Geometrical Structures of Partially Oxidized Rhodium Cluster Cations, Rh_6O_m^+ ($m = 4, 5, 6$), Revealed by Infrared Multiple Photon Dissociation Spectroscopy

Kohei Koyama¹, Toshiaki Nagata¹, Satoshi Kudoh¹, Ken Miyajima¹, Douwe M. M. Huitema², Valeriy Chernyy², Joost M. Bakker², Fumitaka Mafuné^{1*}

¹*Department of Basic Science, School of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo 153-8902, Japan*

²*Radboud University, Institute for Molecules and Materials, FELIX Laboratory, Toernooiveld 7c, 6525 ED Nijmegen, the Netherlands*

ABSTRACT: Infrared multiple photon dissociation (IR-MPD) spectra of Rh_6O_m^+ ($m = 4\text{--}10$) are obtained in the $300\text{--}1000\text{ cm}^{-1}$ spectral range using the free electron laser for infrared experiments (FELIX) via dissociation of Rh_6O_m^+ or $\text{Rh}_6\text{O}_m^+\text{-Ar}$ complexes. The spectra are compared with the calculated spectra of several stable geometries obtained by density functional theory (DFT) structural optimization. The spectrum for Rh_6O_4^+ shows prominent bands at 620 and 690 cm^{-1} , and is assigned to a capped-square pyramidal Rh atom geometry with three bridging O atoms and one O atom in a hollow site. Rh_6O_5^+ displays bands at 460 , 630 , 690 , and 860 cm^{-1} , and has a prismatic Rh geometry with three bridging O atoms and two O atoms in a hollow site. Rh_6O_6^+ shows three intense bands around $600\text{--}750\text{ cm}^{-1}$ and multiple weak bands in the range of $350\text{--}550\text{ cm}^{-1}$. This species has a prismatic Rh geometry with four bridging O atoms and two O atoms in a hollow site. Considering that Rh_6O_m^+ ($m \leq 3$) adopts tetragonal bipyramidal Rh_6 structures, the change at $m = 4$ to capped bipyramidal and at $m = 5$ to prismatic geometries results in a reduction of the number of triangular hollow sites. Since NO preferentially binds on a

triangular hollow site through the N atom, the geometry change lowers the possibility of NO dissociative adsorption.

1. Introduction

Rhodium is used in automobile catalytic converters to remove harmful gases, such as nitric oxide (NO), from the exhaust.¹⁻⁵ The mechanism of NO reduction by Rh has been studied for many years using gas-phase clusters. Their use is advantageous for understanding the behavior of N and O atoms at the atomic and molecular level, since the number of Rh, N, and O atoms involved in the reaction is well defined.⁶⁻¹¹ For instance, Mackenzie et al. investigated the reduction of NO on rhodium clusters by single collision reactivity experiments performed by Fourier transform mass spectrometry in the gas phase. The experiments suggested that the first NO molecule predominantly adsorbs dissociatively on Rh_n^+ clusters ($n < 17$). When a second NO molecule is adsorbed, N_2 was found to desorb, leaving behind O atoms. Although several NO molecules can consecutively be adsorbed and reduced on Rh_n^+ , the clusters exhibit a limited NO reduction ability. For Rh_6^+ , four NO molecules can be reduced yielding N_2 before the remaining oxygen atoms disrupt NO reduction; further NO molecules only adsorb onto Rh_6O_4^+ clusters.⁶⁻⁹

Harding et al. calculated the geometrical structures of stable $\text{Rh}_6\text{O}_{1-4}^+$ clusters and studied the adsorption form of NO on Rh_6O_4^+ using density functional theory (DFT).^{12,13} The calculations suggest that stable clusters have an ~~octahedral~~ tetragonal bipyramidal (octahedral) or capped-square pyramidal structure. Based on optimized geometrical structures, the dissociation pathways of NO on Rh_6O_4^+ were calculated, showing that at least three distinct pathways are possible. However, they are all unlikely due to the high internal energy of reactants required and the existence of a high reaction barrier. To verify the reaction mechanism, the geometrical structure of stable Rh_6O_4^+ needs to be experimentally determined.^{12,13}

