Adsorption Forms of NO on Rh_n^+ ($n = 6\text{--}16$) Revealed by Infrared Multiple Photon Dissociation Spectroscopy

Toshiaki Nagata^{1 §}, Kohei Koyama¹, Satoshi Kudoh¹, Ken Miyajima¹, 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:

The adsorption of NO on cationic Rh clusters, Rh_n^+ ($n = 6\text{--}16$), was studied by IRMPD spectroscopy using FELIX in combination with DFT calculations. The IRMPD spectra show that NO adsorbs molecularly on an on-top site of Rh_n^+ for all n studied, while for $n = 7, 12, 13$ and 14 evidence is found for second, bridging, adsorption site. Indeed, the DFT calculations suggest that molecular NO adsorption on a bridge site is more stable than on an on-top site for $n = 7$. Part of the NO adsorbs dissociatively on Rh_n^+ , and the ratio of dissociative adsorption depends on the size, n . For Rh_n^+ ($n = 6, 8, 9$), the dissociative form of NO is predicted more favorable than the molecular form by the DFT calculations, but experimentally observed ratios of dissociative adsorption were less than the prediction. The activation barrier existing between the molecular and dissociative adsorption was considered to hinder the NO dissociation.

1. Introduction

Rhodium is one of the most important elements in catalysts. As it has a function to catalytically reduce NO, it has been used as three-way catalytic converters in the aftertreatment system of automobiles.¹ The mechanism of NO reduction has been investigated for a few decades and the form in which NO adsorbs on a surface is known to be sensitive to temperature and surface coverage: NO adsorbs molecularly on all Rh surfaces at low temperatures (<170 K), and it dissociates upon heating, when coverage is low.²⁻⁴ The most stable form of NO on Rh(111) corresponds to the hollow (μ_3) site one at 0.5 ML coverage, which changes to one on-top (μ_1) site and two hollow site adsorbates for a coverage of 0.75 ML.⁵ The mechanism of NO reduction also strongly depends on the chemical environment. In the presence of CO, the Rh(111) surface is initially covered with mainly N atoms (N(a)), which were generated from the reaction of NO and CO to give N(a) and CO₂. A NO molecule then reacts with N(a) to form N₂O, and the N₂-O bond on the surface is cleaved to release N₂.⁶⁻⁹

As the reaction path varies depending on reaction conditions, the use of a gas-phase cluster for investigation of the reaction mechanism can be very instructive: As all atoms and molecules involved in the clusters can be probed using mass spectrometry, the reaction can be monitored in a controlled manner.¹⁰⁻¹³ Direct decomposition of NO by isolated Rh_n^{+/-} clusters in the gas phase has been observed using collision-based experiments.¹⁴⁻¹⁶ Mass spectrometric analysis shows that after the adsorption of two NO molecules on a cluster, N₂ was produced and released from the cluster leaving the dioxide cluster. These results were interpreted as resulting from the dissociative adsorption of NO, generating N atoms that can migrate on the surface of the cluster. It was suggested that the reaction is driven by heat generated upon NO

adsorption to the isolated $\text{Rh}_n^{+/-}$ in vacuum. Indeed, no decomposition of NO was observed under thermalized conditions at 300 K, whereas the release of N_2 was clearly observed at higher temperatures (>800 K), indicating that NO was reduced on the clusters for $n \geq 7$.¹⁷

According to DFT calculations using the LANL2DZ effective core potential and basis set to describe Rh atoms, the most stable geometry of $\text{Rh}_6^+(\text{NO})$ comprises a tetragonal bipyramid Rh_6^+ cluster with NO adsorbed molecularly on an on-top site of the Rh_6^+ cluster with its N atom pointing inwards, with an adsorption energy of -1.5 eV.¹⁷ In the dissociation reaction pathway, a transition state existed with an energy barrier of $+1.1$ eV relative to the reactants, Rh_6^+ and NO. After this transition state, the complex falls into another minimum, where the N and O atoms are separately adsorbed on hollow sites on the cluster, which is 1.2 eV lower than the geometry before adsorption.

For Rh_7^+ , Xie and coworkers predicted that NO adsorbs in molecular form on a hollow Rh_7^+ site, with an energy of -2.0 eV.¹⁸ In addition, a transition state exists for the dissociation of NO, with an energy barrier of $+1.7$ eV from the molecularly adsorbed $\text{Rh}_7^+(\text{NO})$ complex. The most stable state where both N and O atoms were separately adsorbed on bridge (μ_2) sites was observed 2.4 eV below the initial state of Rh_7^+ and NO. As the transition state was found to be 0.3 eV lower in energy than the initial state, NO could adsorb dissociatively on Rh_7^+ .

Thus, according to the calculations there exists a transition state toward dissociation of NO, which needs to be overcome for the catalytic reduction of NO over Rh clusters. However, there is no experimental evidence on how and where NO adsorbs on the Rh_n^+ cluster under thermalized conditions. Taking into account these previous

studies, we prepared $\text{Rh}_n^+(\text{NO})$ clusters in a helium carrier gas in a good thermal equilibrium at 173–263 K and observed the vibrational spectra of the clusters using infrared multiple photon dissociation (IRMPD) spectroscopy. Then, the geometrical structures of the clusters were determined by comparison to the results of DFT calculations, a proven method for structure determination of clusters.¹⁹⁻²⁶

2. Experimental methods

The adsorption forms of NO on rhodium cluster ions, Rh_n^+ ($n = 6\text{--}16$), were investigated via IRMPD spectroscopy using a molecular beam instrument coupled to the free electron laser for infrared experiments (FELIX).²⁷ Gas-phase Rh_n^+ cluster ions were prepared by pulsed laser ablation of a Rh metal rod at 20 Hz in a He carrier gas. 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 pulse⁻¹. Ablation took place in a 4 mm diameter cluster growth channel filled with He carrier gas that was introduced through a first pulsed valve at a stagnation pressure of 0.7 MPa.

