The effects of charge transfers on the adsorption of CO on small Mo doped Pt clusters


Abstract: The interaction of carbon monoxide with platinum alloy nanoparticles is an important problem in the context of fuel cell catalysis. In this work, molybdenum doped platinum clusters are studied in the gas phase, in order to obtain a better understanding of the fundamental nature of the Pt–CO interaction in the presence of a dopant atom. For this purpose, Ptₙ⁺ and MoPtₙ⁺⁺ (n=3–7) clusters are studied by combined mass spectrometry and density functional theory calculations, making it possible to investigate the effects of Mo doping on the reactivity between platinum clusters and CO. In addition, infrared photodissociation spectroscopy is used to measure the stretching frequency of CO molecules adsorbed on Ptₙ⁺ and MoPtₙ⁺⁺ (n=3-14), allowing an investigation of dopant induced charge redistributions within the clusters. These electronic charge transfers are correlated to the observed changes in reactivity.

Introduction

Platinum nanoparticles are widely used because of their high activity in a number of catalytic processes. For instance, in direct methanol (DMFC) and direct ethanol (DEFC) fuel cells, the alcohols are oxidized on a Pt catalyst, producing carbon dioxide, protons and electrons.[1,2] Fuel cells based on biofuels are a promising alternative for the combustion of fossil fuels as a source of energy, but the high reactivity of the platinum catalysts towards carbon monoxide is a major drawback. Carbon monoxide, which can be generated as reaction intermediate at the cell’s anode, adsorbs on the surface of the Pt nanoparticles thereby reducing the number of active sites and thus the fuel cell’s performance.[3] The interaction of CO with Pt has been studied intensively in the past decades, both experimentally and theoretically.[4-5] Diverse models have been suggested to describe the atop bonding mechanism between CO and Pt. Of the most used are the Blyholder model,[7] its more quantitative refinement the m-o model,[8] and the d-band center model.[9,10] In the Blyholder model bonding is attributed to electron transfer from the occupied 5s molecular orbital (MO) of CO to the empty Pt d-states and back-donation of electrons from occupied Pt d-states to the CO 2π* MO, which is unoccupied in the free CO molecule. The hybridized level between the empty Pt d-states and the 2π* MO of CO is antibonding in C–O, but bonding in Pt–C.[11]

Despite the extensive efforts of previous research, it remains challenging to experimentally probe the influence of the charge at the reactive site and of binding site coordination on the CO adsorption energy. This is a direct consequence of the difficulty to measure and control parameters such as the reactive site’s charge state and coordination number.

Small clusters in the gas phase have proven to be ideal model systems to investigate fundamental aspects of complex reactions.[12-15] The good control over the cluster size, composition and charge state allows to distinguish the effects of these parameters on the studied reactions. Moreover, the high-vacuum conditions of a gas-phase experiment eliminate the contaminating agents that could affect the reaction mechanism. For small sized clusters, ranging from two to a few tens of atoms, direct comparison between experiment and quantum-chemical calculations is possible.[16,17]

Gas-phase experiments on complexes of CO with transition metal clusters, including Pt clusters, elucidated a correlation between the partial charge at the binding site and the cluster–CO interaction strength.[16-21] Here, infrared (IR) action spectroscopy was used to measure the stretching frequencies of the adsorbed CO molecules (νCO) as a function of the kind of atoms in the cluster, its size, and charge state. νCO proved to be a sensitive parameter for the electronic charge distribution within the clusters. Within the conceptual framework of the Blyholder model, a larger electronic density at the binding site enhances the back-donation to the CO 2π* antibonding MO, thereby weakening the C–O bond and lowering νCO.