In our previous study, the geometrical structures of $\text{Rh}_6\text{O}_{6-12}^+$ were investigated by thermal desorption spectrometry and DFT calculations.¹⁴ Rh_6O_6^+ was found to have a prismatic structure with O atoms occupying bridging sites, while $\text{Rh}_6\text{O}_{10,12}^+$ exhibits a more open geometry with some O atoms bound to top sites. In addition, O_2 molecules are weakly bound to $\text{Rh}_6\text{O}_{10}^+$ in $\text{Rh}_6\text{O}_{12}^+$. Under oxygen-rich conditions, the threshold energies of O_2 release from $\text{Rh}_6\text{O}_{8,10}^+$ clusters, estimated by thermal desorption spectrometry, are consistent with the calculated binding energies of O_2 to $\text{Rh}_6\text{O}_{6,8}^+$ clusters. However, estimating the threshold energies for O or O_2 release from $\text{Rh}_6\text{O}_{1-6}^+$ clusters was not possible under our experimental conditions, due to the higher binding energies.

In the present study, we investigated $\text{Rh}_6\text{O}_{3-10}^+$ clusters using infrared multiple photon dissociation (IRMPD) spectroscopy and determined their geometrical structures by comparison to the results of DFT calculations, a proven method for structure determination of clusters.¹⁵⁻¹⁹ According to our previous study, the release of one oxygen molecule from Rh_6O_m^+ is endothermic, with the required energy depending on stoichiometry: ~ 2 eV for $m \leq 6$, 1.0–1.5 eV for $m = 7, 8, 9$, and less than 0.5 eV for $m \geq 10$.¹⁴ As typical molecular vibrations of Rh_6O_m^+ are found around 800 cm^{-1} (0.1 eV), the absorption of at least several photons is required to induce dissociation for any Rh_6O_m species. Although previous reports suggest that it is possible to sequentially absorb multiple photons using an intense FELIX fluence,^{20,21} the number of absorbed photons is limited, reducing the probability for clusters with $m \leq 6$ to release O_2 using FELIX. In our current study, we have not observed dissociation of Rh_6O_6^+ in the $300\text{--}1000\text{ cm}^{-1}$ wavenumber range. To be able to record IR spectra for Rh_6O_m^+ clusters containing only a few O atoms ($m \leq 6$), weakly bound complexes of the clusters with Ar atoms were

formed, which dissociate upon the absorption of only a few photons.^{20,21} Photoabsorption can then be probed by mass spectrometry as the loss of Ar atoms from the clusters. For clusters containing more O atoms ($m = 7, 8, 10$), we observe direct dissociation through O₂ loss and use this loss channel to signal the IR absorption.

2. Experimental methods

The geometrical structures of rhodium oxide cluster ions, Rh₆O_{*m*}⁺ ($m = 4, 5, 6$), were investigated via IRMPD spectroscopy using a molecular beam instrument¹⁵ coupled to the free electron laser for infrared experiments (FELIX).²² Gas-phase Rh_{*n*}O_{*m*}⁺ cluster ions were prepared by pulsed laser ablation of a rhodium metal rod at 10 Hz in a He carrier gas in the presence of O₂. The metal rod (99.9%) was vaporized using the focused second harmonic of a Nd:YAG laser at a typical pulse energy of 25 mJ. Ablation took place in a 4-mm diameter cluster growth channel filled with He carrier gas seeded with 0.016% oxygen that was introduced through a pulsed valve at a total stagnation pressure of 0.7 MPa.

The formation of Rh_{*n*}O_{*m*}Ar_{*p*}⁺ was accomplished by admixing 0.6% argon gas in the carrier gas and cooling the cluster source with liquid N₂. The concentrations of oxygen and argon gases were tuned using mass flow and pressure controllers to maximize the number of clusters of interest. In addition, the partial pressures of oxygen and argon in the cluster source chamber were monitored by a residual gas analyzer.