NO diluted by He gas (~0.5%, stagnation pressure of 0.1 MPa) was introduced into the reaction gas cell after the growth channel through a second valve. Prepared Rh_n^+ collides with NO molecules to form $\text{Rh}_n^+(\text{NO})_m$ clusters in a thermalized condition in He buffer gas. To record IR spectra for $\text{Rh}_n^+(\text{NO})_m$ clusters, weakly bound complexes of the clusters with Ar atoms were formed, which dissociate upon the absorption of only a few photons. Photoabsorption can then be probed by mass spectrometry as the loss of Ar atoms from the clusters. The formation of $\text{Rh}_n^+(\text{NO})\text{Ar}$ was accomplished by admixing 0.3%–4% Ar gas in the carrier gas and cooling the gas to 173–263 K with liquid N₂ in the reaction gas cell. The concentrations of NO and Ar gases were tuned

using mass flow and pressure controllers to maximize the number of clusters of interest. In addition, the partial pressures of NO and Ar 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 $0.25\text{--}20 \text{ mJ pulse}^{-1}$ before use. The spectral bandwidth was kept at $0.2\text{--}0.3\%$ root mean square of the central frequency. 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 was operated at twice the FELIX repetition rate of 10 Hz allowing for the recording of reference mass spectra in between FELIX pulses.

To obtain the IRMPD spectra, the branching ratio $R(\nu)$ of Ar tagged clusters $\text{Rh}_n(\text{NO})_m^+ \text{Ar}_p$ ($p = 1, 2$) to the total number of clusters $\text{Rh}_n(\text{NO})_m^+ \text{Ar}_p$ ($p = 0, 1, 2$) was calculated. The IRMPD intensity is then calculated as the logarithmic ratio $-\ln(R(\nu)/R_0)$, with $R(\nu)$ and R_0 the branching ratios with and without irradiation, respectively. The 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 $\text{Rh}_n^+(\text{NO})$ ($n = 6-10$) and simulate their vibrational spectra, DFT calculations were performed using the Gaussian09 program.²⁸ Becke's three-parameter hybrid density functional with the Lee-Yang-Parr correlation functional (B3LYP)^{29, 30} was used for all calculations. First, to obtain the lowest energy structures of molecularly adsorbed $\text{Rh}_n^+(\text{NO})$, more than twenty initial geometries in which one NO molecule was placed around Rh_n^+ at random were optimized for all conceivable spin states using the LanL2DZ basis set for Rh atoms³¹ and the 6-31G(d) basis sets for N and O atoms^{32, 33} to reduce calculation costs. In addition, to obtain the lowest energy structures of dissociatively adsorbed $\text{Rh}_n^+(\text{NO})$, more than one hundred essentially randomly set initial geometries were optimized for all conceivable spin states using the same basis sets. Several lowest energy geometries obtained for each cluster were re-optimized using the SDD basis set for Rh atoms³⁴ and the aug-cc-pVDZ basis sets for the N and O atoms.³⁵ Harmonic vibrational frequencies for all clusters were calculated at the same level of theory and are presented unscaled throughout this work. 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). Anharmonic frequencies were also calculated for $\text{Rh}_6^+(\text{NO})$ by numerical differentiation to estimate variation from the harmonic frequencies. Natural bond orbital (NBO) analysis was performed for $\text{Rh}_7^+(\text{NO})$ to investigate the charge and spin distribution.³⁶

³⁷ Transition states were calculated for NO migration on Rh_7^+ and dissociation on Rh_8^+ using the quadratic synchronous transit-guided quasi-Newton (STQN) method to estimate the reaction barriers.^{38, 39} Vibrational frequencies were calculated for the

obtained transition state structures, yielding one single imaginary frequency, suggesting that these structures correspond to the first-order saddle points.

4. Results and discussion

All experimentally obtained spectra contain resonances in the 1500–2000 cm^{-1} spectral range, and in the range below 700 cm^{-1} . Bands in the 1500–2000 cm^{-1} spectral range can unambiguously be assigned to the stretching mode of NO, indicating that NO is molecularly adsorbed on Rh_n^+ . When the NO molecule adsorbs dissociatively, no band should appear in this spectral range and instead only bands would appear below 700 cm^{-1} . The exact frequency of the NO stretch vibration (free NO: 1876 cm^{-1} ⁴⁰) is a signature of the binding motif: NO bound to an on-top site in general will have a higher stretch vibrational frequency than bridge-bound NO or NO bound on hollow sites. In the following, we will discuss the experimental spectrum for each Rh_n^+ system individually and compare it to calculated spectra for the stable structural isomers obtained using DFT. In case both molecularly and dissociatively bound NO is found, we will try where possible to estimate their ratios based on the observed spectral intensities in comparison with the calculated IR intensities. Extensive calculations for $\text{Rh}_n^+\text{-NO}$ ($n = 6\text{--}8$) allow us to make conclusive assignments, whereas we can only tentatively assign the spectra for $\text{Rh}_n^+\text{-NO}$ ($n = 9, 10$). No calculations were carried out for $\text{Rh}_n^+\text{-NO}$ ($n = 11\text{--}16$), but we present their experimental spectra nevertheless, as we are able to identify the binding site for molecular NO.

4.1. Adsorption forms of NO on Rh_6^+

Figure 1(a) shows the IRMPD spectrum for $\text{Rh}_6^+(\text{NO})$. A prominent band is found at 1815 cm^{-1} with weaker bands below 700 cm^{-1} . The 1815 cm^{-1} band is direct

evidence for the presence of molecularly bound NO. Indeed, one of the stable geometries of $\text{Rh}_6^+(\text{NO})$ calculated comprises Rh atoms forming a tetragonal bipyramid with a NO molecule adsorbed via the N atom on an on-top site (isomer 6B). The most stable geometry is a tetragonal bipyramid Rh with separate N and O atoms, both of which adsorb on hollow sites (isomer 6A). In addition, two stable geometries with dissociatively adsorbed NO were found: one with N and O adsorbed on two different hollow sites (isomer 6C, +0.24 eV), and one with the N adsorbed on a hollow, and O on a bridge site (isomer 6D, +0.37 eV).

Thus, the band at 1815 cm^{-1} should be assigned to the stretch mode of NO adsorbing on the on-top site. Indeed, the DFT calculations suggest that NO adsorbing on the bridge site (+0.41 eV) and the hollow site (+0.42 eV) are less stable, giving weakened NO stretch vibrations at 1665 and 1478 cm^{-1} , respectively. Although the DFT calculations predict a higher wavenumber for the NO stretch (1925 cm^{-1}) than the experimental one, the value was lowered to 1889 cm^{-1} in an anharmonic calculation, thereby getting closer to the experimental one.

