



Computational Chemistry Workshops  
West Ridge Research Building-UAF Campus  
9:00am-4:00pm, Room 009

Electronic Structure - July 19-21, 2016

Molecular Dynamics - July 26-28, 2016

## Predicting the Structures of Rhodium Carbonyl Clusters

The structures of neutral rhodium carbonyl clusters containing two, four, and six rhodium atoms have been known for some time.

This exercise uses the tools of group theory and symmetry to help in understanding the vibrational spectra of these complexes which then allows us to better determine their structure.

The attached paper by Ingmar Swart, Frank M. F. de Groot, Bert M. Weckhuysen, David M. Rayner, Gerard Meijer, and André Fielicke *The Effect of Charge on CO Binding in Rhodium Carbonyls: From Bridging to Terminal CO*, J. Am. Chem. Soc. **2008**, *130*, 2126-2127 investigates the structures of the monocation rhodium carbonyl clusters via infrared multiphoton dissociation spectroscopy (IR-MPD), comparing experimental results to those predicted from computational modeling.

This is an ideal problem to apply the simple tools of group theory to predict distinguishing features in the IR spectrum of each possible structure.

For this exercise, the focus will primarily be on the  $\nu_{\text{CO}}$  stretching frequencies. The stretching frequencies of terminally bound CO ligands ( $2060\text{--}2100\text{ cm}^{-1}$ ) are typically well separated from those of bridging CO ligands ( $1750\text{--}1900\text{ cm}^{-1}$ ), and so these vibrations could form separate basis sets for symmetry analysis.

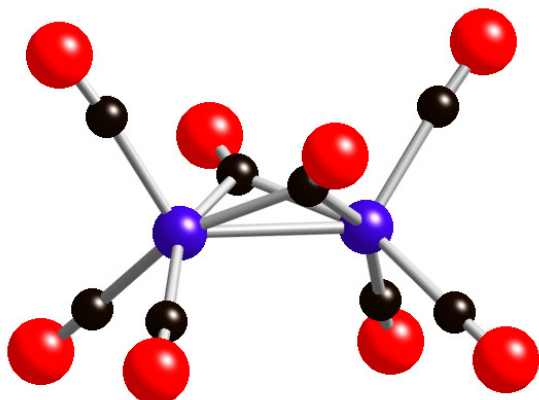
Although static images from the paper are given below, PDB files each of these structures are also available in the appropriate directory and can be visualized with applications such as Jmol and VMD.

## Exercise

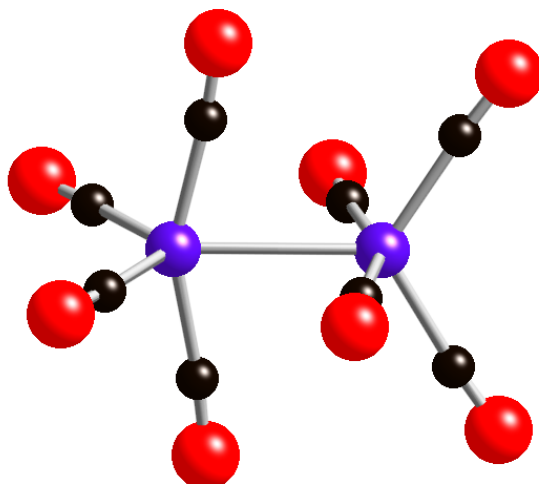
1. Predict how many  $\nu_{\text{CO}}$  stretching frequencies one would see in the IR spectrum for only the  $[\text{Rh}_4(\text{CO})_{12}]^{0/+}$  complexes, since they have very high symmetry.
2. Write a representation for the  $\nu_{\text{CO}}$  stretching frequencies in each structure and determine how many peaks one would expect to see in the terminal and bridging CO regions of the IR spectrum.

The idea is to predict the structures of  $[\text{Rh}_4(\text{CO})_{12}]^{0/+}$  complexes based both on the experimental structures of neutral species and calculations performed on both neutral and analogous charged complexes.

