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Multiphoton ionization of metal cluster complexes $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$: Determination of the ionization energy and coordination energy of the complex ions

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Abstract

Multiphoton ionization and the subsequent dissociation process of metal cluster complexes $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$, prepared in a supersonic jet, were studied by means of multiphoton ionization with time-of-flight (TOF) mass detection. The ionization energies of $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ were determined to be 7.95 and 8.3 eV, respectively, from the laser wavelength at the ionization threshold. The coordination energies of $Os_3(CO)_{12}^+$ and $Ir_4(CO)_{12}^+$ ions were also determined to be 1.6 and 1.2 eV, respectively, from the excitation energy needed to cause the appearance of fragment ions. The observed values agreed reasonably well with the ones calculated by using the density functional theory method.
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Keywords: Metal cluster complex; Ionization energy; Coordination energy; Multiphoton ionization

1. Introduction

There are many studies of polynuclear metal cluster complexes because of their usefulness, for example, as catalyst [1]. Recently some polynuclear metal cluster complexes have attracted attention as the ion source for cluster secondary-ion mass spectroscopy (SIMS) [2], which is a potential tool for the analysis of surfaces by means of low-damage sputtering [3]. To utilize a polynuclear metal cluster complex as an ion beam source, we need to ascertain the basic properties of the complex in the gas phase. However, there are only a few studies of polynuclear metal cluster complexes in the gas phase.

Mizota et al. [2] proposed that metal cluster complexes $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ be used as ion sources in cluster SIMS. They measured the mass spectra of these complexes by photoionization and electron-ionization methods and found that the features of the mass spectra obtained by the two methods are very different from each other. The former method gives strong bare-metal cluster signals, Os_n^+ (n = 1–3) and Ir_n^+ (n = 1–4), and no or very weak signals of parent and fragment ions, $Os_3(CO)_n^+$ or $Ir_4(CO)_n^+$ (n = 1–12), whereas the latter method gives a strong signal of the parent and fragment ions. Mizota et al. could not explain well the reason for the difference between the two methods, because little information existed about the basic properties of these cluster complexes in the gas phase.

Green et al. measured the photoelectron spectrum of $Os_3(CO)_{12}$ in the vapor phase and determined the ionization energy [4,5]. However, there were no data on the ionization energy of $Ir_4(CO)_{12}$, and there was no report on the stability of these metal cluster complex ions. The knowledge of the fundamental properties of the metal cluster complexes could be used to determine the distribution of the fragment ions. In this study, we determined the ionization energies of these metal cluster complexes and the coordination energies of the cluster complex ions by using multiphoton ionization mass spectroscopy.

2. Experimental

We used commercial samples of $Os_3(CO)_{12}$ (Strem Chemicals, Inc., 99%) and $Ir_4(CO)_{12}$ (Strem Chemicals, Inc., 98%) without further purification.

Fig. 1 shows a schematic diagram of the experimental apparatus. The metal cluster complex was kept in a container made

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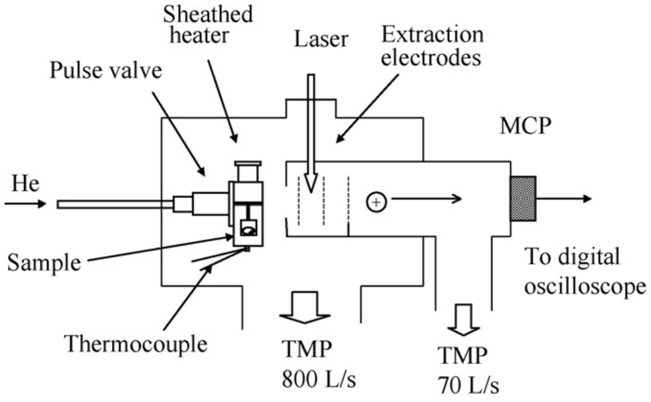

Fig. 1. A schematic diagram of the experimental apparatus.

of pure copper and heated by a sheath heater to sublime the complex. Temperatures of 400 and 450 K were used for $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$, respectively. A supersonic nozzle was designed to prepare the sample in a He-seeded molecular beam; the nozzle consisted of a pulse valve (Parker Hanefin, 0.8 Ø, 10 Hz, duration 250 μs), and a container for the metal cluster complex made of pure copper with a T-shaped channel (1 mm Ø) (Fig. 1). The helium gas ejected from the valve passed through the main channel (19 mm long) to push away the sample vapor supplied from the side channel connected at the center of the main channel. The stagnation pressure of helium was kept at 0.1 MPa.