A significant amount of research in the field of gas-phase clusters has been devoted to the influence of doping on the properties of clusters such as their structures,[22,23] optical responses,[24,25] and reactivity.[26,27] All these studies have shown that a single dopant atom can strongly influence the clusters’ properties. This research is relevant in the context of fuel cells catalysts, since it is well-known that upon alloying the CO tolerance of platinum based fuel cells can be improved considerably.[3] In a recent combined mass spectrometry and density functional theory (DFT) study, some of the current
authors studied the effect of doping on the reactivity of gas-phase Pt clusters (XPt\(_n^+\); X = Mo, Nb, Sn, and Ag; 13 \(\leq n \leq 23\)) towards CO.\[28\] This work showed that a single dopant atom can reduce the interaction strength of Pt clusters with CO and that this effect depends on the type of dopant atom. More specifically, Mo and Nb doping reduced the CO adsorption energy, whereas only minor changes were induced by Ag and Sn doping.

In the current work we explore this intriguing behavior in more depth, focusing on correlated effects of Mo doping on electronic charge redistributions and the Pt clusters’ reactivities towards CO. The reactions of Mo doped Pt\(_n^+\) (3 \(\leq n \leq 14\)) clusters with CO are investigated in a low pressure collision cell by means of mass spectrometry and the CO stretching frequencies (\(v_{\text{CO}}\)) of the cluster–CO complexes are measured using IR photodissociation spectroscopy. For interpretation of the experimental observations, DFT calculations are performed for Pt\(_n^+\) and MoPt\(_n^+\) (3 \(\leq n \leq 7\)).

**Results and Discussion**

**Dissociation rates of cluster–CO complexes**

Figure 1 illustrates the formation of metal cluster carbonyl complexes by interaction of the Pt clusters with CO in a low pressure collision cell. The pressure dependent formation of CO complexes by Pt\(_n^+\) and MoPt\(_n^+\) is shown for three sizes \(n = 4, 5\) and 8. Kinetic data for other sizes are available as Supporting Information. The plotted quantity is the CO pressure \(P_{\text{CO}}\) dependent intensity of the cluster–CO signal in the mass spectra, normalized by the sum of the intensities of the bare cluster and its CO complex. A first observation is that for a given \(P_{\text{CO}}\), the smallest clusters, Pt\(_n^+\) and MoPt\(_n^+\), form the least CO complexes. This behavior can easily be explained by the small heat capacity of those four-atom clusters. When a cluster–CO complex is formed, its heat of formation is redistributed over the vibrational degrees of freedom of the cluster. Small clusters, with few degrees of freedom, heat up more than larger clusters thereby reducing the lifetime of the cluster–CO complex as it is not stabilized by further collisions. Hence, these complexes have low intensities in the mass spectra.\[28,29\] Under the applied experimental conditions no CO complexes are observed for \(n \leq 3\). More interestingly, Figure 1 reveals a size dependent influence of the dopant atom on the CO-complex formation, which one can see by comparing pure and doped clusters with the same number of atoms. For \(n = 4\) and 5, CO complex formation is reduced upon Mo doping, whereas no apparent change upon doping is seen for \(n = 8\).

Quantitative information of the clusters’ reactivity can be extracted from the kinetic data, by assuming the following reaction mechanism for cluster M:

\[
\begin{align*}
\text{M} + \text{CO} &\rightarrow \text{M}(\text{CO}) \\
\text{M}(\text{CO}) &\rightarrow \text{M} + \text{CO}
\end{align*}
\]

where (1) and (2) represent the reactions in and after the collision cell, respectively.\[26,29\] \(k_f\) and \(k_D\) are the reaction rates for formation and dissociation of the CO complex, respectively. The coupled temperature dependent rate equations corresponding to (1) and (2) can be solved as a function of \(P_{\text{CO}}\):

\[
[M(\text{CO})] = \frac{k_f}{k_f + k_D} \frac{P_{\text{CO}}}{T_{\text{CO}}} \left(1 - e^{-\frac{k_f}{k_f + k_D}} \left(1 - e^{-\frac{k_D}{k_f + k_D}} e^{rac{k_D}{k_f + k_D} T_{\text{CO}}} \right)\right)
\]