## Calculated structures of $\text{Rh}_2(\text{CO})_8$



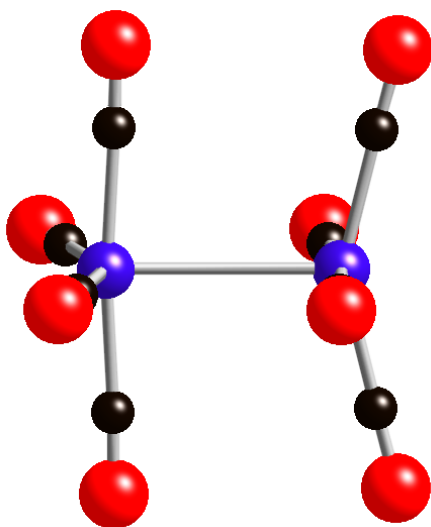
All Bridging COs



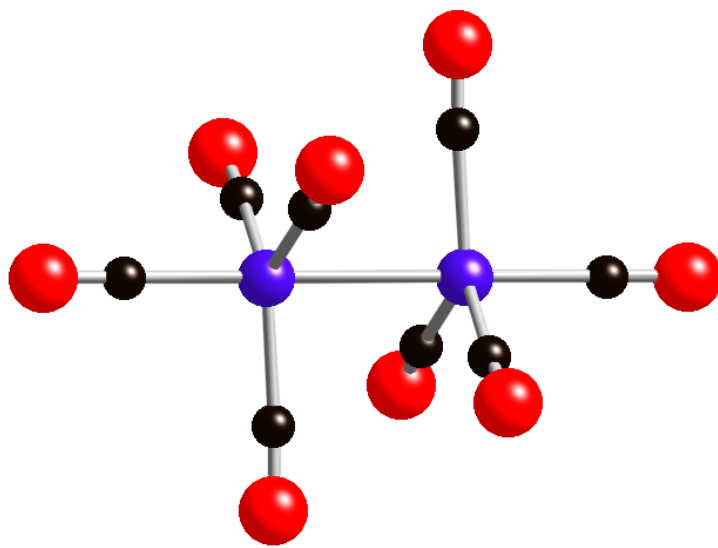
All Terminal COs

The bridged structure is slightly lower in energy than the all-terminal structure, in agreement with experiment.