According to the DFT calculation, the structure with molecular NO has only two weak bands at 366 and 526 cm^{-1} with IR intensities of 0.3% and 0.2% relative to the most intense band at 1925 cm^{-1} (1667 km mol^{-1}). However, more than three bands are clearly discernable in the $300\text{--}700\text{ cm}^{-1}$ range in Figure 1(a), suggesting spectral contributions by other isomers. The intense band at 1815 cm^{-1} appears to be composed of only one peak: indeed, a spectrum obtained using a lower IR fluence (shown in red in Figure 1a) gives no evidence for multiple bands, suggesting that there is only one geometrical structure present with molecularly adsorbed NO, namely isomer 6B. It is thus likely that the other isomers have dissociatively adsorbed NO. Isomer 6A is

predicted to have bands at 351, 442, 507, 565 cm^{-1} and a weaker one at 713 cm^{-1} ; isomer 6C has predicted bands at 463, 485, 598 and 677 cm^{-1} and isomer 6D at 443, 488, 566 and 634 cm^{-1} . From an analysis of the vibrations calculated by DFT for the different isomers (see Figure S1), the bands at 600–650 cm^{-1} should be assigned specifically to isomers with one O atom on a bridge site. Based on these predicted bands of the isomers, we assign the observed bands to isomer 6A at 455 cm^{-1} , to 6B at 550 and 1815 cm^{-1} , and to 6D at 620 cm^{-1} . We rule out the presence of isomer 6C for lack of evidence of the strongest predicted band at 463 cm^{-1} . The weaker band predicted for isomer 6A at 565 cm^{-1} could be hidden in the red shoulder of the band at 550 cm^{-1} . It is somewhat unsatisfactory that predicted bands at 366 cm^{-1} for isomer 6B is not observed in the IRMPD spectrum. We cannot help but notice that the pattern of the experimental bands is quite similar to the pattern predicted for isomer 6A; however, given the large mismatch in frequencies (an unusual scaling factor of ~ 1.24 for the harmonic frequencies would be required), we rule out an assignment to 6A alone.

Here, the question arises on a ratio of the dissociatively adsorbed form to the molecularly adsorbed form. To estimate this ratio, the observed IRMPD intensities are supposed to increase linearly with the theoretical IR intensities. Setting the band intensity at 1815 cm^{-1} be unity, the relative band intensity at 455 cm^{-1} is 4.0×10^{-4} . Note that the band intensity at 1815 cm^{-1} was estimated from the high-resolution spectrum, because the high-intensity scan shown in Figure 1(a) was found to be saturated. The band at 455 cm^{-1} has been assigned to a vibrational excitation of isomer 6A with a predicted IR spectral intensity of 33.0 km mol^{-1} . If both species 6A and 6B were present in a 1:1 ratio, the intensity of the 455 cm^{-1} band would be 2.0×10^{-2} with respect to that of the 1815 cm^{-1} band, which is 50 times higher than that actually observed. Hence, the

ratio of the dissociatively adsorbed form (6A) to the molecularly adsorbed one (6B) are estimated to be 2.0%. When using other bands at 455 cm^{-1} assigned to 6A and at 550 cm^{-1} assigned to 6B (relative intensity of the former to the latter is 0.48), the ratio of the dissociatively adsorbed form to the molecularly adsorbed one would be 3.5%. Thus, while the IRMPD spectrum contains contributions from several isomers, and the dissociative and molecular forms are near-isoenergetic, the molecularly adsorbed form is surely dominant for $\text{Rh}_6^+(\text{NO})$.

4.2. Adsorption forms of NO on Rh_7^+

Figure 2(a) shows the IRMPD spectrum for $\text{Rh}_7^+(\text{NO})$. Two intense bands appear at 1600 and 1825 cm^{-1} with at least five weaker bands below 700 cm^{-1} . As discussed above, bands in $1500\text{--}2000\text{ cm}^{-1}$ spectral range can readily be assigned to molecularly adsorbed NO on Rh_7^+ . Since there are two observed bands, there must be two isomers present. The relatively large frequency difference between the two bands suggests two different adsorption sites.

According to the DFT calculations, the most stable geometry of $\text{Rh}_7^+(\text{NO})$ is formed by a capped octahedral Rh structure with a NO molecule adsorbing on a bridge site (isomer 7A), with a predicted vibrational band at 1712 cm^{-1} . An isomer 7C (+0.11 eV) with molecular NO adsorbed on a bridge site is of a pentagonal bipyramid Rh cluster, now with a predicted vibrational band at 1734 cm^{-1} . A stable geometry (7D, +0.13 eV) has NO molecularly adsorbed on an on-top site, with a predicted band at 1931 cm^{-1} . All the structures are shown in Figures 2(b), (d), and (e). For the capped octahedral isomers 7A and 7D with molecular NO, NO is adsorbed on the capping atom of the Rh cluster. This capping atom is considered quite active, which is illustrated by

its spin density in bare Rh_7^+ , which is higher (NBO 2.01 and Mulliken 1.96) than those of the other atoms (NBO 1.60–1.76 and Mulliken 1.56–1.76). Upon adsorption of NO, the spin density is found to be greatly reduced (NBO 0.68 and Mulliken 0.65), indicating the strong electronic interaction between the Rh atom and NO.

We assign the prominent bands at 1600 and 1825 cm^{-1} to structural isomers with NO adsorbed on the bridge and the on-top sites, respectively. The band at 1600 cm^{-1} could contain contributions from each of the two bridge-adsorbed structural isomers, 7A and 7C, although the lower IR fluence spectrum does not show clear evidence that the band is composed of two peaks. The proximity in energy of the two predicted resonances could mean they obscure each other.