The molecular beam was irradiated by a UV laser pulse and ionized by multiphoton absorption. The mass spectra of the ions were measured by using a linear-TOF mass spectrometer. The free flight length of the flight tube was 0.57 m, and the mass resolution was 200. Ions were detected by a micro-channel plate (MCP, Hamamatsu Photonics) detector mounted on the end of the flight tube. The signal of the MCP detector was collected by a digital oscilloscope (Tektronix, TDS3012) and sent to a computer through a GPIB interface.

For the ionization light source, a UV output from a ultraviolet laser (Spectra Physics, MOPO-HF) or a dye laser (Continuum, ND6000) with the frequency doubled by a second harmonic generation crystal (Inrad, Autotracker) was used. The laser beam was focused at the center of the ionization room by a concave mirror ($R = 700$). In some cases, the unfocused beam was used to minimize the higher-order multiphoton effects. The laser power had to be kept at less than a few hundred microjoules per pulse to observe the ions of the metal cluster complexes. When the laser power was higher than this, we could observe only the bare-metal cluster ions (Me_n^+) because of the photodissociation of Me–CO bonds caused by excess photon absorption.

The delay time between the ejection of He from the pulse valve and the firing of the laser was controlled using a delay pulse generator (Stanford, DG535). The delay time was set by observing the mass spectrum of the sample. Usually there were minimum and maximum delay times during which signal from the supersonic jet could be observed, and the difference between the minimum and maximum delay times was more than several hundred microseconds if the sample was pre-mixed in He gas. In the case of metal cluster complexes, however, this duration was less than a hundred microseconds, and the optimum delay time was close to the minimum delay time for the pre-mixed samples in the supersonic jet. This difference of optimum duration times suggests that the cluster complexes existed only in the front part of the supersonic jet.

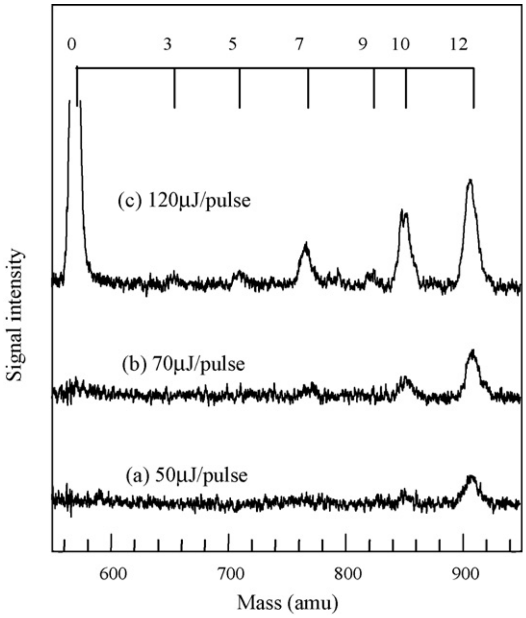

Fig. 2. Mass spectra of $Os_3(CO)_{12}$ ionized by a UV laser ($\lambda = 284$ nm) and dependence of the spectra on laser power. The numbers at the top of the figure represent the numbers of COs in the fragment ion $Os_3(CO)_n^+$.

3. Results and discussions

3.1. Multiphoton ionization of $Os_3(CO)_{12}$

The metal cluster complex $Os_3(CO)_{12}$ was ionized by a laser ($\lambda = 284$ nm) at various laser powers (Fig. 2). Broad features were observed in the mass spectra because of the overlap of the unresolved isotope peaks of osmium (^{188}Os, ^{189}Os, ^{190}Os, and ^{192}Os). When the power of the laser was too high, the absorption of an excess number of photons caused the dissociation of Os–CO and Os–Os bonds, and only metal cluster ions, Os_n^+ ($n = 1$–3), were observed in the mass spectra. This result agrees with the observation of Mizota et al. [2]. We kept the laser power below 100 μJ/pulse (laser duration: 8 ns, power density: less than 5×10^{12} W/m^2) to minimize the effect of multiphoton absorption and were able to observe the parent ion, $Os_3(CO)_{12}^+$. The peak of $Os_3(CO)_{12}^+$ was observed in the mass spectrum, and other peaks were negligibly small when the laser power was low (<50 μJ/pulse) (Fig. 2a). As the laser power increased, the signal of the fragment ions, $Os_3(CO)_n^+$, became stronger (Fig. 2b), and the strong signal of the bare-metal cluster ion, Os_3^+, appeared and became prominent when the laser power was higher than 100 μJ/pulse (Fig. 2c).