where \(k_f\) is the Boltzmann constant, \(T_{\text{CO}}\) the temperature of the CO gas, and \(t_1\) and \(t_2\) the times the cluster spends inside the collision cell and between the cell and the entrance of the mass spectrometer, respectively. \([M(\text{CO})] / [M]_0\) is the normalized abundance of the M(\text{CO}) complexes, relative to the initial amount of cluster M in the beam. A derivation of Eq. (3) can be found in the Supporting Information. Eq. (3) can be fit to the normalized abundances with \(k_0\) as sole fitting parameter if the forward reaction rate, \(k_f\), is approximated by the hard-sphere collision rate.\[29,30\] These fits are presented in Figure 1 as solid lines. The satisfactory quality of the fits suggests that assuming \(k_f\) values from hard-sphere collision theory is a fairly good approximation. The extracted \(k_0\) values for cluster source temperatures of 130 K and 300 K are presented in Figure 2. Error bars on the \(k_0\) values include both fitting errors and model uncertainty on the \(k_f\) values (which were assumed to be hard-sphere collision rates) by assessing the change in \(k_0\) for a variation of the forward rates with 10%. Dissociation rates are higher at 300 K than at 130 K, which is expected since at a lower source temperature, the clusters are colder prior the interaction with CO and the dissociation rate after CO adsorption is lower. One can also note a general decrease in \(k_0\) for

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Figure 1. Three examples of normalized abundance as a function of the CO pressure in the reaction cell for Pt\(_4^+\)(CO) and MoPt\(_4^+\)(CO) \((n = 4, 5\) and 8). Fits of the experimental data using Eq. (3) are shown as continuous lines. The source temperature is kept at 130 K for these measurements.

Figure 2. Dissociation rates \(k_0\) for the Pt\(_n^+\)(CO) and MoPt\(_n^+\)(CO) complexes \((n=4-10)\) at source temperatures of 130 K and 300 K.
increasing cluster size. This is due to the larger heat capacity of the larger clusters. Finally, and most importantly, upon Mo doping the dissociation rates for \( n = 4–7 \) increase (although at 130 K the \( k_0 \) increase for \( n = 7 \) is not larger than the error bar). The enhancement is most pronounced for \( n = 5 \) and 6. For \( n = 8–10 \), \( k_0 \) values do not change significantly upon doping under the applied experimental conditions. Assuming that changes in heat capacities are negligible upon doping (see Supporting Information for details), the observed increase in \( k_0 \) induced by Mo can be attributed to a decrease in the CO binding energy, which will be discussed in more detail below.

**Stretching frequencies of the adsorbed CO molecules**

Complementary information about the effect of Mo doping on the interaction between Pt\(^{\text{+}}\) clusters and CO is obtained by measurements of the internal stretching frequencies of adsorbed CO molecules, \( \nu_{\text{CO}} \). Those are measured via photodissociation of the clusters–CO complexes following multiple photon absorption of infrared light from the free electron laser FHI FEL (see methods section). The photodissociation of Pt\(^{\text{+}}\)(CO) and MoPt\(^{\text{+}}\)(CO) (\( n = 3–6 \)) complexes in the 2000–2150 cm\(^{-1}\) range is shown in Figure 3. The center of each observed band was determined by a Gaussian fit (solid lines in Figure 3) of the data.

![Figure 3: Photodissociation spectra of Pt\(^{\text{+}}\)(CO) and MoPt\(^{\text{+}}\)(CO) (n=3–6) in the 2000–2150 cm\(^{-1}\) range. Gaussian fits (solid lines) provide the center and the width of the bands corresponding to the CO stretching mode \( \nu_{\text{CO}} \).](image)