For each of the two bridge-bound isomers, 7A and 7C, three bands in the 300–700 cm^{-1} spectral range are predicted, namely at 325 cm^{-1} (0.8 km mol^{-1}), 439 cm^{-1} (5.4 km mol^{-1}) and 581 cm^{-1} (1.5 km mol^{-1}) for 7A, and 328 cm^{-1} (0.8 km mol^{-1}), 402 cm^{-1} (1.3 km mol^{-1}) and 483 cm^{-1} (1.7 km mol^{-1}) for 7C. However, five of these (the ones at 325 and 581 cm^{-1} for 7A and all bands for 7C) are so weak that they likely fall under the noise level in the IRMPD spectrum. The on-top bound isomer 7D can contribute two more bands. Hence, for the five bands observed in the 300–700 cm^{-1} range, only three can be attributed to molecularly bound isomers, so it appears likely that at least one isomer with NO dissociatively adsorbed contributes. Indeed, a stable geometry (7B, +0.07 eV) found is a capped tetragonal bipyramid Rh cluster with separate N and O atoms adsorbed on a hollow and bridge site, respectively, predicting rather intense vibrational bands at 476 cm^{-1} (10.5 km mol^{-1}), 607 cm^{-1} (27.7 km mol^{-1}), 649 cm^{-1} (54.9 km mol^{-1}), and 707 cm^{-1} (4.3 km mol^{-1}). Considering these predictions, we assign the observed bands at 475 and 1600 cm^{-1} to isomer 7A, the bands at 575 and

620 cm^{-1} to 7B, and those at 320, 545 and 1825 cm^{-1} to 7D. Due to the large number of bands observed, some of them could obscure each other.

The appearance of bands for both molecularly and dissociatively bound isomers in the same spectral range gives the opportunity to estimate their ratio. The presence of the isomer of Rh_7^+ with NO adsorbed dissociatively (isomer 7B) relative to the most stable isomer 7A would be 9.3%, considering that the band intensities of the IRMPD spectrum at 620 and 1600 cm^{-1} and the IR spectral intensities by the DFT calculations at 649 and 1712 cm^{-1} , under the assumption that the 620 cm^{-1} band are solely due to isomer 7B. Similarly, it would be 18.5%, considering that the observed band intensities at 575 and 1600 cm^{-1} and the calculated IR spectral intensities at 607 and 1712 cm^{-1} . Thus, contribution of the dissociative form of NO in $\text{Rh}_7^+(\text{NO})$ is surely more than that in $\text{Rh}_6^+(\text{NO})$. As discussed later, the presence of isomer 7D would be ~70% relative to that of isomer 7A, under the assumption that the 1600 and 1825 cm^{-1} bands correspond to isomers 7A and 7D, respectively. Thus, NO in the dissociative form (7B) would account for 5–10% of the total amount of $\text{Rh}_7^+(\text{NO})$ isomers (7A, 7B, and 7D).

4.3. Adsorption forms of NO on Rh_8^+

Figure 3(a) shows the IRMPD spectrum for $\text{Rh}_8^+(\text{NO})$. A single prominent band appears at 1810 cm^{-1} with several bands below 700 cm^{-1} . Compared with $\text{Rh}_6^+(\text{NO})$, the contribution of the bands below 700 cm^{-1} appears larger. The prominent band at 1810 cm^{-1} straightforwardly indicates that there is an isomer with NO molecularly adsorbed on the on-top site of Rh_8^+ . Indeed, the DFT calculations yield a stable geometry of $\text{Rh}_8^+(\text{NO})$ comprising a Rh bi-capped octahedron (bisdisphenoid)

with a NO molecule adsorbed on an on-top site, and a predicted vibrational band at 1897 cm^{-1} (isomer 8B, Figure 3(c)). A geometrical isomer with a molecular NO on a bridge site was also found, the formation energy of which is $+0.29\text{ eV}$ higher than isomer 8B. Consistently with the results for $\text{Rh}_7^+(\text{NO})$, the vibrational band of this isomer was predicted at 1637 cm^{-1} , substantially lower than the observed value.

The DFT calculation also identified an isomer with separate N and O atoms on hollow sites as the most stable form (8A, Figure 3(b)), the formation energy of which is 0.13 eV lower than isomer 8B. The calculations predict for this structure vibrational bands at 405 cm^{-1} (6.5 km mol^{-1}), 483 cm^{-1} (9.2 km mol^{-1}), 543 cm^{-1} (25.6 km mol^{-1}), 628 cm^{-1} (2.4 km mol^{-1}) and 675 cm^{-1} (1.2 km mol^{-1}). In addition, an isomer 8C comprising Rh atoms forming a bi-capped octahedron and separate N and O atoms on hollow sites exists at $+0.19\text{ eV}$ higher than isomer 8A, with vibrational bands at 351 cm^{-1} (12.3 km mol^{-1}), 428 cm^{-1} (17.4 km mol^{-1}), 468 cm^{-1} (16.4 km mol^{-1}), 589 cm^{-1} (8.3 km mol^{-1}) and 674 cm^{-1} (1.8 km mol^{-1}). Considering these predicted bands, the observed bands are assigned to isomer 8A at 460 , 550 , 605 , and 640 cm^{-1} and to 8B at 480 , and 1810 cm^{-1} . The presence of the isomer of Rh_8^+ with NO adsorbed dissociatively (8A) relative to the isomer with NO adsorbed molecularly (8B) would be 26% , considering that the band intensities of the IRMPD spectrum at 605 and 1810 cm^{-1} and the IR spectral intensities by the DFT calculations at 628 and 1897 cm^{-1} . In other words, NO adsorbed on Rh_8^+ in the dissociative form (8A) would account for $\sim 21\%$ of the total $\text{Rh}_8^+(\text{NO})$ isomers.

4.4. Adsorption forms of NO on Rh_9^+ and Rh_{10}^+

Although the IRMPD spectra of Rh_9^+ and Rh_{10}^+ were obtained, we have not

found a conclusive assignment for these systems. For $\text{Rh}_9^+(\text{NO})$, all isomers found consist of a Rh_9 capped square antiprism. The most stable form, structure 9A, comprises tri-capped trigonal prismatic Rh_9^+ with separate N and O atoms on hollow sites (see Figure 4(b)). The calculation predicts vibrational bands at 374 cm^{-1} (5.4 km mol^{-1}), 434 cm^{-1} (16.2 km mol^{-1}), 540 cm^{-1} (54.0 km mol^{-1}), 571 cm^{-1} (0.5 km mol^{-1}) and 715 cm^{-1} (6.4 km mol^{-1}). The second most stable geometry of $\text{Rh}_9^+(\text{NO})$, isomer 9B, involves molecular NO adsorbed on an on-top site, the formation energy of which is $+0.06\text{ eV}$ higher than the most stable isomer. For this geometry, a strong absorption band is predicted at 1889 cm^{-1} ($1685.9\text{ km mol}^{-1}$), which is considered to correspond to the observed prominent band at 1810 cm^{-1} . Isomer 9B contributes only bands with limited IR intensity below 700 cm^{-1} , just like a geometrical isomer with molecular NO adsorbed on another on-top site also found (9C, $+0.13\text{ eV}$). These structures are shown in Figures 4(c) and (d).