Interestingly, there were “magic numbers” in the intensity pattern of the fragment ions, $Os_3(CO)_n^+$ ($n = 3$–11, Fig. 2). The intensity of the fragments with $n = 10$ and 7 were strong, but no or very weak signals of the fragment ions were observed at

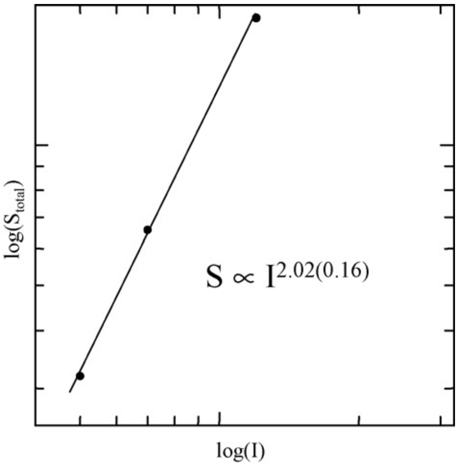

Fig. 3. The dependence of the signal intensity of $Os_3(CO)_n{}^+$ on the laser intensity. I: Laser intensity. S: Sum of the signal intensities of $Os_3(CO)_n{}^+$. The wavelength of the laser was 284 nm.

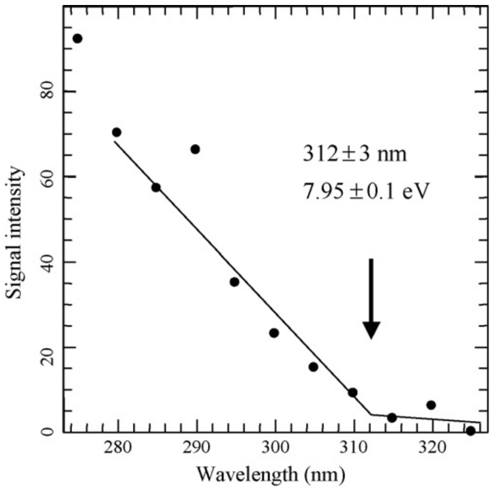

Fig. 4. The dependence of the ionization efficiencies on the laser wavelength. The rising point was observed at 312 nm.

$n = 11$, 8, and 4. Actually, this magic number was not due to the difference in the stabilities of the fragment ions. The "magic number" strongly depended on the laser wavelength, and can be explained by the excess energy in the multiphoton absorption of the cluster complex. This fact will be used to determine the coordination energy of the Os–CO bond in a later part of this paper.

The signal intensity of the parent ion, $Os_3(CO)_{12}{}^+$, showed a second-order dependence on the laser power, and we concluded that the cluster complex was ionized by two-photon absorption. The sum of the signal intensities of all the fragment ions except the metal cluster ion, $S_{\text{total}} = \sum S_{Os_3(CO)_n{}^+}$, also showed a second-order dependence on laser intensity (Fig. 3). The result of the linear fit gave a slope of 2.02, suggesting that the ionization was a two-photon process. However, we could not determine a reliable power dependence of the $Os_3{}^+$ signal, because the slope was too steep. We believe that the difference reflects the difference between the production mechanisms of the fragment ions and the metal cluster ions.

Similar measurements were made in the wavelength region of 272–320 nm to determine the ionization efficiency of the cluster complex. In the region of 272–296 nm, the plot of the sum of the signal intensities of the fragment ions versus the laser power showed that the ionization was a two-photon process and that higher-order processes can be neglected. When the wavelength was longer than 300 nm, the signal from the two-photon ionization became weaker, and we could not measure a mass spectrum with a good signal-to-noise (S/N) ratio with low laser power. In this region, the effect of the three-photon process was also observed. For example the double logarithmic plot of the signal intensity against the laser power at $\lambda = 314$ nm gave a slope of 2.8, suggesting that the contribution from the three-photon process cannot be neglected. The ordinate of the two-photon ionization efficiency curve (Fig. 4) shows the coefficient of the second-order term in the fit of the signal intensities and the laser power assuming a second-order polynomial. The efficiency of the two-photon ionization for the cluster complex increased monotonically in the region of the wavelength shorter than 312 nm, and no special feature like a band structure was observed. This fact suggests that the two-photon energy of 312 nm (7.95 ± 0.1 eV), is the rising point of the efficiency curve, that is, the threshold of the two-photon ionization.

We determined that the two-photon ionization energy of $Os_3(CO)_{12}$ is 7.95 eV. However, this value is slightly higher than that reported by Green et al. They measured the photoelectron spectrum of gaseous $Os_3(CO)_{12}$, and reported that the ionization energy for the lowest peak is 7.83 eV. This should be close to the vertical ionization energy. On the other hand, our value was determined from the threshold of the two-photon ionization and should be between the vertical and adiabatic ionization energies. So we would expect their energy value to be slightly higher than the present result. We believe that the reason for this discrepancy is the difference in the temperatures of the cluster complexes: they measured the photoelectron spectrum at high temperature (400 K), whereas we used a supersonic jet. The cluster complex has 12 Os–CO bonds. Because these bonds should be weak and the frequency of the rocking vibration of the bonds should be low, the low-frequency vibrational mode can contribute to the internal energy of the complex at high temperature, and this contribution can affect the apparent ionization energy.