The results are summarized in Figure 4(a), showing \( \nu_{\text{CO}} \) up to \( n = 14 \). A zoom in the \( n = 3–7 \) size range is presented in Figure 4(b). For the pure Pt\(^{\text{+}}\) clusters there is an overall decrease in \( \nu_{\text{CO}} \) with increasing cluster size. This behavior has been observed previously and is well understood in terms of the electron density at the binding Pt site.\(^{[19]}\) The overall positive charge of 1 e of the cationic cluster is distributed over a larger number of (surface) atoms for increasing cluster size, reducing the electron deficiency for each Pt atom. According to the Blyholder model, this produces a higher back-donation of electron density into the 2\( \pi^* \) antibonding orbital of CO, reducing its vibrational frequency. For the doped MoPt\(^{\text{+}}\)(CO) clusters \( \nu_{\text{CO}} \) is found to be constant for the smaller clusters (\( n = 3–5 \)) and to decrease for \( n > 5 \). Furthermore, the frequency shift observed for a given cluster size upon replacement of one Pt atom by a Mo atom is found to depend non-uniformly on the cluster size. One observes shifts to higher frequencies for \( n = 3, 14 \), to lower frequencies for \( n = 5–7 \), or no apparent shifts (larger than the 1 e error) for \( n = 4, 8–13 \). The size dependent shifts in frequency upon Mo doping can be traced back to the electron density at the Pt binding site, as will be described in the following sections.

**Clusters’ structures, CO adsorption energies and stretching frequencies**

The most stable structures of the Pt\(^{\text{+}}\)(CO) and MoPt\(^{\text{+}}\)(CO) complexes with \( n = 3–7 \), as obtained by density functional theory (DFT) calculations, are presented in Figure 5. Minimum energy structures of the bare Pt\(^{\text{+}}\) and MoPt\(^{\text{+}}\) (\( n=3–7 \)) clusters are provided as Supporting Information. For \( n = 3, 5 \) and 7 the Mo only has minor effect on the geometry, while for \( n = 4 \) and 6 significant structural reorganization takes place, adopting slightly more planar structures upon doping. For all doped clusters, CO adsorbs atop at a Pt atom. Isomers with the CO molecule adsorbed on the Mo dopant were found to be at least 1 eV less stable than the structures of Figure 5. The calculated spin multiplicities and CO adsorption energies of the minimum energy configurations are detailed in Table 1.

**Table 1.** Spin multiplicities 2S+1, CO adsorption energies, CO stretching frequencies and Löwdin charges at the reactive Pt site of the Pt\(^{\text{+}}\) and MoPt\(^{\text{+}}\) clusters (\( n = 3–7 \))

<table>
<thead>
<tr>
<th>Cluster</th>
<th>2S+1 bare cluster</th>
<th>2S+1 CO complex</th>
<th>( E_{\text{ads}} ) / eV</th>
<th>( \nu_{\text{CO}} ) / cm(^{-1})</th>
<th>Charge at Pt binding site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(^{\text{+}})</td>
<td>4</td>
<td>2</td>
<td>-2.42</td>
<td>2121</td>
<td>+0.32</td>
</tr>
</tbody>
</table>
Calculated CO stretching frequencies of Pt\(^n\)+ and MoPt\(^n\)-1+(CO) are listed in Table 1 and compared in Figure 4(c). Consistent with the experiment, \(\nu_{\text{CO}}\) of Pt\(^n\)+ (CO) is found to decrease with increasing cluster size and upon Mo doping \(\nu_{\text{CO}}\) downshifts for \(n = 3\) and \(4\) and upshifts for \(n = 5-7\). Assuming that upon Mo doping the clusters’ heat capacities are affected only slightly, the experimentally obtained CO dissociation rates \(k_D\) depend directly on \(E_{\text{ads}} = E_{\text{clusters}\text{+CO}} - E_{\text{clusters}} - E_{\text{CO}}\), i.e. larger \(k_D\) values correspond to complexes with weaker bound CO. A detailed description of the relation between \(k_D\) and \(E_{\text{ads}}\) is given in Ref. [28]. Based on the experimental results in Figure 2 one thus expects that Mo doping reduces the CO bonding for \(n = 5-7\). Calculated results are in good agreement with those predictions.

