Cluster Compounds

Effects of Charge Transfer on the Adsorption of CO on Small Molybdenum-Doped Platinum Clusters

Piero Ferrari,^[a] Jan Vanbuel,^[a] Nguyen Minh Tam,^[b] Minh Tho Nguyen,^[c] Sandy Gewinner,^[d] Wieland Schöllkopf,^[d] André Fielicke,^[e] and Ewald Janssens^{*[a]}

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 have been studied in the gas phase to obtain a better understanding of the fundamental nature of the Pt-CO interaction in the presence of a dopant atom. For this purpose, Pt_n^+ and $MoPt_{n-1}^+$ (n=3-7) clusters were studied by combined mass spectrometry and density functional

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 platinum catalyst to produce carbon dioxide, protons, and electrons.^[1,2] Fuel cells based on biofuels are a promising alternative to the combustion of fossil fuels as a source of energy, but the high reactivity of the platinum catalysts towards carbon monoxide, which can be generated as a reaction intermediate at the cell's anode, is a major drawback. Carbon monoxide is adsorbed on the surface of the platinum nanoparticles, thereby reducing the number of active sites and thus the performance of the fuel cell.^[3] The interaction of CO with platinum has been studied intensively in the past decades, both experimentally and theoretically.^[4–6] Diverse models have been suggested to describe the bonding mecha-

[a] P. Ferrari, J. Vanbuel, Prof. Dr. E. Janssens Laboratory of Solid State Physics and Maanetism KU Leuven, Celestijnenlaan 200D, 3001 Leuven (Belgium) E-mail: ewald.janssens@kuleuven.be [b] Dr. N. M. Tam Computational Chemistry Research Group & Faculty of Applied Sciences Ton Duc Thang University, Ho Chi Minh City (Vietnam) [c] Prof. Dr. M. T. Nguyen Department of Chemistry, KU Leuven, Celestijnenlaan 200F 3001 Leuven (Belgium) [d] S. Gewinner, Dr. W. Schöllkopf Fritz-Haber-Institut der Max-Planck-Gesellschaft Faradayweg 4-6, 14195 Berlin (Germany) [e] Dr. A. Fielicke Institut für Optik und Atomare Physik, Technische Universität Berlin Hardenbergstrasse 36, 10623 Berlin (Germany) Supporting information and the ORCID identification numbers for the authors of this article can be found under http://dx.doi.org/10.1002/

theory calculations, making it possible to investigate the effects of molybdenum doping on the reactivity of platinum clusters with CO. In addition, IR photodissociation spectroscopy was used to measure the stretching frequency of CO molecules adsorbed on Pt_n^+ and $MoPt_{n-1}^+$ (n=3-14), allowing an investigation of dopant-induced charge redistribution within the clusters. This electronic charge transfer is correlated with the observed changes in reactivity.

nism between CO and transition metal atoms. Of the most used are the Blyholder model,^[7] its more quantitative refinement, the π - σ model,^[8] and the d-band center model.^[9,10] In the Blyholder model, bonding to platinum is attributed to electron transfer from the occupied 5 σ molecular orbital (MO) of CO to the empty platinum d states and the back-donation of electrons from occupied platinum d states to the CO $2\pi^*$ MO, which is unoccupied in the free CO molecule. The hybridized level between the empty platinum d states and the $2\pi^*$ MO of CO is antibonding in C–O, but bonding in Pt–C.^[11]

Despite the extensive efforts of previous research, it remains a challenge to experimentally probe the influence of the charge at the reactive site and binding-site coordination on the CO adsorption energy. This is a direct consequence of the difficulty in measuring and controlling parameters such as the charge state and coordination number of the reactive site.

Small clusters in the gas phase have proven to be ideal model systems for investigating the fundamental aspects of complex reactions.^[12–15] The good control over cluster size, composition, and charge state allows the effects of these parameters on the studied reactions to be distinguished. 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 transitionmetal clusters, including platinum clusters, elucidated a correlation between the partial charge at the binding site and the strength of the cluster–CO interaction.^[18–21] Hitherto, IR action spectroscopy has been used to measure the stretching frequencies of the adsorbed CO molecules (ν_{CO}) as a function of the nature of the atoms in the cluster, its size, and charge state. ν_{CO} proved to be a parameter sensitive to the electronic

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charge distribution within clusters. Within the conceptual framework of the Blyholder model, a larger electronic density at the binding site enhances the back-donation to the CO $2\pi^*$ antibonding MO, thereby weakening the C–O bond and lowering $\nu_{\rm CO}$.

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 properties of clusters. This research is relevant in the context of fuel cell catalysts, because 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 gasphase platinum 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 platinum clusters towards CO and that this effect depends on the type of dopant atom. More specifically, molybdenum and niobium doping reduced the CO adsorption energy, whereas only minor changes were induced by silver and tin doping.