We estimated the effect of the temperature in the following way: the density of states (DOS) of the cluster complex was calculated by following the Beyer-Swinehart algorithm [6] assuming harmonic vibration, and the vibrational frequencies of $Os_3(CO)_{12}$ were calculated by using the density function theory (DFT) method. Then, the distribution function was obtained by multiplying the DOS(E) and by the Boltzmann factor $\exp((Ek_B/T)$. From this calculation, the maximum distribution of internal energy was found to be approximately 1 eV at 400 K. Although there is another factor, the Franck(Condon factor, that also affects the transition probability, this internal energy can cause an error in the determination of the ionization energy.

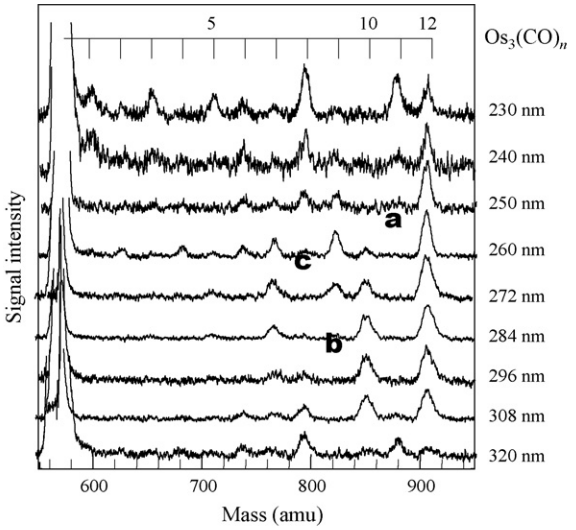

Fig. 5. The dependence of the photo-fragmentation of the cluster complex cation of $Os_3(CO)_n{}^+$ on the wavelength of the laser. The laser power and intensity scale are different from each other (see text). Bold characters show the rising points of (a) 2-photon, $n = 11$, (b) 3-photon, $n = 9$, and (c) 3-photon, $n = 8$.

3.2. Determination of the Os–CO coordination energy in the ion

Fig. 5 shows typical mass spectra of $Os_3(CO)_{12}$ photo-ionized by the laser in the wavelength region of 230–320 nm. In each measurement the laser power was adjusted so that the metal cluster complex absorbed several photons. The intensity scale of each spectrum was set appropriately that the two-photon signal gave similar intensity. The S/N ratios of the mass spectra measured at 230–250 nm were poor because the laser was not stable in this wavelength region.

It is apparent that the fragmentation pattern strongly depended on the laser wavelength. As mentioned in the early part of this paper, there were some magic numbers in the mass spectra; however, the numbers depended strongly on the laser wavelength. This result suggests that the fragmentation pattern was determined not by the stability of the fragment ions but by the total energy of the absorbed photons. Because there was no collision between the cluster complexes in the mass spectrometer, the important parameters should be the threshold wavelength at which the fragment ions appear and the number of photons absorbed. The total photon energy at the threshold should be equal to the energy difference between $Os_3(CO)_{12}$ and $Os_3(CO)_{12-n}{}^+ + n_{CO}$, which does not depend much on the intermediate reaction paths.

There were threshold wavelengths at which the fragment ions appear (Fig. 5): $n = 11$, 252 nm (a); $n = 9$, 284 nm (b); and $n = 8$, 257 nm (c). By considering the energy relations, we concluded that (a) corresponds to two-photon ionization, and (b) and (c) to three-photon ionization. Fig. 6 shows the plot of the appearance potential against the number of COs in the fragment ions. The plot shows the linear relation between the number of COs dissociated and the absorbed energy. The simple explanation fort the linear relationship is that the coordination energy of the Os–CO bond of the metal cluster complex did not depend strongly on the number of COs remaining in the complex, and the coordination energy of the bond was determined to be 1.6 eV (Fig. 6).

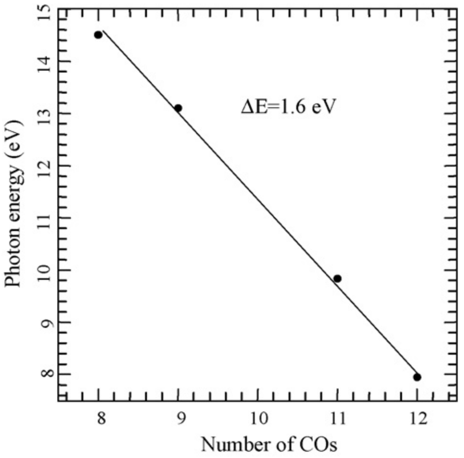

Fig. 6. The plot of the appearance energy of the fragment ion against the number of COs in the $Os_3(CO)_n{}^+$ fragment. The Os–CO bond energy was determined to be 1.6 eV from the slope of the plot.