The mixture of clusters and carrier gas was expanded in vacuum to form a molecular beam. The beam first passed through a 2 mm diameter skimmer to enter a differentially pumped vacuum chamber and was then shaped by a 1 mm diameter aperture to match the IR laser beam. The cluster beam was overlapped by a counter-propagating

IR laser beam, which ascertained the spatial overlap of the cluster beam with the IR laser beam. The typical FELIX output consists of a pulse train (macropulse) of ~ 7 microseconds length with transform limited, ps duration micropulses at a 1 GHz repetition rate. The typical macropulse energy of 50 mJ pulse^{-1} was attenuated to $10\text{--}20 \text{ mJ pulse}^{-1}$ before use. The spectral shape is near-Gaussian; the root mean square bandwidth was kept at $0.2\text{--}0.3 \%$ of the central frequency, translating into a FWHM of 3.8 cm^{-1} at 800 cm^{-1} . After interaction with the IR laser, all cluster ions were analyzed using a reflectron time-of-flight (TOF) mass spectrometer. To correct for source fluctuations, the experiment is operated at twice the FELIX repetition rate of 5 Hz allowing for the recording of reference mass spectra in between FELIX pulses. From the raw mass spectra for each wavelength, depletion spectra are constructed, where the depletion $D(\nu)$ is given by the ratio $(I_{\text{on}}(\nu) - I_{\text{off}})/I_{\text{off}}$ of the number of ions detected with ($I_{\text{on}}(\nu)$) and without (I_{off}) the IR laser at frequency ν . A value of $D(\nu) < 0$ thus implies the loss of ions due to IR induced dissociation, whereas a value of $D(\nu) > 0$ implies an increase of the number of ions detected due to dissociation of larger species. To obtain the IRMPD spectra, the branching ratio $R(\nu)$ of all Ar tagged clusters $\text{Rh}_6\text{O}_4^+\text{Ar}_p$ ($p = 1, 2$) to the total number of clusters $\text{Rh}_6\text{O}_4^+\text{Ar}_p$ ($p = 0, 1, 2$) was calculated. The IRMPD intensity is then calculated as the ratio $(R_0 - R(\nu))/R_0$, with $R(\nu)$ and R_0 the branching ratios with and without irradiation, respectively. Both the depletion and IRMPD spectra were normalized on the IR macropulse energy. All IR frequencies were calibrated using a grating spectrometer.

3. Computational methods

To determine the stable geometries of Rh_6O_m^+ ($m = 3, 4, 5, 6$) and simulate their vibrational spectra, DFT calculations were performed using the Gaussian09 program.²³ Becke's three-parameter hybrid density functional²⁴ with the Lee-Yang-Parr correlation functional²⁵ (B3LYP) was used for all calculations. First, to obtain the lowest energy structures of Rh_6O_5^+ , $\text{Rh}_6\text{O}_5\text{Ar}^+$ and Rh_6O_6^+ , more than one hundred essentially randomly set initial geometries were optimized for ~~all possible spin states~~ spin states $2S+1 = 2, 4, 6, 8$ using the LanL2DZ basis set for Rh atoms²⁶ and the 6-31G(d) basis sets for O and Ar atoms^{27,28} to reduce calculation costs. Several lowest energy geometries obtained for each cluster were re-optimized using the SDD basis set for Rh atoms²⁹ and the aug-cc-pVDZ basis sets for the O and Ar atoms.³⁰ For Rh_6O_3^+ and Rh_6O_4^+ , structures with dissociatively adsorbed oxygen reported by Harding et al. were initially adopted and re-optimized.¹² Harmonic vibrational frequency computations for all clusters were carried out at the same level of theory. The calculated spectra were produced by convoluting the unscaled harmonic vibrations with a Gaussian lineshape function with a 15 cm^{-1} full width at half maximum (FWHM). The IR intensities of the typical bands are given in the supporting information.

4. Results and discussion

4.1. Infrared multiple photon dissociation

Figure 1 shows mass spectra of rhodium oxide cluster cations complexed with Ar atoms, $\text{Rh}_6\text{O}_m^+\text{Ar}_p$ ($m = 3-6$; $p = 0, 1, 2$). The number of oxygen atoms in the clusters was fine-tuned by controlling the concentration of oxygen in the carrier gas used for cluster preparation. Upon irradiation of the cluster beam with an IR laser pulse at

680 cm^{-1} the peak intensities of $\text{Rh}_6\text{O}_m^+\text{Ar}_{1,2}$ (indicated by vertical arrows) decrease, while those of Rh_6O_m^+ increase to the same extent, suggesting that $\text{Rh}_6\text{O}_m^+\text{Ar}_{1,2}$ clusters release the Ar atom(s) to form Rh_6O_m^+ on absorbing IR photons. The Ar atoms are bound so weakly that they do not affect the geometrical structures and the bonding nature of the clusters (see Figure S1). This is confirmed by DFT calculations, predicting binding energies of 0.22 and 0.13 eV for a first and second Ar atom to Rh_6O_4^+ , respectively (see Figure S2).