In the current work we explored this intriguing behavior in more depth, focusing on correlated effects of molybdenum doping on electronic charge redistributions and the reactivities of the platinum clusters towards CO. The reactions of molybdenum-doped Pt_n⁺ ($3 \le n \le 14$) clusters with CO have been investigated in a low-pressure collision cell by means of mass spectrometry, and the CO stretching frequencies (ν_{CO}) of the cluster–CO complexes were measured by IR photodissociation spectroscopy. For interpretation of the experimental observations, DFT calculations were performed on Pt_n⁺ and MoPt_{n-1}⁺ ($3 \le n \le 7$).

Results and Discussion

Dissociation rate constants of cluster-CO complexes

Figure 1 illustrates the formation of metal cluster-carbonyl complexes through the interaction of the platinum clusters



Figure 1. Three examples of normalized abundance as a function of the CO pressure in the reaction cell for $Pt_n^+(CO)$ and $MOPt_{n-1}^+(CO)$ (n=4, 5, 8). Fits of the experimental data by using Equation (3) are shown as continuous lines. The source temperature was kept at 130 K for these measurements.

with CO in a low-pressure collision cell. The pressure-dependent formation of CO complexes of Pt_n^+ and $MoPt_{n-1}^+$ is shown for three cluster sizes (n = 4, 5, 8). Kinetic data for other sizes are available in the Supporting Information. The CO pressure (P_{CO}) is plotted against the intensity of the signal of the cluster-CO complex 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_{CO} , the smallest clusters, Pt₄⁺ and MoPt₃⁺, form the least CO complexes. This behavior can easily be explained by the small heat capacity of these 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 were observed for $n \leq 3$. More interestingly, Figure 1 reveals a size-dependent influence of the dopant atom on the cluster-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 molybdenum doping, whereas no apparent change upon doping is seen for n=8.

Quantitative information on the reactivities of the clusters can be extracted from the kinetic data by assuming the reaction mechanism for cluster M presented in Equations (1) and (2):

$$M + CO \underset{k_{D}}{\overset{k_{f}}{\longrightarrow}} M(CO)$$
(1)

$$\mathsf{M}(\mathsf{CO}) \xrightarrow{k_{\mathsf{D}}} \mathsf{M} + \mathsf{CO}$$
⁽²⁾

in which reaction (1) represents the reaction in the collision cell and reaction (2) is the reaction thereafter.^[26,29] The parameters $k_{\rm f}$ and $k_{\rm D}$ are the rate constants for the formation and dissociation of the CO complex, respectively. The coupled temperature-dependent rate equations corresponding to reactions (1) and (2) can be solved as a function of $P_{\rm CO}$, according to Equation (3):

$$\frac{[M(CO)]}{[M]_{0}} = \frac{k_{f} P_{CO}}{k_{f} P_{CO} + k_{D} k_{B} T_{CO}} e^{-k_{D} t_{2}} (1 - e^{-(k_{f} \frac{P_{CO}}{k_{B} T_{CO}} + k_{D}) t_{1}})$$
(3)

in which k_B is the Boltzmann constant, T_{CO} is the temperature of the CO gas, t_1 and t_2 are the times the cluster spends inside the collision cell and between the cell and the entrance of the mass spectrometer, respectively, and $[M(CO)]/[M]_0$ is the normalized abundance of the M(CO) complexes relative to the initial amount of cluster M in the beam. A derivation of Equation (3) can be found in the Supporting Information. Equation (3) can be fitted to the normalized abundances with k_D as sole fitting parameter if the forward reaction rate constant, 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 hardsphere collision theory is a fairly good approximation. The ex-



tracted $k_{\rm D}$ values for cluster source temperatures of 130 and 300 K are presented in Figure 2. Error bars on the $k_{\rm D}$ values include contributions from both fitting errors and model uncertainty in the $k_{\rm f}$ values (which were assumed to be hard-sphere collision rates) by assessing the change in $k_{\rm D}$ for a variation of



Figure 2. Dissociation rate constants $k_{\rm D}$ for the $Pt_{n^+}(CO)$ and $MoPt_{n-1^+}(CO)$ complexes (with n = 4-10) at source temperatures of 130 and 300 K.