3.3. Ionization energy and the Ir–CO coordination energy of $Ir_4(CO)_{12}$

We carried out a similar experiment to determine the ionization energy and the Ir–CO coordination energy of the $Ir_4(CO)_{12}$ metal cluster complex. In the Ir experiment, however, we needed a higher sublimation temperature (450 K) than that of the osmium cluster complex to observe the mass spectrum by two-photon ionization. Actually this temperature was limited

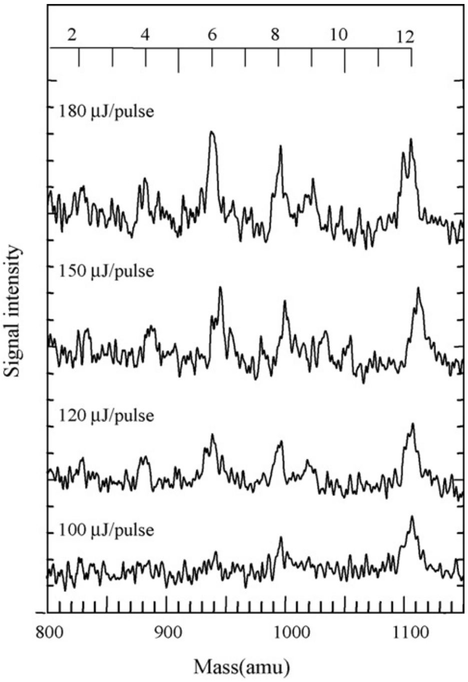

Fig. 7. Mass spectra of $Ir_4(CO)_{12}$ ionized by a UV laser (λ = 272 nm) and dependence of the spectra on the laser power. The numbers at the top of the figure represent the number of COs in the $Ir_3(CO)_n{}^+$ fragment ion.

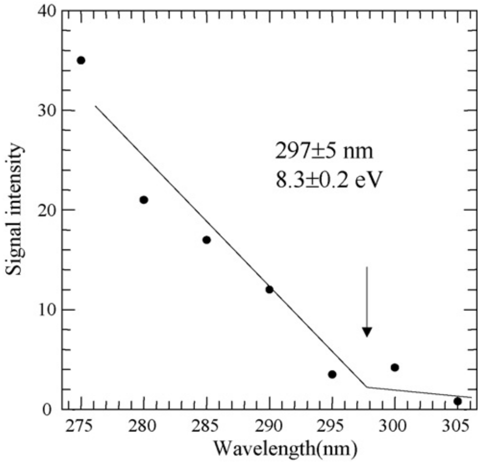

Fig. 8. The dependence of the ionization efficiencies on the laser wavelength. The rising point is observed at 297 nm.

by the thermal dissociation of the complex, and the vapor pressure of $Ir_4(CO)_{12}$ could not be increased enough to measure its mass spectrum with as good a S/N ratio as was obtained for $Os_3(CO)_{12}$.

The typical mass spectra of $Ir_4(CO)_{12}$ and its dependence on the applied laser power were measured (Fig. 7). The wavelength of the UV laser was 272 nm. Because the optical conditions were slightly different from those used for the osmium cluster, the absolute power of the laser cannot be compared with that in Fig. 2. When the laser power was weak, we observed the signal of the molecular ion, $Ir_4(CO)_{12}^+$, and the signal of the fragment ions was weak. With increased laser intensity, the intensity of the fragment ions, $Ir_4(CO)_n^+$, increased. With higher laser power, the signal of the bare-metal cluster, Ir_4^+, became prominent in the mass spectrum, and this result agrees with the experimental result of Mizota et al. [2]. Although the S/N ratio was not as good as that of osmium cluster, the fragmentation and its power dependence were similar to those observed for $Os_3(CO)_{12}$. We can also see magic numbers in the fragment ions, and the double logarithmic plot of the signal intensity and laser power again showed a second-order dependence.

Fig. 8 shows the dependence of the ionization efficiency on the laser wavelength. There was a threshold at 297 nm, and the two-photon ionization energy was determined to be 8.3 ± 0.2 eV. This value is slightly higher than that of $Os_3(CO)_{12}$ (7.95 eV). We believe that this difference corresponds to the difference in the ionization energies of the metal atoms (Os: 8.7 eV, Ir: 9.1 eV).