4.2. IRMPD spectra of Rh_6O_m^+ ($m = 4, 5, 6$)

Figure 2(a) shows the IRMPD spectrum for Rh_6O_4^+ . Prominent bands are found at 490, 615 and 690 cm^{-1} with a weaker band just below 400 cm^{-1} . According to the previous report of Harding et al., the most stable geometry of Rh_6O_4^+ calculated by PBE/SDD is highly symmetric, with Rh atoms forming a tetragonal bipyramid. The second most stable geometry (0.10 eV higher) found is capped-square pyramidal.¹² In our extensive structure search, we have optimized geometrical structures of Rh_6O_m^+ ($m = 4, 5, 6$) using B3LYP/SDD and calculated their vibrational spectra. The different functional reverses the energetic order found by Harding et al.: we found the capped square pyramid structure, with three bridging O atoms and one O atom in a hollow site to be the most stable Rh_6O_4^+ structure, while the second most stable one is the tetragonal bipyramid with four O atoms in hollow sites. Both structures are shown in Figures 2(b) and (c). The spin state of the most stable capped square pyramid is quartet, and the relative energies increase by +0.06, +0.07 and +0.29 eV for doublet, sextet and octet, respectively. The IRMPD spectrum is fully consistent with the vibrational spectrum of the capped-square pyramid predicting three intense bands at 520, 605, and 690 cm^{-1} (unscaled values). The

highly symmetric tetragonal bipyramid should exhibit dominant vibrational bands at 565 cm^{-1} , which do not appear in the IRMPD spectrum and no band above 655 cm^{-1} . It is worth noting that both Pd_6O_4^+ and Co_6O_4^+ adopt tetragonal bipyramidal geometries, probably due to the higher number of bonds between the metal atoms.^{31–34} The bands appearing at 495, 615 and 690 cm^{-1} are common to Rh_6O_m^+ ($m = 4, 5, 6$) and are assigned to vibrations of bridging oxygen atoms in the Rh–O–Rh framework.

Figure 2(d) shows the IRMPD spectrum of Rh_6O_5^+ . Bands appearing at 460, 475, 630, 690, and 860 cm^{-1} are discernible. The calculated most stable geometry is a prism with three bridging O atoms and two O atoms in a hollow site. This geometry is highly symmetric, D_{3h} . In addition, another geometry exists, consisting of the most stable Rh_6O_4^+ structure plus one O atom adsorbed on a hollow site, with a formation energy +1.16 eV higher than the most stable one. Bands at 460, 630, and 690 cm^{-1} in the IRMPD spectrum are most likely due to the most stable structure, for which only three vibrational bands are predicted for the wavenumber range studied due to its high symmetry. The presence of Ar atoms breaking the symmetry may explain the splitting of the band predicted at 460 cm^{-1} . Nevertheless, an additional band at 860 cm^{-1} remains unidentified. According to the DFT calculations, bands in this wavenumber region can generally be assigned to vibrations involving a terminal oxygen atom, --Rh--O . However, such geometries have not been found for stable isomers. They are considered to be energetically unfavorable, and the terminal oxygen would rather form a bridge structure instead. In our calculations, all starting structures with a terminal oxygen, relaxed into structures containing a bridging oxygen atom. We also examined the possibility of stabilizing the terminal oxygen by the tagging Ar atom, which may contribute to the band at 860 cm^{-1} . Calculations of the stable geometries of $\text{Rh}_6\text{O}_5^+\text{Ar}$ indicated that no such structures exist, and the Ar atom does not

appreciably change the geometry of Rh_6O_5^+ (see Figure S2). Most likely, the band at 860 cm^{-1} can be assigned to a combination band of bending motions of Rh–O–Rh at 426 and 439 cm^{-1} .