Without the conclusive assignment, it is difficult to estimate the ratio of the dissociative adsorption to the molecular adsorption of NO on Rh_9^+ . However, the DFT calculations on the five stable isomers of $\text{Rh}_9^+(\text{NO})$ with NO adsorbed dissociatively suggest that IR spectral intensity of the strongest band appearing below 700 cm^{-1} is $16.6\text{--}77.9\text{ km mol}^{-1}$ and varies within a factor of 5 at most in the different isomers. Hence, we are able to estimate very roughly the value from the band intensities of the IRMPD spectrum and the IR spectral intensities by the DFT calculations, which should be regarded only as a guide. Assuming that the bands at 490 and 1810 cm^{-1} of the IRMPD spectrum in Figure 4(a) correspond to the bands at 540 cm^{-1} (54.0 km mol^{-1}) of the isomer 9A and at 1889 cm^{-1} (1686 km mol^{-1}) of the isomer 9B, respectively, the ratio would be 6%. In addition, taking other stable isomers into consideration, the ratio

of dissociative adsorption to the molecular adsorption of NO on Rh_9^+ would be 4%–19%.

For $\text{Rh}_{10}^+(\text{NO})$, the most stable form of $\text{Rh}_{10}^+(\text{NO})$ comprises bi-capped square antiprismatic Rh_{10}^+ with molecular NO on an on-top site (10A, Figure 5(b)). The calculation predicts a vibrational band at 1882 cm^{-1} , which is consistent with the observed prominent band at 1810 cm^{-1} . The second most stable geometry of $\text{Rh}_{10}^+(\text{NO})$ involves molecular NO adsorbing on an on-top site of edge-sharing bi-octahedral Rh_{10}^+ (10B, Figure 5(c)), the formation energy of which is +0.08 eV higher than the most stable isomer. This geometry predicts a strong absorption band at 1884 cm^{-1} ($1910.3\text{ km mol}^{-1}$) (see Figure 5(c)). An isomer of $\text{Rh}_{10}^+(\text{NO})$ with dissociated NO was also found, at a formation energy of 0.15 eV higher than the most stable isomer, contributing adsorption bands below 700 cm^{-1} . Assuming that the bands at 480 and 1810 cm^{-1} of the IRMPD spectrum in Figure 5(a) correspond to the bands at 512 cm^{-1} (51.1 km mol^{-1}) of the isomer 10C and at 1882 cm^{-1} ($1723.5\text{ km mol}^{-1}$) of the isomer 10A, respectively, the ratio of the dissociative adsorption to the molecular adsorption of NO on Rh_{10}^+ can be estimated to be 13% as a guide.

4.5. Molecular adsorption of NO on Rh_n^+ clusters

Figure 6 shows IRMPD spectra of $\text{Rh}_n^+(\text{NO})$ ($n = 11\text{--}16$) in $1400\text{--}1980\text{ cm}^{-1}$ spectral range. As discussed above, the peaks around 1600 and 1800 cm^{-1} correspond to the molecular NO adsorption on the bridge and on-top sites, respectively. While we have not carried out DFT calculations for these systems, it is apparent that all systems exhibit at least one form of molecular NO adsorption: The spectra show that NO adsorbs on an on-top site of Rh_n^+ for all n studied; an additional adsorption of NO on a

bridge site analogous to $n = 7$ is observed for $n = 12, 13$ and 14 .

How does the observation of molecularly bound NO on all species investigated compare to the energetic ordering of isomers found in the calculations? For this, the formation energies of the isomers for different n are summarized in Figure 7 and Table 1. For ease of comparison, the energies are shown in Figure 7 as relative to that of the most stable isomer with molecularly adsorbed NO on the on-top site (labeled as m_o). It is directly evident that the m_o isomer is not the most stable species found for $n = 6-9$, but the formation energy is at most only 0.13 eV higher than that of the most stable form, which makes their formation in a source kept at a temperature of 223 K very likely.

For $n = 7$, the isomer with molecular NO on the bridge site (m_b , 7A) is more stable than the one on the on-top site (m_o , 7D). Thus, observation of the m_b isomer specific to Rh_7^+ among Rh_n^+ ($n = 6-10$) is consistent to the calculated formation energies. However, the IRMPD intensity observed for the more stable isomer 7A with NO on the bridge site is comparable in the abundance to that for isomer 7D with NO on the on-top site for Rh_7^+ . If we assume that the band at 1600 cm^{-1} is solely due to isomer 7A, with a calculated IR intensity of 993 km mol^{-1} , and the band at 1810 cm^{-1} to isomer 7D, 1802 km mol^{-1} , a ratio of NO adsorbing on the on-top site to that adsorbing on the bridge site would be 0.7 from the band intensities of the IRMPD spectrum. Focusing on the ratio, we changed temperature of the reaction gas cell between 173–263 K, where NO adsorbed on Rh_7^+ by collision in the buffer He gas, finding no appreciable changes in the ratio. This suggests that the isomeric ratio between 7A and 7D does not correspond to the equilibrium ratio.

It is known that the most stable geometry of bare Rh_7^+ is pentagonal bipyramid

(pb) based on the IRMPD study and DFT calculations.⁴¹ It could thus be expected that the entrance complex is formed by a NO molecule adsorbed on the pentagonal bipyramid Rh_7^+ . In our experiments, we observe mostly structures involving a capped octahedral (co) system. To understand how such a structural transformation may take place, we consider the potential energy surface of NO adsorption onto pentagonal Rh_7^+ , most likely on an on-top site (pb- m_o) followed by the formation of stable isomers of $\text{Rh}_7^+(\text{NO})$ (co- m_b) after passing several intermediate and transition states (see Figure 8). We found two pathways from the pb- m_o structure towards the co- m_b isomer, one through a bridging structure (pb- m_b , -1.75 eV from Rh_7^+ and NO) which is separated from pb- m_o (-1.65 eV) by a transition state, TS1, at -1.36 eV (right-hand side in Figure 8), and another through an on-top (co- m_o) structure at -1.72 eV. The transition states towards the latter, TS1', is lower by 0.15 eV than TS1 (-1.51 eV vs. -1.36 eV). Hence, the isomer with NO on the on-top site is considered to be formed in a comparable extent to the isomer with NO on the bridge site in spite of the difference in the formation energy.