## Calculated structures for $[\text{Rh}_2(\text{CO})_8]^+$

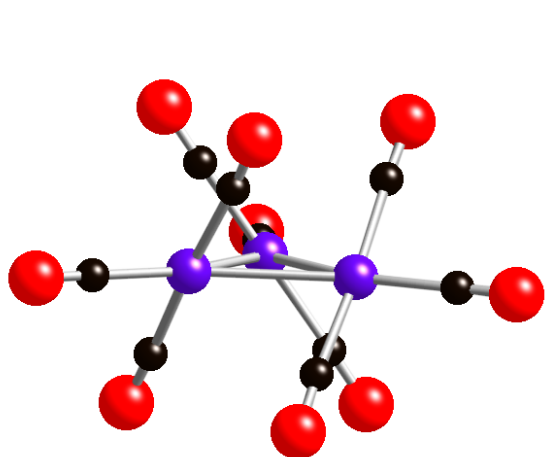


Lowest Energy Structure

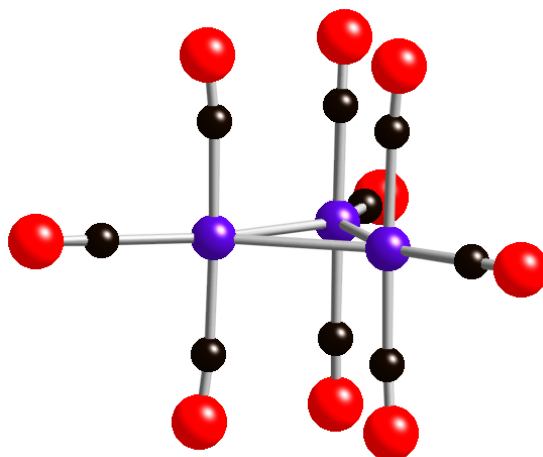


Another Possible Structure for  $[\text{Rh}_2(\text{CO})_8]^+$

### Calculated Structures for $[\text{Rh}_3(\text{CO})_9]^+$

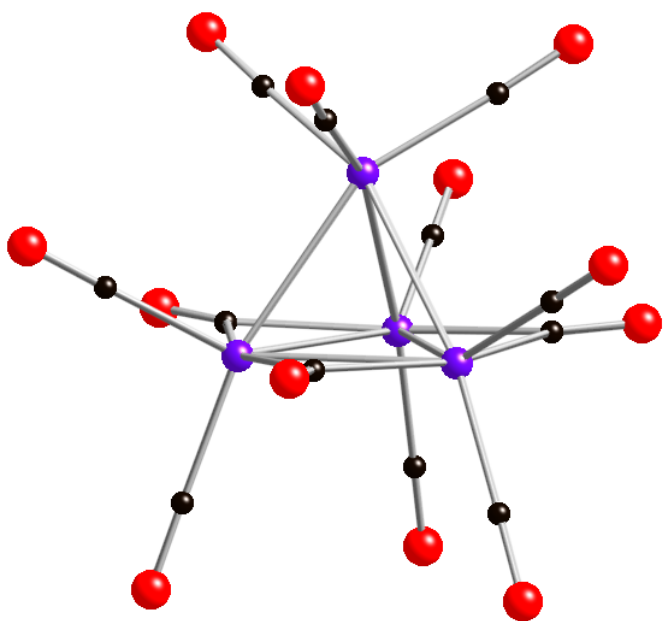


Lowest Energy Structure

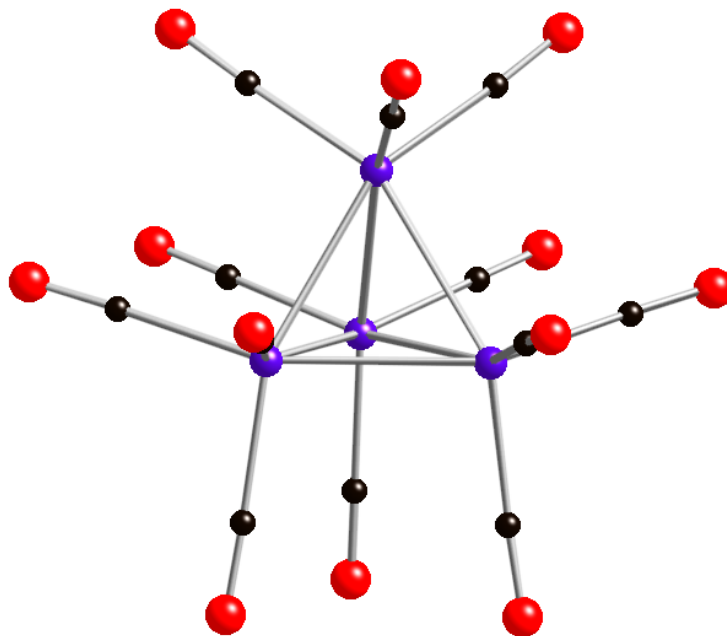


Another Possible Structure for  $[\text{Rh}_3(\text{CO})_9]^+$

### Calculated structures of $\text{Rh}_4(\text{CO})_{12}$ , $[\text{Rh}_4(\text{CO})_{12}]^+$



Known Structure of Neutral Cluster



Proposed Monocationic Structure

The neutral structure agrees with experiment.