Figure 2(g) shows the IRMPD spectrum of Rh_6O_6^+ . It is dominated by a strong band centered at 690 cm^{-1} with weaker sidebands at 630 and 705 cm^{-1} . The band at 690 cm^{-1} appears saturated; when the laser power is attenuated, the intensities of the two sidebands decrease more drastically than the intensity of the middle band. Further, four weaker bands at 355 , 430 , 500 , and 545 cm^{-1} are visible. The calculated most stable structure is a prism with five bridging O atoms and one O atom in a hollow site. In addition, DFT calculations showed the existence of a rather open geometry ($+0.11\text{ eV}$ higher in formation energy). While both predicted spectra could account for the strong band at 680 cm^{-1} in the experimental spectrum, the two sidebands and the four bands between 350 – 550 cm^{-1} are only accounted for by the most stable prismatic structure. The apparent mismatch in the intensity distribution of the three bands between calculated and experimental spectra could well be explained by the saturation of the 680 cm^{-1} band.

4.3. Other clusters

For larger Rh_6O_m^+ ($m \geq 6$) clusters, we investigated the IR spectral properties without tagging Ar atoms. For these species, depletion spectra are shown in Figure 3, which we display in columns based on an odd or even number of constituent oxygen atoms. The spectra can be divided in spectra that exhibit depletion (loss), those that exhibit growth (gain) and one that exhibits a mixture of the two. Evidently, Rh_6O_m^+ ($m = 7$ and 10) exhibits depleted ion intensities between 600 – 720 cm^{-1} due to photoabsorption, whereas Rh_6O_m^+ ($m = 5, 6$) shows a growth. The spectrum for Rh_6O_9^+ shows no change

and that for Rh_6O_8^+ shows a mixture of gain and depletion. For both odd- and even-numbered oxygen species, the depletion and gain signals coincide: there is loss for Rh_6O_7^+ and simultaneous gain for Rh_6O_5^+ at 650 cm^{-1} . For the even species, the situation is slightly more complex: there is loss for $\text{Rh}_6\text{O}_{10}^+$ centered at 670 cm^{-1} , which is mirrored by a (relatively broad) gain signal in Rh_6O_8^+ . The spectrum of $\text{Rh}_6\text{O}_{10}^+$ exhibits a weaker depletion between $800\text{--}920\text{ cm}^{-1}$, which is also observed for Rh_6O_8^+ as a gain. At the same time, a loss for Rh_6O_8^+ centered at 640 cm^{-1} is reflected by a gain in Rh_6O_6^+ . We therefore conclude that the IRMPD excitation of Rh_6O_m^+ ($m = 7, 8, 10$) results in release of O_2 :

According to our previous study using thermal desorption spectrometry, the threshold energies for O_2 molecule release were 1.2, 1.3, 1.4, and 0.5 eV for $m = 7, 8, 9$, and 10.¹⁴ In addition, the dissociation energies obtained by DFT calculations were 1.9 eV for $m = 6$. Hence, dissociation was observed for structures with a dissociation energy as high as 1.3 eV under the present experimental conditions. This energy translates into a number of more than 10 absorbed photons. It is somewhat surprising that no depletion is observed for the Rh_6O_9^+ cluster given the similarity of the observed thermal desorption energies; this will be discussed below.

It is of interest to note that all bands observed for Rh_6O_m^+ ($m = 7, 8, 10$) are close to the maximum of the IRMPD spectra for the Ar-tagged Rh_6O_m^+ ($m = 4, 5, 6$) clusters, but with a substantially larger spectral width. This is likely caused by the requirement to absorb more IR photons to overcome the desorption energy of O_2 to the $\text{Rh}_6\text{O}_{m-2}^+$ ($m = 7, 8, 10$) cluster than for desorption of Ar.³⁵ In the multiple photon absorption process, an IR photon is absorbed in a particular vibrational mode, followed by statistical re-

distribution of the energy over all degrees of freedom of the cluster through intramolecular vibrational redistribution (IVR). After IVR, the previously excited vibrational mode can absorb another photon. Repeating this photoabsorption and IVR cycle leads to a gradual heating of the cluster. As a result, the resonance of the vibrational mode is redshifted due to the anharmonicity of the vibrational potential, causing broadening and red-shifting of the vibrational bands.³⁶ While this same picture is valid for the Ar-tagged species it is expected that broadening effects are more pronounced for O₂ loss as the typical binding energy of Ar (0.2 eV) is much lower than that for O₂ (1.0 eV).