The dependence of the mass spectrum of $Ir_4(CO)_{12}$ on the wavelength of the ionization laser was measured (Fig. 9). In each measurement the laser power was adjusted so that the metal cluster complex absorbed several photons. The intensity scale of each spectrum was set appropriately that the two-photon signal gave similar intensity. The appearance of the fragment ions clearly depended on the wavelength of the laser, as was the case for the osmium cluster complex. The asterisk (*) indicates the threshold of the appearance of the fragment ions. There were two-photon thresholds for $n = 11$ at 260 nm and $n = 10$ at 242 nm, and also three-photon thresholds for $n = 8$ at 278 nm and $n = 7$ at 260 nm. Fig. 10 plots the appearance potential and the number of COs in the fragment ions. The plot shows the linear relation between them, and we obtained 1.2 eV for the Ir–CO coordination energy in the ion complex. The coordination energy did not strongly depend on the number of COs in the fragment ion, as was also observed for the osmium cluster complex. The coordination energy of Ir–CO was slightly lower than that of Os–CO (1.6 eV).

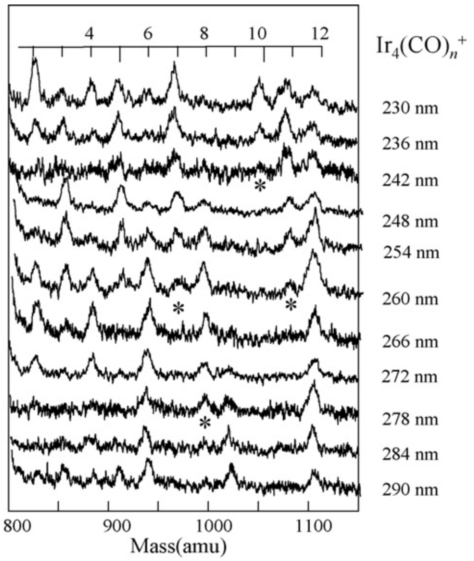

Fig. 9. The dependence of the photofragmentation of cluster complex cation $Ir_4(CO)_n^+$ on the wavelength of the laser. The laser power and intensity scale are different from each other (see text). * shows the appearance point of the fragment ion.

3.4. Comparison of the observed results with DFT calculations

The structures and energies of $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ were calculated by using the DFT method (Gaussian 03 program [7], B3LYP method) and compared with the experimental results.

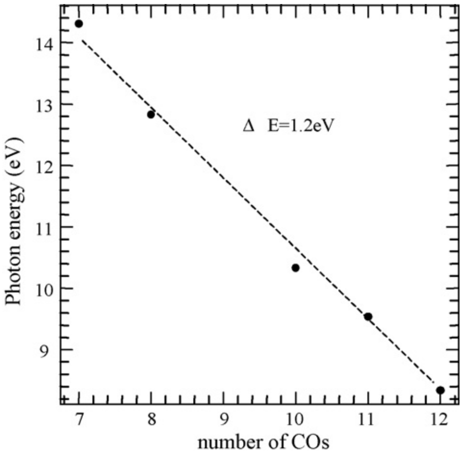

Fig. 10. The plot of the appearance energy of the fragment ion against the number of COs in the $Ir_4(CO)_n^+$ fragment ion. The Ir—CO bond energy was determined to be 1.2 eV from the slope of the plot.

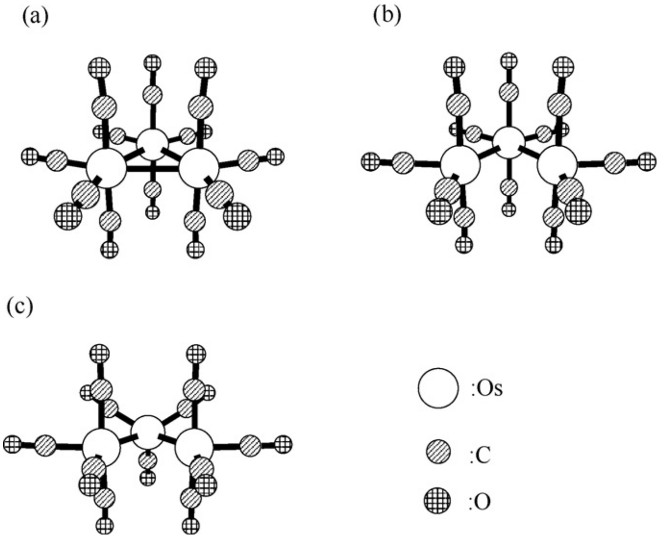

Fig. 11. Calculated structures of the Os cluster complexes: (a) $Os_3(CO)_{12}$, (b) $Os_3(CO)_{12}^+$, and (c) $Os_3(CO)_{11}^+$.

We used LANL2DZ for the heavy metal atoms (Os, Ir) and 6-311G** for the light atoms (C, O) as the basis sets.