The effect of Mo doping and the electronic charge transfers

Considering the Blyholder model to describe the Pt–CO interaction, dopant induced electronic charge redistribution is expected to affect both the CO adsorption energy and the \(\nu_{\text{CO}}\) stretching frequency. Therefore, atomic Löwdin charges were calculated for the clusters and their CO complexes. The local charges on the preferential CO adsorption site in the bare clusters are given in Table 1. For the monometallic Pt\(^n\)+ clusters, the positive charge at the Pt binding site decreases monotonously with cluster size from +0.32 e for Pt\(^3\)+ to +0.17 e for Pt\(^7\)+. This decrease correlates with the redshift of \(\nu_{\text{CO}}\) (Figure 4a) and confirms that the amount of back-donation, from the metal to CO, determines the redshift of \(\nu_{\text{CO}}\).

Mo doping has an effect on the Löwdin charges at the reactive Pt atom. A comparison of the charge distributions in Pt\(^n\)+ and MoPt\(^n\)-1+(CO) shows that transfer of electron density from Mo to Pt reduces the positive charge at the Pt binding site of +0.32 e in Pt\(^3\)+ to +0.22 e in MoPt\(^2\)+. On the other hand, electron transfer from Pt to Mo is found for the larger cluster sizes (\(n = 5-7\)) in which the Pt atom binding to CO is more positively charged in MoPt\(^n\)-1+ than in Pt\(^n\)+. For \(n = 4\) there is no apparent charge transfer.

The effect of Mo doping on the charge redistribution is visualized for \(n = 3\) and \(5\) in Figure 6. In pure Pt clusters, the positive +1 e charge of the cationic cluster is almost equally distributed over the atoms, giving to each Pt a more positive charge in Pt\(^n\)+ than in Pt\(^n\)+. However, in MoPt\(^n\)+, Mo donates electron density to Pt, ending up with a positive charge of +0.60 e, in opposition to MoPt\(^n\)-1+, where transfer of electron density is seen from Pt to Mo, leaving Mo with the smaller charge of +0.12 e.