In Figure 4, the gain spectrum for Rh₆O₆⁺ is compared to calculated IR spectra for candidate structures for Rh₆O₈⁺ and the depletion spectrum of Rh₆O₁₀⁺ to candidate structures for Rh₆O₁₀⁺. At first glance, it is directly clear that for all structures more IR bands are expected than the single one observed. For Rh₆O₈⁺ the most prominent discrepancy is the lack of any observed bands below 600 cm⁻¹. While unsatisfactory for a structural assignment, this could be rationalized by a sudden “cut-off” of the signal: to exceed the threshold energy for the desorption of O₂ to occur, the number of absorbed photons required is inversely proportional to the frequency ν . Previously, a non-linear frequency dependence of the photon flux required for detection of thermionic emission by neutral Nb clusters upon resonant IR excitation was observed.³⁵ This resulted in an abrupt cut-off of IR bands below a certain threshold frequency. Under the current conditions, with a near-constant macropulse energy, it is conceivable that such excitation limitations could lead to a similar sudden frequency cut-off for observed desorption.

Given such limitations, the spectra for Rh₆O_{7,8,10}⁺ may not lead to a unique identification of geometrical structures, but some of them are worth discussing in

comparison with the results by DFT calculations. The IRMPD spectrum for Rh_6O_8^+ in Figure 4(a), the same as the gain spectrum of Rh_6O_6^+ in Figure 3(c), shows a prominent broad band at 640 cm^{-1} . DFT calculations suggested several stable geometries of Rh_6O_8^+ as shown in Figure 4(b–d). All structures have a common geometry of a prism with eight bridging O atoms, which is similar to the geometries of Rh_6O_5^+ and Rh_6O_6^+ : As the number of O atoms increases, the oxygen atoms, adsorbed on the hollow sites of the prism in Rh_6O_5^+ and Rh_6O_6^+ , appear to migrate to the bridge sites. None of the spectra is sufficiently different to assign the experimental spectrum to a specific structure, but they are all at least consistent with the observation of no band at frequencies higher than 700 cm^{-1} .

For the IRMPD spectrum for $\text{Rh}_6\text{O}_{10}^+$ shown in Figure 4(e), the same spectrum as shown in Figure 3(a), similar arguments can be made: a prominent band appears at 670 cm^{-1} , which has a tail to the lower wavenumber range. In addition, a broad but much weaker band appears between $800\text{--}920\text{ cm}^{-1}$, which, as was discussed for the spectrum of $\text{Rh}_6\text{O}_5^+\text{-Ar}$, is evidence for the existence of a terminal O atom. The calculated stable geometries of $\text{Rh}_6\text{O}_{10}^+$ with the vibrational spectra are shown in Figure 4(f–h). The geometries of the stable isomers are similar with a Rh prism structure with nine bridging O atoms and one terminal oxygen atom. The similarity in the geometrical structures is reflected in the characteristic vibrational spectra comprising bands in 500 , 650 , and 920 cm^{-1} . Nevertheless, despite the presence of a terminal oxygen for the structure in Figure 4(h), its calculated spectrum does not exhibit the characteristic Rh–O stretch mode at 920 cm^{-1} . This is because the R–O bond of the terminal oxygen is weak and elongated ($1.77\text{ \AA}$ for structure Figure 4(h) versus $1.68\text{ \AA}$ for the other two), so that the vibrational mode is red-shifted by $\sim 180\text{ cm}^{-1}$ and is now part of the structure around 700 cm^{-1} . In analogy

to Rh_6O_8^+ , it is difficult to draw conclusions about a structural assignment. While all structures predict bands near the 670 cm^{-1} band observed, the spectral resolution of the observed band is insufficient to eliminate certain candidate structures. What is more, while a broadening of bands such as observed for the $800\text{--}920\text{ cm}^{-1}$ feature, such a strong mismatch between predicted IR intensities and IR depletion makes it difficult to rule out structure 4(h) as carrier of the main intensity of the absorption spectrum. One only could speculate that the relative strength of the 670 cm^{-1} band is due to resonance effect of the presence of multiple vibrational bands.³⁶