## The Effect of Charge on CO Binding in Rhodium Carbonyls: From Bridging to Terminal CO

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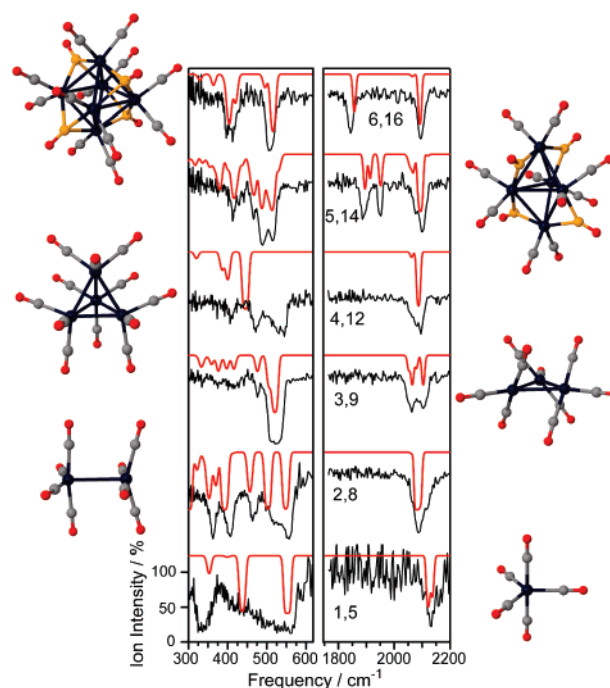
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Changing the electron density of a catalyst can have a profound influence on its selectivity and activity. For this reason, electronic promoter materials are often added to a catalyst to tailor the electron density of the active particle and to obtain optimal performance.<sup>1</sup> Despite the widespread use of electronic promoters, the mechanisms responsible for the observed effect(s) are often poorly understood. For CO oxidation over a Pt catalyst, the activity increases with electron density.<sup>2</sup> In contrast, the hydrogenation of CO over cobalt- and rhodium-based catalysts is found to be more active and more selective upon reducing the electron density of the metal particles.<sup>3,4</sup> This change in electron density also leads to a decrease in the ratio of bridge to linear-bound CO but the mechanism behind this destabilization of bridge-bound CO is unknown.<sup>3,5</sup>

We address the issue of charge-induced changes in the binding of CO to metal centers by focusing on rhodium carbonyls as models. Rhodium-based catalysts have been used for many reactions involving CO.<sup>6</sup> The structures of the neutral saturated carbonyl complexes containing two, four, and six Rh atoms are well-known,<sup>7–10</sup> but little is known about the charged complexes. We establish the structures of the cations by infrared multiple photon dissociation (IR-MPD) spectroscopy. By comparing the structures of the cationic species with structures of the corresponding neutral complexes, information regarding the effect of charge on the binding geometry of CO is obtained.

The experimental procedures for IR-MPD spectroscopy have been described in detail elsewhere.<sup>11–13</sup> Briefly, a molecular beam of cluster complexes, generated in a laser ablation source coupled with a reaction channel, is overlapped with a counter-propagating beam of IR photons delivered by the Free Electron Laser for Infrared eXperiments (FELIX).<sup>14</sup> When the laser frequency is resonant with an IR-active vibration of a complex, it can absorb several photons and subsequently undergo fragmentation. The vibrational spectra are obtained by monitoring the changes in the cluster mass distribution as a function of IR frequency. The experimental spectra are complemented with density functional theory (DFT) calculations (B3LYP/TZVP, see Supporting Information) to obtain information on cluster geometries and electronic structure.<sup>15</sup>