These charge distributions are correlated with the observed shifts in \(\nu_{\text{CO}}\) upon doping. If there is electron density transferred from Mo to Pt, a larger back-donation is accepted from Pt to the 2π* antibonding orbital of CO, decreasing the C–O bond strength and the CO stretching frequency. In contrast,
when electron density is transferred from Pt to Mo, less back-
donation is possible and v\text{CO} increases. This close correlation
between the atomic charge at the Pt binding site and v\text{CO} allows
predictions about the charge transfers in the clusters to be made
using the measured v\text{CO}. Such empirical models have been used
before to understand trends on measured v\text{CO} values of CO
adsorbed on different monometallic transition metal clusters in
different charge states: (Rh,Co,Ni)\text{\textsuperscript{110}}\text{CO} and
(Ni,Pd,Pt)\text{\textsuperscript{110}}\text{CO} \text{\textsuperscript{110}}. The main assumption of the model is
that v\text{CO} is mainly affected by the electron population at the 2π*
 antibonding orbital of CO, P(2π*). Since this antibonding orbital
is populated by back-donation of electron charge from the
reactive site to the CO molecule, P(2π*) is proportional to the
excess charge at this site. One can propose a model that
assumes a linear dependence between v\text{CO} and this excess charge.
In an ideal metallic cluster the charge is equally
distributed over the surface atoms and one gets:
\[ v_{\text{CO}} = v_{\text{CO}}^\text{\textsuperscript{m}} + \Delta v_{\text{CO}}^{\text{ex}} = \frac{d\varepsilon}{\pi r} \] (4)
where v\text{CO} is the frequency in the limit of an infinite
number of atoms on the cluster, \Delta v\text{CO}^{\text{ex}} is the induced frequency
shift due to the interaction of the dipole moment of CO with the
electric field of the charged cluster (which shifts the charge
distribution within the CO molecule), z the total charge of the
cluster in e, d a proportionality constant, and n the number
of surface atoms of the cluster (which for the small sizes studied
here equals the number of atoms in the cluster, n). For \Delta v\text{CO}^{\text{ex}} the
following expression is used:\textsuperscript{110}
\[ \Delta v_{\text{CO}}^{\text{ex}} = 1395 \text{ cm}^{-1} \left( \frac{z}{\pi r^2} \right) \] (5)
in which r is the distance from the center of the cluster to the
center of the CO molecule, r = r\text{Cl} + r\text{C/O} with r\text{Cl} the
radius of the cluster, which is assumed spherical (r\text{Cl} = r\text{Cl}^{1/3} with
r\text{Cl} the radius of the atom obtained from the bulk density), r\text{C/O}
the covalent radius of the carbon atom in a typical M–C bond
(r\text{C} = 0.52 Å) and r\text{C/O} the C–O distance (r\text{C/O} = 1.15 Å). The pre-factor
1395 cm\textsuperscript{-1} is obtained from DFT simulations.\textsuperscript{110} A fit of Eq. (4) to the
experimentally measured v\text{CO} values is shown in Figure 7(a)
and yields v\text{CO} = 2035 ± 1 cm\textsuperscript{-1} and d = 146 ± 7 cm\textsuperscript{-1}.
Since this fit predicts the smooth evolution of v\text{CO} with size,
deviations between the fit and the measured values (Fig 7(a))
may be related to a non-uniform distribution of the charge. If this
idea is correct Eq. (4) can again be used, but now to predict
the local charges at the reactive Pt site. Therefore the term z/n, in
Eq. (4) is replaced by Q, the fractional charge at the reactive
site and Q is calculated using the fitted v\text{CO} and d values and the
measured v\text{CO} for the pure Pt\textsuperscript{5+} and doped MoPt\textsuperscript{5+} clusters.
The resulting Q values are shown in Figure 7(b) for n = 3–14
together with excess charges as obtained from DFT calculations
for n = 3–7. Error bars on the modelled Q values are propagated
from the uncertainties on fitted v\text{CO} and d, and the measured v
values using Eq. (4). For sizes for which DFT calculations are
available, the fractional charges Q obtained by both methods
agree well. Based on this good agreement for n ≤ 7, the transfer
electron density can be estimated for the larger sizes using
the measured v\text{CO}. In particular, for n = 14 v\text{CO} is redshifted upon
Mo doping (see Figure 4-a). This suggests that the CO binding
Pt site in MoPt\textsuperscript{5+} is less positively charged than that in Pt\textsuperscript{5+}
and indicates an electron transfer from Mo to Pt. This was also seen
in DFT calculations on the larger Pt\textsuperscript{19+}CO and MoPt\textsuperscript{18+}CO
clusters.\textsuperscript{28} The empirical model yields local charges of +0.08 e
and +0.02 e on the reactive sites in Pt\textsuperscript{14+}CO and MoPt\textsuperscript{13+}CO,
respectively. Bader charge analysis, used in Ref.\textsuperscript{28} for
Pt\textsuperscript{19+}CO and MoPt\textsuperscript{18+}CO gave local charges of +0.08 e
and +0.01 e, respectively.