4.4. Interpretation of the reactivity of Rh_6O_m^+ towards NO

Thus, we have determined the geometrical structures of Rh_6O_m^+ ($m = 4, 5, 6$) using IRMPD spectroscopy. The most important finding is that all structures are based on a capped square pyramid Rh structure with oxygen atoms that tend to bridge Rh–Rh bonds, occupying the adsorption sites of Rh clusters. This is in contrast to Harding et al, who find that tetragonal bipyramid ~~octahedral~~ structures dominate at low energies.¹² While we could not decisively characterize the structures of Rh_6O_m^+ ($m = 7\text{--}10$) all calculations indicate this motif for larger clusters, too. According to the reported gas-phase ~~CID~~ single collision reactivity experiments performed by Fourier transform mass spectrometry ~~experiments~~—and the relevant DFT calculations, two NO molecules, dissociatively adsorbed on Rh_6^+ , are reduced to form Rh_6O_2^+ and N_2 .^{7,12} The adsorption and reduction further proceeded on Rh_6O_2^+ , leaving the oxygen atoms on the cluster and releasing N_2 into the gas phase. However, the reduction was terminated completely at the stage of Rh_6O_4^+ .⁷ DFT calculations supported the following reaction scheme¹². The dissociative adsorption of NO onto the energetically stable Rh_6O_4^+ geometries was

generally endothermic, whereas at least three exceptional exothermic reaction channels existed, leading to the dissociative adsorption on the energetically unstable Rh_6O_4^+ .¹² However, an activation barrier existed between the molecularly and dissociatively adsorbed forms, kinetically hindering the dissociation of NO.¹² Our current study on structural determination of Rh_6O_4^+ indicates that the adsorption of the fourth NO proceeds over the capped pyramidal structures. A plausible scenario is that NO was molecularly adsorbed on the capped-square pyramidal geometry of Rh_6O_4^+ , bridging two Rh atoms, and did not dissociate on the cluster, since the dissociation is endothermic by +1.62 eV.¹² NO molecules adsorbed in a different way, forming unstable structures at energies of +1.0 and +1.6 eV higher than the most stable one, could exothermically dissociate (−0.28 and −0.97 eV), but the activation energies are +2.7 and +1.1 eV, respectively.¹²

DFT calculations indicated that Rh atoms form tetragonal bipyramidal structures in Rh_6O_m^+ for $m \leq 3$.¹² In our calculations, those in Rh_6O_m^+ were found to have a capped pyramidal geometry for $m = 4$ and a prismatic geometry for $m = 5$ and 6, which are now confirmed by the current spectroscopic experiments. The change of geometry of the Rh framework at $m = 4$ reduces the number of triangular hollow sites, on which N atoms prefer to sit when NO adsorbs dissociatively, from eight to six,^{38,39} with only two triangular hollow sites available for Rh_6O_4^+ . For Rh_6O_5^+ , which has a prismatic structure, no sites are left. While evidence for dissociative or molecular adsorption of NO onto Rh_6O_4^+ is still lacking, it is highly likely that the change of geometry at $m = 4$ is an important factor in preventing the reduction of two NO molecules over Rh_6O_4^+ ; the further change for $m = 5$ and 6 certainly will prevent NO dissociative adsorption. We are currently investigating the nature of NO adsorption on Rh_6O_4^+ .