Fig. 11 shows the calculated structures of $Os_3(CO)_{12}$ (Fig. 11a) and $Os_3(CO)_{12}^+$ (Fig. 11b). The neutral complex has D_{3h} symmetry, and this symmetry is broken when the complex is ionized. In the case of the neutral complex, the osmium atoms are situated at the apex of an equilateral triangle, and the distance between the osmium atoms, r(Os–Os), was calculated to be 0.297 nm. However, in the cationic complex, the osmium atoms make an isosceles triangle, and the distances between the two atoms are 0.291 nm (sides) and 0.317 nm (base). The energy difference between the neutral and cationic complexes was calculated to be 7.77 eV and is compared with the experimental value in Table 1. The calculation reproduces the experimental value well. Fig. 11c shows the optimized structure of the fragment ion, $Os_3(CO)_{11}^+$. The CO which coordinated the Os atom at the apex dissociated, and the configuration of the remaining CO molecules changed significantly. The energy difference between $Os_3(CO)_{12}^+$ and $Os_3(CO)_{11}^+$ + CO was calculated to be 1.16 eV and is shown as the coordination energy of Os–CO in Table 1. The calculated value is slightly smaller than the experimental value. The experimental value was determined by the observation of the threshold photon energy of the appearance potential. This energy corresponds to the reaction barrier and may be larger than the energy difference between the bottom of the potential curves of $Os_3(CO)_{12}^+$ and $Os_3(CO)_{11}^+$. So, the structure difference between $n = 11$ and $n = 12$ complexes might affect the apparent dissociation energy.

Table 1
Observed and calculated ionization energies and Me—CO bond energies of metal cluster complexes (in eV)

	Ionization energy		Me–CO coordination energy	
	Observed[a]	Calculated[b]	Observed[c]	Calculated[b]
$Os_3(CO)_{12}$	7.95	7.77	1.6	1.16
$Ir_4(CO)_{12}$	8.3	8.05	1.2	1.19

[a] Determined from the rising point of the two-photon ionization.

[b] Gaussian 03, B3LYP method. Basis sets. Os, Ir: LANL2DZ, C, O: 6-311G**. Zero-point energy is corrected.

[c] Determined from the rising point of the multiphoton dissociation.

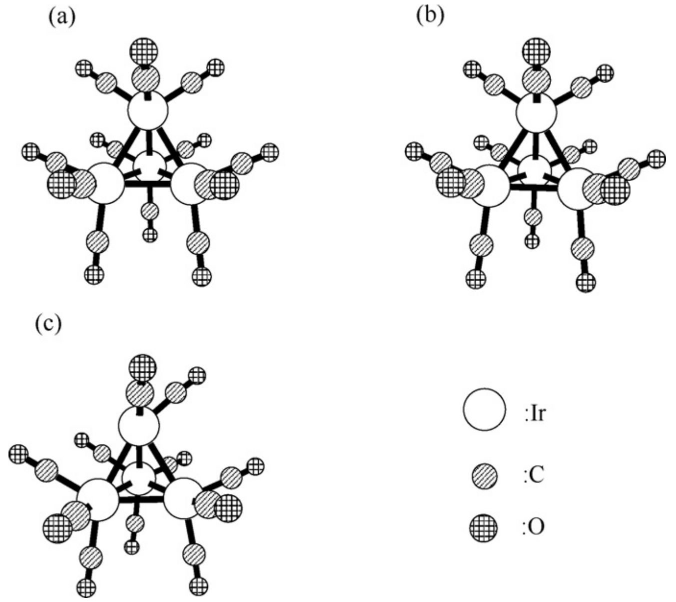

Fig. 12. Calculated structures of the Ir cluster complexes: (a) $Ir_4(CO)_{12}$, (b) $Ir_4(CO)_{12}^+$, and (c) $Ir_4(CO)_{11}^+$.

Fig. 12a shows the results of the calculation for the $Ir_4(CO)_{12}$ complex. In this case, the structure did not change much on ionization (Fig. 12b). The neutral and cationic complexes have the same symmetry, and the bond distance changed by only 0.002 nm (0.274–0.276 nm). The ionization energy was calculated to be 8.05 eV, which agrees reasonably well with the experimental value (Table 1). Fig. 12c shows the optimized structure of $Ir_4(CO)_{11}^+$; the configuration of CO around the Ir atoms did not change very much, except that one CO was removed from $Ir_4(CO)_{12}^+$. Table 1 shows the energy difference between the calculated energies of $n = 11$ and $n = 12$ as the coordination energy of Ir–CO. This time, the calculation reproduced the observed one reasonably well.

