The following full text is a preprint version which may differ from the publisher's version.

For additional information about this publication click this link.
http://hdl.handle.net/2066/181161

Please be advised that this information was generated on 2020-06-21 and may be subject to change.
Adsorption Forms of NO on Rh$_n^+$ ($n = 6$–$16$) Revealed by Infrared Multiple Photon Dissociation Spectroscopy

Toshiaki Nagata$^1$, Kohei Koyama$^1$, Satoshi Kudoh$^1$, Ken Miyajima$^1$, Joost M. Bakker$^2$, 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$_n^+$ ($n = 6$–$16$), 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.\textsuperscript{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.\textsuperscript{2-4} The most stable form of NO on Rh(111) corresponds to the hollow (\(\mu_3\)) site one at 0.5 ML coverage, which changes to one on-top (\(\mu_1\)) site and two hollow site adsorbates for a coverage of 0.75 ML.\textsuperscript{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 CO\(_2\). A NO molecule then reacts with N(a) to form N\(_2\)O, and the N\(_2\)–O bond on the surface is cleaved to release N\(_2\).\textsuperscript{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.\textsuperscript{10-13} Direct decomposition of NO by isolated Rh\(_n^{+/−}\) clusters in the gas phase has been observed using collision-based experiments.\textsuperscript{14-16} Mass spectrometric analysis shows that after the adsorption of two NO molecules on a cluster, N\(_2\) 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 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 $n \geq 7$.\cite{17}

According to DFT calculations using the LANL2DZ effective core potential and basis set to describe Rh atoms, the most stable geometry of Rh$_6^{+}$(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.\cite{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.\cite{18} In addition, a transition state exists for the dissociation of NO, with an energy barrier of $+1.7$ eV from the molecularly adsorbed Rh$_7^{+}$(NO) complex. The most stable state where both N and O atoms were separately adsorbed on bridge ($\mu_2$) 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 \( \text{Rh}_n^+ \)(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.\textsuperscript{19-26}

2. Experimental methods

The adsorption forms of NO on rhodium cluster ions, \( \text{Rh}_n^+ \) \((n = 6–16)\), were investigated via IRMPD spectroscopy using a molecular beam instrument coupled to the free electron laser for infrared experiments (FELIX).\textsuperscript{27} Gas-phase \( \text{Rh}_n^+ \) 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 \( \text{Rh}_n^+ \) collides with NO molecules to form \( \text{Rh}_n^+\)(NO)\(_m\) clusters in a thermalized condition in He buffer gas. To record IR spectra for \( \text{Rh}_n^+\)(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 \( \text{Rh}_n^+\)(NO)Ar was accomplished by admixing 0.3\%–4\% Ar gas in the carrier gas and cooling the gas to 173–263 K with liquid N\(_2\) 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 0.25–20 mJ pulse$^{-1}$ before use. The spectral bandwidth was kept at 0.2–0.3% 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 Rh\textsubscript{n}\textsuperscript{+}(NO) (n = 6–10) and simulate their vibrational spectra, DFT calculations were performed using the Gaussian09 program.\textsuperscript{28} Becke's three-parameter hybrid density functional with the Lee-Yang-Parr correlation functional (B3LYP)\textsuperscript{29,30} was used for all calculations. First, to obtain the lowest energy structures of molecularly adsorbed Rh\textsubscript{n}\textsuperscript{+}(NO), more than twenty initial geometries in which one NO molecule was placed around Rh\textsubscript{n}\textsuperscript{+} at random were optimized for all conceivable spin states using the LanL2DZ basis set for Rh atoms\textsuperscript{31} and the 6-31G(d) basis sets for N and O atoms\textsuperscript{32,33} to reduce calculation costs. In addition, to obtain the lowest energy structures of dissociatively adsorbed Rh\textsubscript{n}\textsuperscript{+}(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 atoms\textsuperscript{34} and the aug-cc-pVDZ basis sets for the N and O atoms.\textsuperscript{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\textsuperscript{-1} full width at half maximum (FWHM). Anharmonic frequencies were also calculated for Rh\textsubscript{6}\textsuperscript{+}(NO) by numerical differentiation to estimate variation from the harmonic frequencies. Natural bond orbital (NBO) analysis was performed for Rh\textsubscript{7}\textsuperscript{+}(NO) to investigate the charge and spin distribution.\textsuperscript{36} Transition states were calculated for NO migration on Rh\textsubscript{7}\textsuperscript{+} and dissociation on Rh\textsubscript{8}\textsuperscript{+} using the quadratic synchronous transit-guided quasi-Newton (STQN) method to estimate the reaction barriers.\textsuperscript{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\(^{-1}\)) 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 Rh\(_n^+\)-NO (\(n = 6−8\)) allow us to make conclusive assignments, whereas we can only tentatively assign the spectra for Rh\(_n^+\)-NO (\(n = 9, 10\)). No calculations were carried out for Rh\(_n^+\)-NO (\(n = 11−16\)), 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 Rh\(_6^+\)(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 Rh₆⁺(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 300–700 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 $\sim 1.24$ 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 $4.0 \times 10^{-4}$. 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 $2.0 \times 10^{-2}$ 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 Rh\(_6^+\)(NO).