The co- m_o structure could directly isomerize into co- m_b , through a relatively high transition state (TS2'; +0.48 eV from co- m_o). However, the isomerization via TS2' is not likely, as the other reaction pathway connecting them through structural rearrangements of Rh_7^+ (co- $\text{m}_\text{o} \leftrightarrow \text{pb-}\text{m}_\text{o} \leftrightarrow \text{pb-}\text{m}_\text{b} \leftrightarrow \text{co-}\text{m}_\text{b}$) also exists, with a somewhat lower energy barrier (TS1; +0.37 eV from co- m_o). This finding suggests that the framework of the Rh cluster deforms more readily than the NO molecule migrates between the adsorption sites.

4.5. Dissociative adsorption of NO on Rh_n^+ clusters

As shown in Figure 7, the isomer with dissociatively adsorbed NO is more stable than the isomer with molecular NO for Rh_8^+ . Nevertheless, an analysis of the observed intensities of the IRMPD bands suggests that the ratio of the isomer 8A with dissociated NO shown in Figure 3(b) is only as much as 26%. This low ratio is probably due to the activation barrier between the molecularly adsorbed and the dissociatively adsorbed forms. Figure 9 shows the reaction pathway from molecularly to dissociatively adsorbed NO on Rh_8^+ : NO, having adsorbed on the on-top site of the bi-capped octahedral Rh_8^+ (-1.72 eV relative to the reactants), is able to dissociate via a transition state at $+0.89$ eV, with N and O atoms adsorbed on the hollow sites (Figure 9(a)). Similarly, dissociation of NO that has adsorbed on the less stable bridge site (-1.43 eV) proceeds via a transition state at $+0.96$ eV (Figure 9(b)) to the same dissociated structure as in Figure 9(a). In both cases, a step elongating the NO bond forms the high transition state, hindering dissociation of NO: The transition state is prohibitively high in energy, even when taking into account the thermal vibrational energy. The DFT calculations indicate that $\text{Rh}_8^+(\text{NO})$ with NO sitting on the on-top site possesses the average vibrational energy of 0.62 and 0.75 eV at 223 and 298 K, respectively. Thus, even if the energy released upon adsorption of NO onto Rh_8^+ is held inside the cluster, the total internal energy is lower than the energy of the transition state. The limited fraction of clusters where dissociation takes place form the high-energy tail of the Boltzmann distribution.

5. Conclusions

Adsorption form of NO on cationic Rh clusters, Rh_n^+ ($n = 6-16$), was

investigated by IRMPD spectroscopy using FELIX and the DFT calculations. The spectra show that a NO molecule adsorbs on an on-top site of Rh_n^+ for all n studied; $n = 7, 12, 13$ and 14 evidence is found for an additional structure where NO is adsorbed on a bridge site. A part of NO adsorbs dissociatively on Rh_n^+ , and the ratio of dissociative adsorption depends on the size, n : For Rh_6^+ , almost all the NO adsorbs molecularly on the on-top site of the tetragonal bipyramid Rh_6^+ . For Rh_7^+ , NO adsorbs molecularly on the on-top and bridge sites of the capped tetragonal bipyramid Rh_7^+ . A part of NO (5–10%) adsorbs dissociatively on Rh_7^+ with N and O atoms on hollow and bridge sites, respectively. For Rh_8^+ , NO adsorbs molecularly on the on-top site of the bi-capped tetragonal bipyramid Rh_8^+ . A part of NO (~21%) adsorbs dissociatively on Rh_8^+ with N and O atoms on different hollow sites. The DFT calculations predicted that the dissociative form of NO is more favorable than the molecular form for Rh_n^+ ($n = 6, 8, 9$) based on their formation energies, but experimentally observed ratios of dissociative adsorption were surely less than the prediction. The activation barrier existing between the molecular and dissociative adsorption was found to hinder the NO dissociation according to the DFT calculations.

ASSOCIATED CONTENT

Supporting Information

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

■ AUTHOR INFORMATION

Corresponding Author

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

Present Address

§(T.N.) Department of Chemistry, Graduate School of Science, Tohoku University, 6-3 Aoba, Aramaki, Aoba-ku, Sendai 980-8578, Japan.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGEMENT

We gratefully acknowledge the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) for the support of the FELIX Laboratory, and thank the FELIX staff, particularly Dr. Britta Redlich for her skillful assistance and Mr. Valeriy Chernyy for the technical support. This work was supported by Grants-in-Aid for Exploratory Research (No. 26620002), for Young Scientists (B) (No. 17K14433), and for JSPS Research Fellow (No. 17J02017) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan (MEXT). The computations were performed using Research Center for Computational Science, Okazaki, Japan. T.N. is grateful for a

Research Fellowship from the Japan Society for the Promotion of Science (JSPS).

■ REFERENCES

- (1) Shimokawabe, M.; Umeda, N. Selective Catalytic Reduction of NO by CO Over Supported Iridium and Rhodium Catalysts. *Chem. Lett.* **2004**, *33*, 534-535.
- (2) Castner, D. G.; Sexton, B. A.; Somorjai, G. A. Leed and Thermal Desorption Studies of Small Molecules (H₂, O₂, CO, CO₂, NO, C₂H₄, C₂H₂ AND C) Chemisorbed on the Rhodium (111) and (100) Surfaces. *Surf. Sci.* **1978**, *71*, 519-540.
- (3) Villarrubia, J. S.; Ho, W. Nitric Oxide Adsorption, Decomposition, and Desorption on Rh(100). *J. Chem. Phys.* **1987**, *87*, 750-764.
- (4) Kao, C. -.; Blackman, G. S.; Van Hove, M. A.; Somorjai, G. A.; Chan, C. -. The Surface Structure and Chemical Reactivity of Rh(111)-(2 × 2)-3NO by HREELS and Dynamical LEED Analysis. *Surf. Sci.* **1989**, *224*, 77-96.
- (5) Loffreda, D.; Simon, D.; Sautet, P. Vibrational Frequency and Chemisorption Site: A DFT-Periodic Study of NO on Pd (111) and Rh (111) Surfaces. *Chem. Phys. Lett.* **1998**, *291*, 15-23.
- (6) Makeev, A. G.; Slinko, M. M. Mathematic Modelling of the Peculiarities of NO Decomposition on Rh(111). *Surf. Sci.* **1996**, *359*, L467-L472.
- (7) Zaera, F.; Gopinath, C. S. Role of Adsorbed Nitrogen in the Catalytic Reduction of NO on Rhodium Surfaces. *J. Chem. Phys.* **1999**, *111*, 8088-8097.
- (8) Zaera, F.; Gopinath, C. S. Evidence for an N₂O Intermediate in the Catalytic Reduction of NO to N₂ on Rhodium Surfaces. *Chem. Phys. Lett.* **2000**, *332*, 209-214.
- (9) Zaera, F. Outstanding Mechanistic Questions in Heterogeneous Catalysis. *J. Phys.*