Finally, we discuss the correlation between transfer of
electron density and CO binding energies. In the Blyholder
interpretation bonding between CO and Pt is attributed to
electron donation from the 5\textsuperscript{0} MO of CO to empty d-orbitals
of Pt as well as the back-donation process. Thus, Mo dopant
induced electron redistribution in the cluster may affect both
interactions in opposite ways, requiring a detailed analysis of the
electronic structure to make conclusions about the effect of
doping. The top panel of Figure 8 presents the partial density
of states (PDOS) of Pt\textsuperscript{5+}CO and MoPt\textsuperscript{5+}, projected on C, on O
and on the Pt d-states. As a reference, the energies of the MOs
of the free CO are indicated by vertical dashed lines. A first
observation from the figure is the strong stabilization of the 4σ
and 5σ MO’s, which under the interaction with Pt are located at
energies around -19 eV and -16.5 eV, respectively. The wave
functions of these states are shown in the bottom panel of
Figure 8. The stabilization is the strongest for the 5σ MO, which
is ascribed to the electronic charge donation from CO to Pt. It is
important to note that the 5σ stabilization is stronger in MoPt\textsuperscript{5+}
than in Pt\textsuperscript{5+}. This is a consequence of the electronic charge
transfer from Pt to Mo in this cluster size, which leads to a larger
density of unoccupied Pt d-states available to interact with CO.
The enhanced 5σ stabilization seems to contradict the result that
upon Mo doping the CO adsorption energy for this size is
reduced. However, this effect gets over-compensated by the
back-donation from occupied d-states of Pt to the antibonding
2π* MO of CO. Located between -14 eV and the Fermi level, E\text{F},
several hybridized states of 2π* character are found in the
PDOS spectra.\textsuperscript{28} Since this MO is empty in the free CO, these
hybridized states are ascribed due to back-donation of
electron density from Pt to CO. Those hybridized states are antibonding for the C-O interaction, but bonding for the Pt-C bond. An inspection of Figure 8 shows that the density of these states is larger in Pt$_5^+$ than in MoPt$_4^+$, especially near $E_F$ due to the lower population of Pt d-states below the Fermi energy in the doped cluster, as a consequence of the Pt to Mo electron transfer. An integration of the density of states of C and O 1 eV below $E_F$ gives around a 50% larger population in Pt$_5^+$ than in MoPt$_4^+$. So we can conclude that for Pt$_5^+$ the effect of charge redistribution upon Mo doping has a stronger influence on the back-donation than on the 5σ $\rightarrow$ d transfer, reducing the CO binding energy. A similar influence of Mo doping, i.e., a reduction of the CO adsorption energy, was observed previously for the Pt$_{10}^+$ cluster. However, in that case, a transfer of electron density from Mo to Pt was observed and the 5σ back-donation was more important than the 2n* hybridization.

Conclusions

In this work, the effect of a single Mo dopant atom on the bonding between CO and small gas-phase Pt$_n^+$ (n=3–14) clusters has been studied. Mass spectrometry was combined with density functional theory calculations in order to investigate the reactivity of the clusters. Theory and experiment are well in agreement, showing that, upon doping, CO binding energies were reduced, in particular for Pt$_3^+$, Pt$_4^+$ and Pt$_7^+$. In addition, electronic charge transfer induced by Mo doping was characterized by IR spectroscopic measurements of the CO stretching frequencies and charge population analysis calculations. Electron transfers were found to be size dependent. We found a correlation between the cluster-CO bond strength and the dopant induced electron transfer; for those sizes with a more positive charge at the Pt binding site, weaker CO binding energies were found. This demonstrates the importance of back-donation of electron density to the CO bonding mechanism. In the Blyholder model both the 5σ sigma donation and the 2n* back-donation are responsible for the Pt-CO bonding. However, these two mechanisms are affected oppositely by the charge at the atomic Pt binding site. This work has shown that in very small Mo doped Pt clusters the effect of reduced 2n* back-donation affects the CO binding more strongly than an enhanced 5σ sigma donation, resulting in an overall reduction of the CO binding energies. In previous studies performed on larger clusters a predominant 5σ sigma donation was found, in contrast to the cluster sizes studied here. This demonstrates the possibility to sensitively control donation and back-donation effects in the Pt-CO interaction by doping and cluster size.