3.5. The intensity distribution of $Os_3(CO)_n^+$ in the electron impact mass spectrum

Mizota et al. measured and compared the mass spectra of metal cluster complexes by photoionization and by electron-ionization methods [2]. The former method gave strong bare-metal cluster signals for Os_n^+ ($n = 1$–3), and no or very weak signals for $Os_n(CO)_m^+$. This is apparently due to the multiphoton absorption dissociation of Me–CO and Me–Me bonds because Mizota et al. used a strong laser. The latter method gave $Os_3(CO)_n^+$ signals including a weak signal of Os_3^+. They also pointed out that the intensity of the peaks of $n = 7$ and 8 are stronger than the other peaks. Fig. 2 in Ref. [2] also indicates that the intensity of the peak of $n = 10$ is weaker than the other peaks. This feature can be explained by assuming that the initial internal energy distribution of $Os_3(CO)_{12}^+$ ionized by electron

Table 2
Peaks in the photoelectron spectrum and the excess internal energy of $Os_3(CO)_{12}$ (in eV)[a]

Peak	$h\nu$–E_k	$h\nu$–E_k–IE	n_{CO}	$Os_3(CO)_n^+$
A	7.83	0	0	12
B	8.28	0.45	0	12
C	8.48	0.65	0	12
D	9.24	1.41	0	12
E	9.60	1.57	0, 1	11, 12
F	10.44	2.61	1	11
G	13.58	5.75	3	9
H	15.05	7.22	4	8

[a] Table 1 in Ref. [5].

impact is similar to that by photoionization with a large excess energy.

Green et al. measured the photoelectron spectrum of $Os_3(CO)_{12}$ and observed several peaks in it [5]. Table 2 lists some of their data. When a cluster complex absorbs a photon with energy $h\nu$ and emits an electron with kinetic energy E_k, the complex ion has an excess energy of ($h\nu$–E_k–IE), where IE is the ionization energy. This excess energy should be discharged by the emission of CO molecules. The maximum number of COs to be emitted, n_{CO}, can be calculated as the integer part of ($h\nu$–E_k–IE)/$E_{CO\text{–}Os}$, where $E_{CO\text{–}Os}$ is the coordination energy, assuming that $E_{CO\text{–}Os}$ does not depend on the number of COs in the complex. This assumption was confirmed for $n_{CO} \leq 4$ in this work (Fig. 6). Table 2 summarizes ($h\nu$–E_k–IE), n_{CO}, and the number of COs in the fragment ion (12–n_{CO}) for each peak observed in the photoelectron spectrum.

The peaks A–F correspond to the peaks $n = 12$–11 in the mass spectrum. The peak H is broad and much stronger than the other peaks, and this may be the reason for the strong peaks at $n = 7, 8$ in the electron impact mass spectrum. There is a gap at around 12 eV in the photoelectron spectrum. This gap corresponds to $n = 10$, and seems to be the reason for the weak peak of $n = 10$ in the mass spectrum. These features become more apparent when we compare the photoelectron spectrum (Fig. 1b in Ref. [3]) and the electron impact mass spectrum (Fig. 2a in Ref. [2]). From these facts, we concluded that the initial distribution of the excess energy of $Os_3(CO)_{12}^+$ ionized by electron impact was similar to that by photoionization with large excess energy, and that the subsequent emission of CO molecules determined the relative intensity of the fragment peaks of $Os_3(CO)_n^+$.

4. Conclusion

We measured the photoionization mass spectra of metal cluster complexes $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ by multiphoton absorption of a UV laser in the wavelength region of 250–320 nm. The laser power was kept at less than 100 μJ/pulse to observe the parent and fragment ions; otherwise the multiphoton dissociation in the neutral complex and the subsequent ionization gave a strong signal of bare-metal cluster ions rather than metal cluster complex ions.

The observation of the threshold energy of the multiphoton absorption for the parent ion and fragment ions enabled us to determine the ionization energy and the coordination energy of the Me–CO bond. Observed values agreed reasonably well with values calculated using DFT method. We have shown that the distribution of the fragment ions in the electron impact mass spectrum, which is an important factor for cluster SIMS, can be explained well by the coordination energy of the Me–CO bond and the distribution of the excess energy of the metal cluster complex ion.

References

[1] B.F.G. Johnson, Transition Metal Clusters, John Wiley and Sons, New York, 1980.
[2] T. Mizota, H. Nonaka, T. Fujimoto, A. Kurokawa, S. Ichimura, Appl. Surf. Sci. 231/232 (2004) 945–948.
[3] N. Winograd, Anal. Chem. 77 (2005) 143A–149A.
[4] J.C. Green, E.A. Seddon, D.M.P. Mingos, J. Chem. Soc., Chem. Commun. (1979) 94–95.
[5] J.C. Green, D.M.P. Mingos, E.A. Seddon, Inorg. Chem. 20 (1981) 2595–2602.
[6] S.E. Stein, B.S. Rabinovitch, J. Chem. Phys. 58 (1973) 2438–2445.
[7] M.J. Frisch, et al., Gaussian 03, Revision B.04, Gaussian, Inc., Pittsburgh, PA, 2003.