5. Conclusions

IRMPD spectra of Rh_6O_m^+ were obtained in the 300–1000 cm^{-1} spectral range. For $4 \leq m \leq 6$, the dissociation energies for releasing O_2 are too high for photodissociation signals to be observed. Instead, Ar release from clusters with weakly bound tagging Ar atoms was observed after multiple photon absorption of IR laser radiation, yielding well-resolved vibrational spectra. The spectra were compared with the vibrational spectra for several stable geometries obtained by DFT structural optimization. Rh_6O_4^+ showed prominent bands at 615 and 690 cm^{-1} and several other bands at higher and lower wavenumbers, allowing assignment to a capped-square pyramidal Rh geometry with three bridging O atoms and one O atom in a hollow site. Rh_6O_5^+ displayed bands at 460, 630, 690 and 860 cm^{-1} and exhibited a prismatic Rh geometry with three bridging O atoms and two O atoms in a hollow site. Most likely, the band at 860 cm^{-1} was due to a combination band or overtone. Rh_6O_6^+ showed three intense bands around 600–750 cm^{-1} together with multiple weak bands between 350–550 cm^{-1} and was identified to have a prismatic Rh geometry with four bridging O atoms and two O atoms in a hollow site. Considering that Rh_6O_m^+ ($m \leq 3$) adopts tetragonal bipyramidal Rh structures, the change of geometry at $m = 4$ results in a reduction of the number of triangular hollow sites, where NO preferentially binds via the N atom, thus lowering the possibility of NO dissociative adsorption. The inference is consistent with the interpretation of experimental results by Mackenzie et al.⁷

For $m \geq 7$, the dissociation energies for releasing O_2 were low enough for direct photodissociation of bare Rh_6O_m^+ clusters. The vibrational spectra exhibited one dominant band around 600–700 cm^{-1} , characteristic of the vibration of bridging oxygen atoms in the Rh–O–Rh framework. The spectra are not sufficient for structural

identification, but consistent with theoretical findings of prismatic structures with bridging oxygen atoms.

■ ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge on the ACS Publication website at DOI:_.

Depletion spectra of $\text{Rh}_6\text{O}_4^+\text{Ar}_2$, $\text{Rh}_6\text{O}_4^+\text{Ar}$, and Rh_6O_4^+ ; Optimized structures of $\text{Rh}_6\text{O}_4^+\text{Ar}$ and $\text{Rh}_6\text{O}_5^+\text{Ar}$; IRMPD spectrum of Rh_6O_3^+ and theoretical vibrational spectra of candidate structures obtained by DFT calculations; IRMPD spectrum of Rh_6O_8^+ and theoretical vibrational spectra of candidate structures obtained by DFT calculations; Geometrical structures and vibrational spectra of stable Rh_6O_9^+ cluster obtained by DFT calculations; Tabulated spin multiplicities and atomic coordinates; IR intensities of the typical bands.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: mafune@cluster.c.u-tokyo.ac.jp Tel: +81-3-5454-6597

Notes

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Figure captions

Figure 1. Mass spectrum of rhodiumoxide cluster cations complexed with Ar atoms, $\text{Rh}_6\text{O}_m^+\text{Ar}_p$ ($m = 3-6$; $p = 0, 1, 2$) without (a) and with irradiation by the IR laser at 680 cm^{-1} .

Figure 2. IRMPD spectra of (a) $\text{Rh}_6\text{O}_4^+\text{-Ar}$, (d) $\text{Rh}_6\text{O}_5^+\text{-Ar}$ and (g) $\text{Rh}_6\text{O}_6^+\text{-Ar}$ accompanied by theoretical vibrational spectra for candidate structures of (b, c) Rh_6O_4^+ , (e, f) Rh_6O_5^+ , and (h, i) Rh_6O_6^+ , as obtained by DFT calculations. Intensity of the band at 698.7 cm^{-1} of panel (e) for Rh_6O_5^+ is 160.3 km mol^{-1} . The grey line in the experimental spectra indicates a zero level.

Figure 3. IR depletion spectra of Rh_6O_m^+ ($m = 6-10$). The intensities have been normalized on the IR macropulse energy. The grey line indicates a zero level.

Figure 4. IR depletion spectra of (a) Rh_6O_8^+ and (e) $\text{Rh}_6\text{O}_{10}^+$, accompanied by theoretical vibrational spectra for candidate structures of (b–d) Rh_6O_8^+ and (f–h) $\text{Rh}_6\text{O}_{10}^+$ obtained by DFT calculations. The grey line in the experimental spectra indicates a zero level.

Figure 1

Figure 2

Figure 3

Figure 4

TOC graphic