4.2. Adsorption forms of NO on Rh\(_7^+\)

Figure 2(a) shows the IRMPD spectrum for Rh\(_7^+\)(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 1500–2000 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 Rh\(_7^+\)(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\textsuperscript{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\textsuperscript{-1} to structural isomers with NO adsorbed on the bridge and the on-top sites, respectively. The band at 1600 cm\textsuperscript{-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\textsuperscript{-1} spectral range are predicted, namely at 325 cm\textsuperscript{-1} (0.8 km mol\textsuperscript{-1}), 439 cm\textsuperscript{-1} (5.4 km mol\textsuperscript{-1}) and 581 cm\textsuperscript{-1} (1.5 km mol\textsuperscript{-1}) for 7A, and 328 cm\textsuperscript{-1} (0.8 km mol\textsuperscript{-1}), 402 cm\textsuperscript{-1} (1.3 km mol\textsuperscript{-1}) and 483 cm\textsuperscript{-1} (1.7 km mol\textsuperscript{-1}) for 7C. However, five of these (the ones at 325 and 581 cm\textsuperscript{-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\textsuperscript{-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\textsuperscript{-1} (10.5 km mol\textsuperscript{-1}), 607 cm\textsuperscript{-1} (27.7 km mol\textsuperscript{-1}), 649 cm\textsuperscript{-1} (54.9 km mol\textsuperscript{-1}), and 707 cm\textsuperscript{-1} (4.3 km mol\textsuperscript{-1}). Considering these predictions, we assign the observed bands at 475 and 1600 cm\textsuperscript{-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 Rh\(^{7+}\)(NO) is surely more than that in Rh\(^{6+}\)(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 Rh\(^{7+}\)(NO) isomers (7A, 7B, and 7D).

4.3. Adsorption forms of NO on Rh\(^{8+}\)

Figure 3(a) shows the IRMPD spectrum for Rh\(^{8+}\)(NO). A single prominent band appears at 1810 cm\(^{-1}\) with several bands below 700 cm\(^{-1}\). Compared with Rh\(^{6+}\)(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 Rh\(^{8+}\)(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 eV higher than isomer 8B. Consistently with the results for Rh⁷+(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 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 Rh⁸⁺ 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 Rh⁸⁺ in the dissociative form (8A) would account for ~21% of the total Rh⁸⁺(NO) isomers.