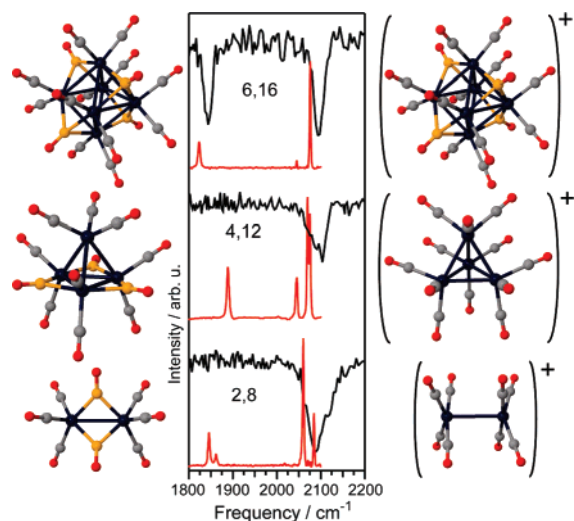
Upon introduction of CO in the reactor channel, the  $\text{Rh}_n^+$  clusters bind multiple CO molecules. The pressure in the reactor channel was increased until the resulting molecular beam distribution did not change anymore, that is, when the clusters were saturated with carbon monoxide.<sup>16</sup> The complexes saturate as  $\text{Rh}(\text{CO})_5^+$ ,  $\text{Rh}_2(\text{CO})_8^+$ ,  $\text{Rh}_3(\text{CO})_9^+$ ,  $\text{Rh}_4(\text{CO})_{12}^+$ ,  $\text{Rh}_5(\text{CO})_{14}^+$ , and  $\text{Rh}_6(\text{CO})_{16}^+$ . The saturation numbers of the cationic rhodium dimer, tetramer, and hexamer are the same as those of the corresponding neutral



**Figure 1.** Experimental (black) and calculated (red) vibrational spectra of  $\text{Rh}_n(\text{CO})_m^+$  complexes. The values  $n, m$  indicate the number of Rh atoms and CO molecules, respectively. The simulated depletion spectra are based on the calculated single photon absorption spectra. In the complex geometries shown next to the graph, C atoms of  $\mu_1$  CO are depicted in gray and C atoms of  $\mu_2$  and  $\mu_3$  CO are shown in yellow.

clusters. Binary tri- and pentanuclear rhodium cluster carbonyls have not been identified before.

The vibrational spectra in the C–O stretching region and the Rh–C stretch and deformation region for complexes with 1–6 metal atoms are shown in Figure 1. Terminally bound CO ligands are present for all complexes (absorption bands between 2060–2100  $\text{cm}^{-1}$ ) but bridging ( $\mu_2$ -CO) and/or face capping ( $\mu_3$ -CO) carbonyls (absorption bands between 1750 and 1900  $\text{cm}^{-1}$ ) are only present for  $\text{Rh}_5(\text{CO})_{14}^+$  and  $\text{Rh}_6(\text{CO})_{16}^+$ . The cationic carbonyl complexes with 1–4 metal atoms therefore contain only terminally bound CO ligands.<sup>17</sup> The DFT calculations confirm this assignment and also predict that vibrational modes associated with bridge bound CO in isomers of complexes with 2–4 metal atoms have significant IR intensities which should be observed experimentally. The cluster structures and the calculated spectra are shown together with the IR-MPD spectra in Figure 1. The calculated and experimental spectra are in good agreement in both the C–O stretching range,  $\nu(\text{CO})$ , as well as in the Rh–C stretch and deformation region,



**Figure 2.** Experimental vibrational spectra of  $\text{Rh}_2(\text{CO})_8^{+/0}$ ,  $\text{Rh}_4(\text{CO})_{12}^{+/0}$ , and  $\text{Rh}_6(\text{CO})_{16}^{+/0}$  (cations, black; neutrals, red; bottom to top) in the  $\nu(\text{CO})$  range. Structures for the neutral complexes are shown on the left and for the cations on the right. In the complex geometries shown next to the graph, C atoms of  $\mu_1$  CO are depicted in gray and C atoms of  $\mu_2$  and  $\mu_3$  CO are shown in yellow.

$\nu/\delta(\text{RhC})$ . Only in the case of  $\text{Rh}_4(\text{CO})_{12}^+$  we find a discrepancy, a band at  $\sim 530 \text{ cm}^{-1}$  is missing in the simulated spectrum. A possible explanation for this discrepancy is that the complex is distorted from the high-symmetry structure ( $T_d$ ) shown in Figure 1 or the presence of a second isomer. The lowest energy isomers identified by the calculations are also the ones whose vibrational spectra are in best agreement with the experimental data.