CO reactivity measurements

The reactivity of the clusters towards CO was studied in a low-pressure collision cell installed in a molecular beam setup with a laser ablation cluster source and a time-of-flight mass spectrometer. Rectangular Mo and Pt targets were ablated by two independent Nd:YAG lasers (532 nm, 10 Hz). Before ablation, He gas was introduced in the source by a pulsed valve (7 bar, 10 Hz) to trigger cluster formation. In this study the source was either maintained at room temperature or cooled down to 130 K by a continuous flow of liquid nitrogen. The cluster beam, composed of a mixture of pure Pt$_n^+$ and single doped MoPt$_n^+$ clusters (n=3-10), was exposed to CO gas in the collision cell. The pressure of CO (P$_{CO}$) was varied in the range between 0 and 0.2 Pa. The intensities of the clusters and their CO complexes are analyzed by time-of-flight mass spectrometry. Under the current conditions only cluster-CO complexes with maximally one CO molecule survive on the timescale of the experiment. Representative mass spectra are available as Supporting Information.

IR spectroscopy measurements

IR spectroscopy experiments were carried out in a dual-target dual-laser cluster setup connected to a beamline of the Infrared Free Electron Laser at the Fritz Haber Institute of the Max Planck Society in Berlin (FHI FEL). A detailed description of the cluster source is available in Ref. 34 and its operation principle is similar to the source used for the CO reactivity measurements. The main difference is that for the IR spectroscopy experiments the CO gas is inserted via a pulsed valve into a reaction channel that is directly connected to the cluster source. The cluster source was kept at room temperature. Pure Pt$_n^+$ and single doped MoPt$_n^+$ clusters and their CO complexes were formed with a size distribution ranging from n=1 to n=14. After production, the cluster beam was collimated by a 2 mm diameter skimmer followed by a 1 mm diameter aperture where clusters interacted with the counter-propagating IR laser beam delivered by the FHI FEL with a repetition rate of 5 Hz. Finally, the cluster size distributions, with and without IR laser excitation, were analyzed by reflection time-of-flight mass spectrometry. The wavelength of the FHI FEL was tuned in the range of the CO stretching mode (2000–2200 cm$^{-1}$). An average pulse energy of 25 mJ and a step size of 2 cm$^{-1}$ were used for the spectroscopy. The bandwidth or the IR radiation was 10-15 cm$^{-1}$ (full width at half maximum).
Density functional theory calculations

Density functional theory (DFT) calculations for bare clusters, Pt\(^n\)\(^+\) and MoPt\(^n\)\(^+\), and their corresponding CO complexes, Pt\(^n\)\(^+\)(CO) and MoPt\(^n\)\(^+\)(CO) (\(n=3-7\)), were carried out using the TPSS exchange-correlation functional as implemented in the ORCA 3.0.3 software package.\(^{[35]}\) For Pt and Mo atoms, 18 and 14 electrons were included in the valence, respectively, while the other electrons are described by the Stuttgart-Dresden ECP(def2-TZVP) pseudopotentials.\(^{[36]}\) All electrons of C and O atoms were treated explicitly with the aug-cc-pVZD basis set.\(^{[37]}\) The selection of this computational level was motivated by the results of Ref. [38], in which the structures of small cationic pure Pt\(^n\)\(^+\) clusters (\(n=3\)-5) were successfully assigned by a combined IR spectroscopy and DFT study. First minimum-energy structures of the bare clusters, Pt\(^n\)\(^+\) and MoPt\(^n\)\(^+\) (\(n=3\)-7), were searched, followed by an independent search of the corresponding CO complexes. This search carried out using the hybrid B3PW91 functional,\(^{[39,40]}\) in conjunction with the aug-cc-pVZ basis sets as implemented in the GAUSSIAN 09 package.\(^{[41]}\) For each structure several spin states were tried and harmonic IR spectra were calculated. The coordinates of the obtained minimum-energy structures are given as Supporting Information. Löwdin populations were calculated to study atomic electronic charge distributions of the bare clusters and their CO complexes.

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Keywords: platinum clusters • Mo doping • carbon monoxide • IR spectroscopy • reactivity