4.4. Adsorption forms of NO on Rh⁹⁺ and Rh¹⁰⁺

Although the IRMPD spectra of Rh⁹⁺ and Rh¹⁰⁺ were obtained, we have not
found a conclusive assignment for these systems. For Rh₉⁺(NO), all isomers found consist of a Rh₉ capped square antiprism. The most stable form, structure 9A, comprises tri-capped trigonal prismatic Rh₉⁺ 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 Rh₉⁺(NO), isomer 9B, involves molecular NO adsorbed on an on-top site, the formation energy of which is +0.06 eV higher than the most stable isomer. For this geometry, a strong absorption band is predicted at 1889 cm⁻¹ (1685.9 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 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 Rh₉⁺. However, the DFT calculations on the five stable isomers of Rh₉⁺(NO) with NO adsorbed dissociatively suggest that IR spectral intensity of the strongest band appearing below 700 cm⁻¹ is 16.6–77.9 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 Rh$_{10}^+(NO)$, the most stable form of Rh$_{10}^+(NO)$ 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 Rh$_{10}^+(NO)$ 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 km mol$^{-1}$) (see Figure 5(c)). An isomer of Rh$_{10}^+(NO)$ 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 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 Rh$_n^+(NO)$ ($n = 11$–16) in 1400–1980 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 $m_0$). It is directly evident that the $m_0$ 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 ($m_0$, 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. 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-mo) followed by the formation of stable isomers of Rh$_7^+$(NO) (co-mb) after passing several intermediate and transition states (see Figure 8). We found two pathways from the pb-mo structure towards the co-mb isomer, one through a bridging structure (pb-mb, −1.75 eV from Rh$_7^+$ and NO) which is separated from pb-mo (−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-mo) 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-mo structure could directly isomerize into co-mb, through a relatively high transition state (TS2’; +0.48 eV from co-mo). However, the isomerization via TS2’ is not likely, as the other reaction pathway connecting them through structural rearrangements of Rh$_7^+$ (co-mo ↔ pb-mo ↔ pb-mb ↔ co-mb) also exists, with a somewhat lower energy barrier (TS1; +0.37 eV from co-mo). 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 Rh$_8^+(NO)$ 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


(9) Zaera, F. Outstanding Mechanistic Questions in Heterogeneous Catalysis. J. Phys.


(21) Fielicke, A.; Ratsch, C.; von Helden, G.; Meijer, G. The Far-Infrared Spectra of Neutral and Cationic Niobium Clusters: Nb\textsubscript{5}\textsuperscript{0+} to Nb\textsubscript{9}\textsuperscript{0+/+}. *J. Chem. Phys.* 2007, 127, 234306.


Figure captions

Figure 1. (a) IRMPD spectrum for Rh$_6^+$ (NO) and (b–e) vibrational spectra of the stable isomers of Rh$_6^+$ (NO) obtained by the DFT calculations. In panel (a), high resolution spectrum in 1550–1900 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 Rh$_7^+$ (NO) and (b–e) vibrational spectra of the stable isomers of Rh$_7^+$ (NO) obtained by the DFT calculations. See caption of Figure 1 for other information.

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

Figure 4. (a) IRMPD spectrum for Rh$_9^+$ (NO) and (b–d) vibrational spectra of the stable isomers of Rh$_9^+$ (NO) obtained by the DFT calculations. See caption of Figure 1 for other information.
Figure 5. (a) IRMPD spectrum for Rh_{10}^{+}(NO) and (b–d) vibrational spectra of the stable isomers of Rh_{10}^{+}(NO) obtained by the DFT calculations. In panel (a), high resolution spectrum in 1500–1900 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 Rh_{n}^{+}(NO) ($n = 11$–$16$).

Figure 7. Formation energies of isomers of Rh_{n}^{+}(NO) ($n = 6$–$10$) 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 Rh_{7}^{+}(NO) showing structural isomerization.

Figure 9. Energy diagram of Rh_{8}^{+}(NO) showing structural isomerization.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6

IRMPD intensity vs. Wavenumber / cm$^{-1}$ for $\text{Rh}_{n}^{+}(\text{NO})$ with $n = 11, 12, 13, 14, 15, 16$. The figure shows the spectral shifts and intensity changes with increasing $n$.
Figure 7
Table 1

Stable adsorption forms of NO on Rh$_n^+$ clusters. *a* energy difference upon adsorption

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