Chem. B **2002**, *106*, 4043-4052.

- (10) Kaldor, A.; Cox, D. M. Recent Advances in the Chemistry of Gas Phase Transition Metal Clusters. *Pure Appl. Chem.* **1990**, *62*, 79-88.
- (11) Böhme, D. K.; Schwarz, H. Gas-Phase Catalysis by Atomic and Cluster Metal Ions: The Ultimate Single-Site Catalysts. *Angewandte Chemie International Edition* **2005**, *44*, 2336-2354.
- (12) Lang, S. M.; Bernhardt, T. M. Gas Phase Metal Cluster Model Systems for Heterogeneous Catalysis. *Phys. Chem. Chem. Phys.* **2012**, *14*, 9255-9269.
- (13) Schlangen, M.; Schwarz, H. Effects of Ligands, Cluster Size, and Charge State in Gas-Phase Catalysis: A Happy Marriage of Experimental and Computational Studies. *Catal. Lett.* **2012**, *142*, 1265-1278.
- (14) Ford, M. S.; Anderson, M. L.; Barrow, M. P.; Woodruff, D. P.; Drewello, T.; Derrick, P. J.; Mackenzie, S. R. Reactions of Nitric Oxide on Rh_6^+ Clusters: Abundant Chemistry and Evidence of Structural Isomers. *Phys. Chem. Chem. Phys.* **2005**, *7*, 975-980.
- (15) Anderson, M. L.; Ford, M. S.; Derrick, P. J.; Drewello, T.; Woodruff, D. P.; Mackenzie, S. R. Nitric Oxide Decomposition on Small Rhodium Clusters, $\text{Rh}_n^{+/-}$. *J. Phys. Chem. A* **2006**, *110*, 10992-11000.
- (16) Harding, D. J.; Davies, R. D. L.; Mackenzie, S. R.; Walsh, T. R. Oxides of Small Rhodium Clusters: Theoretical Investigation of Experimental Reactivities. *J. Chem. Phys.* **2008**, *129*, 124304.
- (17) Tawaraya, Y.; Kudoh, S.; Miyajima, K.; Mafuné, F. Thermal Desorption and Reaction of NO Adsorbed on Rhodium Cluster Ions Studied by Thermal Desorption Spectroscopy. *J. Phys. Chem. A* **2015**, *119*, 8461-8468.

- (18) Xie, H.; Ren, M.; Lei, Q.; Fang, W. Nitric Oxide Adsorption and Reduction Reaction Mechanism on the Rh_7^+ Cluster: A Density Functional Theory Study. *J. Phys. Chem. A* **2011**, *115*, 14203-14208.
- (19) Fielicke, A.; Meijer, G.; von Helden, G. Infrared Spectroscopy of Niobium Oxide Cluster Cations in a Molecular Beam: Identifying the Cluster Structures. *J. Am. Chem. Soc.* **2003**, *125*, 3659-3667.
- (20) Fielicke, A.; Kirilyuk, A.; Ratsch, C.; Behler, J.; Scheffler, M.; von Helden, G.; Meijer, G. Structure Determination of Isolated Metal Clusters Via Far-Infrared Spectroscopy. *Phys. Rev. Lett.* **2004**, *93*, 023401.
- (21) Fielicke, A.; Ratsch, C.; von Helden, G.; Meijer, G. The Far-Infrared Spectra of Neutral and Cationic Niobium Clusters: $\text{Nb}_5^{0/+}$ to $\text{Nb}_9^{0/+}$. *J. Chem. Phys.* **2007**, *127*, 234306.
- (22) Garand, E.; Goebbert, D.; Santambrogio, G.; Janssens, E.; Lievens, P.; Meijer, G.; Neumark, D. M.; Asmis, K. R. Vibrational Spectra of Small Silicon Monoxide Cluster Cations Measured by Infrared Multiple Photon Dissociation Spectroscopy. *Phys. Chem. Chem. Phys.* **2008**, *10*, 1502-1506.
- (23) Kerpál, C.; Harding, D. J.; Hermes, A. C.; Meijer, G.; Mackenzie, S. R.; Fielicke, A. Structures of Platinum Oxide Clusters in the Gas Phase. *J. Phys. Chem. A* **2013**, *117*, 1233-1239.
- (24) Kiawi, D. M.; Bakker, J. M.; Oomens, J.; Buma, W. J.; Jamshidi, Z.; Visscher, L.; Waters, L. B. F. M. Water Adsorption on Free Cobalt Cluster Cations. *J. Phys. Chem. A* **2015**, *119*, 10828-10837.
- (25) Lang, S. M.; Bernhardt, T. M.; Kiawi, D. M.; Bakker, J. M.; Barnett, R. N.; Landman, U. Cluster Size and Composition Dependent Water Deprotonation by

- Free Manganese Oxide Clusters. *Phys. Chem. Chem. Phys.* **2016**, *18*, 15727-15737.
- (26) Koyama, K.; Nagata, T.; Kudoh, S.; Miyajima, K.; Huitema, D. M. M.; Chernyy, V.; Bakker, J. M.; Mafuné, F. Geometrical Structures of Partially Oxidized Rhodium Cluster Cations, Rh_6O_m^+ ($m = 4, 5, 6$), Revealed by Infrared Multiple Photon Dissociation Spectroscopy. *J. Phys. Chem. A* **2016**, *120*, 8599-8605.
- (27) Oepf, D.; van der Meer, A.; van Amersfoort, P. The Free-Electron-Laser User Facility FELIX. *Infrared Phys. Technol.* **1995**, *36*, 297-308.
- (28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. Gaussian 09. **2013**, Revision E.01.
- (29) Becke, A. D. Density-functional Thermochemistry. III. the Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
- (30) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B* **1988**, *37*, 785-789.
- (31) Hay, P. J.; Wadt, W. R. Ab Initio Effective Core Potentials for Molecular Calculations. Potentials for K to Au Including the Outermost Core Orbitals. *J. Chem. Phys.* **1985**, *82*, 299-310.
- (32) Ditchfield, R.; Hehre, W. J.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. IX. an Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1971**, *54*, 724-728.
- (33) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. further Extensions of Gaussian-Type Basis Sets for use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1972**, *56*, 2257-2261.