In Figure 2 we compare the vibrational spectra of the neutral (taken from ref 10) and cationic species. It is immediately clear that cationic and neutral  $\text{Rh}_2(\text{CO})_8$  and  $\text{Rh}_4(\text{CO})_{12}$  have different structures. The neutral complexes have two and three bridge-bound carbonyl ligands, respectively,<sup>7,10</sup> whereas all CO molecules are terminally bound in  $\text{Rh}_2(\text{CO})_8^+$  and  $\text{Rh}_4(\text{CO})_{12}^+$ . Removing an electron from the neutral complexes thus leads to a destabilization of the bridge bound carbonyl ligands. In contrast,  $\text{Rh}_6(\text{CO})_{16}$  does not undergo a structural rearrangement. The metal cores of the cations retain the structure of the neutral compounds.

DFT calculations were performed for neutral complexes as well as for cations in the structure of the neutral clusters to compare the electronic structures. The calculations identify the correct ground state isomers of the neutral complexes. For  $\text{Rh}_2(\text{CO})_8$ , the neutral complex with only terminally bound CO molecules is just 0.09 eV higher in energy. The calculations show that the highest occupied molecular orbital (HOMO) of the complex with the bridging carbonyls is doubly occupied and can be thought of as a combination of rhodium d-orbitals with antibonding  $2\pi^*$  orbitals of the bridging CO ligands, the classic back-donation of M–CO binding. The HOMO is bonding with respect to the Rh– $\mu_2$ –CO bonds. Ionization removes an electron from the HOMO. Mulliken overlap population analysis shows that the electron density in a single Rh– $\mu_2$ –CO bond is reduced by 12% upon removing one electron from the neutral cluster. The  $\text{Rh}_2(\text{CO})_8^+$  complex is unstable in the structure of the neutral. It is a transition state that is +0.65 eV higher in energy than the isomer with only terminally bound CO. Consequently the complex will undergo a charge induced structural rearrangement. According to our calculations, the accompanying reorganization in electronic structure results in a lengthening of the Rh–Rh bond (see Supporting Information). A similar argument holds for  $\text{Rh}_4(\text{CO})_{12}$ . The HOMO is involved in the binding of the

three bridge-bonded CO molecules. Upon removing one electron, the electron density between the rhodium atoms and the bridging CO ligands is reduced by 38%. The destabilization of the bridge-bonded CO molecules leads to a complex with only terminally bound CO. As shown by the experimental and calculated vibrational spectra, the high symmetry ( $T_d$ ) complex  $\text{Rh}_6(\text{CO})_{16}$  does not undergo structural rearrangement upon removal of an electron. The HOMO of  $\text{Rh}_6(\text{CO})_{16}$  is involved in the binding of the face-capping CO. It has  $t_2$  symmetry and is fully occupied, that is, there are six electrons in three equivalent orbitals. This results in a very stable complex. Removing one electron from the HOMO reduces the electron density between the rhodium atoms and the face-capping carbonyl ligands by only 4%, and hence the complex does not undergo reorganization.

In conclusion, a complete series of saturated cationic rhodium carbonyl complexes  $\text{Rh}_n(\text{CO})_m^+$  ( $n = 1-6$ ) has been structurally characterized. It is shown that the removal of an electron from a metal carbonyl cluster can selectively destabilize bridge-bonded CO molecules. These results provide a possible explanation for effects of promoter materials that are observed for CO bonding on transition-metal catalysts,<sup>2,3</sup> providing information that contributes to understanding the origin of electronic promoter effects in catalysis in general.

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**Supporting Information Available:** Description of the computational procedure and detailed results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (17) The spectra exhibit saturation and broadening of the  $\mu_1$  band(s) when repeated at 20 times the IR fluence but no new absorptions. This confirms that noise does not mask low strength transitions. Saturation of the depletion via the  $\mu_1$  band(s) confirms that other isomers are not present in significant quantities.

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