excess energy deposited in the molecules upon ionization leads to M—CO bond cleavages which could be rationalized by comparing mass and photoelectron spectra. The M—CO bond energy was found to lie between 1.4 and 2.5 eV, increasing for more fragmented molecules. The dissociation mechanism seems to disfavor the generation of vibrationally excited CO fragments implying that internal energy is stored in the cation. The onset of one site double ionization was estimated to be between 20.8 and 22.4 eV. At 26 eV, more efficient double ionization where one electron was ionized from the metals and one from the ligands was observed. The energy gap between ionization from the ligands and ionization from the metal core was more than 1 eV smaller for double than for single ionization because of Coulomb repulsion effects. Finally, we observed that CO bond cleavage is possible. Thus, the remaining carbon atom is inserted in the metal core of the molecule, resulting in the structure shown in Figure 1.

The findings of this article might open up new research directions. For example, one might ask whether the shift of the valence shape resonance extends to even higher photon energies when centers with more metal atoms are used, and if so, what the maximum photon energy is and whether there is a connection to the type of ligand. In addition, the dependence of the shape resonance on the metal's group in the periodic table of elements might be investigated. Finally, calculations will be needed in order to understand these effect in detail.

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