- (34) Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H. Energy-Adjusted *Ab Initio* Pseudopotentials for the Second and Third Row Transition Elements. *Theor. Chim. Acta* **1990**, 77, 123-141.
- (35) Dunning, T. H., Jr. Gaussian Basis Sets for use in Correlated Molecular Calculations. I. the Atoms Boron through Neon and Hydrogen. *J. Chem. Phys.* **1989**, 90, 1007-1023.
- (36) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1.
- (37) Reed, A. E.; Weinstock, R. B.; Weinhold, F. Natural Population Analysis. *J. Chem. Phys.* **1985**, 83, 735-746.
- (38) Peng, C.; Bernhard Schlegel, H. Combining Synchronous Transit and Quasi-Newton Methods to Find Transition States. *Israel J. Chem.* **1993**, 33, 449-454.
- (39) Peng, C.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. Using Redundant Internal Coordinates to Optimize Equilibrium Geometries and Transition States. *J. Comput. Chem.* **1996**, 17, 49-56.
- (40) Hallam, H. E., Ed.; In *Vibrational Spectroscopy of Trapped Species: Infrared and Raman Studies of Matrix-isolated Molecules, Radicals and Ions*; John Wiley & Sons: London, 1973.
- (41) Harding, D. J.; Gruene, P.; Haertelt, M.; Meijer, G.; Fielicke, A.; Hamilton, S. M.; Hopkins, W. S.; Mackenzie, S. R.; Neville, S. P.; Walsh, T. R. Probing the Structures of Gas-Phase Rhodium Cluster Cations by Far-Infrared Spectroscopy. *J. Chem. Phys.* **2010**, 133, 214304.

Figure captions

Figure 1. (a) IRMPD spectrum for $\text{Rh}_6^+(\text{NO})$ and (b–e) vibrational spectra of the stable isomers of $\text{Rh}_6^+(\text{NO})$ obtained by the DFT calculations. In panel (a), high resolution spectrum in $1550\text{--}1900\text{ cm}^{-1}$ is also shown as a curve in red, which was obtained by scanning the wavelength of the dim IR light (1/20). Spectral intensities of the bands in panel (b–e) are shown in the unit of km mol^{-1} , and the peak height corresponds to the IR spectral intensity given by the DFT calculations. The formation energy calculated from the most stable isomer and the spin state are shown in each panel. Blue, red, and dark-cyan balls stand for N, O, and Rh atoms, respectively.

Figure 2. (a) IRMPD spectrum for $\text{Rh}_7^+(\text{NO})$ and (b–e) vibrational spectra of the stable isomers of $\text{Rh}_7^+(\text{NO})$ obtained by the DFT calculations. See caption of Figure 1 for other information.

Figure 3. (a) IRMPD spectrum for $\text{Rh}_8^+(\text{NO})$ and (b–d) vibrational spectra of the stable isomers of $\text{Rh}_8^+(\text{NO})$ obtained by the DFT calculations. See caption of Figure 1 for other information.

Figure 4. (a) IRMPD spectrum for $\text{Rh}_9^+(\text{NO})$ and (b–d) vibrational spectra of the stable isomers of $\text{Rh}_9^+(\text{NO})$ obtained by the DFT calculations. See caption of Figure 1 for other information.

Figure 5. (a) IRMPD spectrum for $\text{Rh}_{10}^+(\text{NO})$ and (b–d) vibrational spectra of the stable isomers of $\text{Rh}_{10}^+(\text{NO})$ obtained by the DFT calculations. In panel (a), high resolution spectrum in $1500\text{--}1900\text{ cm}^{-1}$ is also shown as a curve in red, which was obtained by scanning the wavelength of the dim IR light (1/10).

Figure 6. IRMPD spectra of $\text{Rh}_n^+(\text{NO})$ ($n = 11\text{--}16$).

Figure 7. Formation energies of isomers of $\text{Rh}_n^+(\text{NO})$ ($n = 6\text{--}10$) plotted by setting the energy of the most stable isomer with molecularly adsorbed NO on an on-top site as 0 eV. Here, m and d stand for molecular and dissociative adsorption and subscript o and b stand for the on-top and bridge sites, respectively.

Figure 8. Energy diagram of $\text{Rh}_7^+(\text{NO})$ showing structural isomerization.

Figure 9. Energy diagram of $\text{Rh}_8^+(\text{NO})$ showing structural isomerization.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table 1

Stable adsorption forms of NO on Rh_n^+ clusters. ^aenergy difference upon adsorption

size	form	site		energy ^a / eV
$n = 6$	dissociative	N: hollow	O: hollow	-1.77
	molecular	NO: on-top		-1.73
	dissociative	N: hollow	O: hollow	-1.53
	dissociative	N: hollow	O: bridge	-1.40
$n = 7$	molecular	NO: bridge		-1.85
	dissociative	N: hollow	O: bridge	-1.78
	molecular	NO: bridge		-1.75
	molecular	NO: on-top		-1.72
$n = 8$	dissociative	N: hollow	O: hollow	-1.85
	molecular	NO: on-top		-1.72
	dissociative	N: hollow	O: hollow	-1.66
$n = 9$	dissociative	N: hollow	O: hollow	-1.71
	molecular	NO: on-top		-1.65
	molecular	NO: on-top		-1.58
$n = 10$	molecular	NO: on-top		-1.79
	molecular	NO: on-top		-1.71
	dissociative	N: hollow	O: hollow	-1.65

TOC graphic