the forward rate constants of 10%. Dissociation rate constants are higher at 300 K than at 130 K, which is expected because at a lower source temperature the clusters are colder prior to the interaction with CO and the dissociation rate constant after CO adsorption is lower. One can also note a general decrease in $k_{\rm D}$ with increasing cluster size. This is due to the larger heat capacity of the larger clusters. Finally, and most importantly, upon molybdenum doping the dissociation rate constants for clusters with n = 4-7 increase (although at 130 K the increase in $k_{\rm D}$ for n = 7 is not larger than the error bar). The enhancement is most pronounced for n=5 and 6. For n=8-10, the $k_{\rm D}$ values do not change significantly upon doping under the applied experimental conditions. Assuming that changes in heat capacities are negligible upon doping (see the Supporting Information for details), the observed increase in $k_{\rm D}$ induced by molybdenum 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 molybdenum doping on the interaction between Pt_n^+ clusters and CO was obtained by measurement of the internal stretching frequencies of the adsorbed CO molecules, ν_{CO} . These were measured by photodissociation of the cluster–CO complexes following multiple photon absorption of IR irradiation from the free electron laser FHI FEL (see the Experimental Section). The photodissociation of Pt_n^+ (CO) and $MOPt_{n-1}^+$ (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.

The results are summarized in Figure 4a, which shows the variation of v_{CO} up to n = 14. A closer look at the systems with n = 3-7 is presented in Figure 4b. For the pure Pt_n^+ clusters there is an overall decrease in v_{CO} with increasing cluster size. This behavior has been observed previously and is well under-



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Figure 3. Photodissociation spectra of Pt_n⁺(CO) and MoPt_{n-1}⁺(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 ν_{cO} .



Figure 4. a) Center of the CO stretching bands for $Pt_n^+(CO)$ (**n**) and $MoPt_{n-1}^+CO)$ (\odot) as a function of cluster size (n=3-14). Error bars represent the uncertainty in the band center of the Gaussian fit. b) Zoom of panel (a) in the size range n=3-7. c) Center of the CO stretching mode for Pt_n^+ and $MoPt_{n-1}^+$ (n=3-7) clusters calculated by DFT.

stood in terms of the electron density at the binding platinum site.^[19] The overall positive charge of +1e of the cationic cluster (where *e* represents the positive elementary charge) is distributed over a larger number of (surface) atoms in clusters of increasing size, which reduces the electron deficiency on each platinum atom. According to the Blyholder model, this produces a higher back-donation of electron density into the $2\pi^*$ antibonding orbital of CO, thereby reducing its vibrational frequency. For the doped MoPt_{n-1}⁺(CO) clusters, ν_{CO} is found to be constant for the smaller clusters (n=3-5) and to decrease for n > 5. Furthermore, the change in frequency observed for a given cluster size upon replacement of one platinum atom by a molybdenum atom is found to depend non-uniformly on



the cluster size. One observes shifts to lower frequencies for n=3,14, to higher frequencies for n=5-7, and no apparent shifts (larger than the 1σ error) for n=4,8-13. The size-dependent shifts in frequency upon molybdenum doping can be traced back to the electron density at the platinum binding site, as will be described in the following sections.

Cluster structures, CO adsorption energies, and stretching frequencies

The most stable structures of the $Pt_n^+(CO)$ and $MOPt_{n-1}^+(CO)$ complexes with n = 3-7, as determined by DFT calculations, are presented in Figure 5. Cartesian coordinates of the minimumenergy structures of the Pt_n^+ and $MOPt_{n-1}^+$ (n=3-7) clusters are provided in the Supporting Information. For n=3, 5, and 7,



Figure 5. DFT-calculated minimum-energy structures of $Pt_n^+(CO)$ and $MoPt_{n-1}^+(CO)$ for n = 3-7. The drawn spheres, in increasing darkness, represent Pt, Mo, C, and O atoms.

the molybdenum only has a minor effect on the geometry, whereas for n=4 and 6, significant structural reorganization takes place, with the clusters adopting slightly more planar structures upon doping. For all the doped clusters, CO is adsorbed on a platinum atom. Isomers with the CO molecule adsorbed on the molybdenum dopant were found to be at least 1 eV less stable than the structures presented in Figure 5. The calculated spin multiplicities and CO adsorption energies of the minimum-energy configurations are detailed in Table 1.

The calculated CO stretching frequencies of Pt_n^+ (CO) and $MoPt_{n-1}^+$ (CO) are also listed in Table 1 and compared in Fig-

Table 1. Spin multiplicities 25+1, CO adsorption energies, CO stretching
frequencies, and Löwdin charges on the reactive platinum site of the Pt _n ⁺
and MoPt_{n-1}^+ clusters ($n = 3-7$).

Bare cluster	25+1 bare cluster	2S+1 CO complex	E _{ads} [eV]	$ u_{ m co}$ [cm ⁻¹]	Charge on Pt binding site [e]
Pt ₃ ⁺	4	2	-2.42	2121	+0.32
MoPt ₂ ⁺	4	4	-2.45	2111	+0.22
Pt_4^+	4	4	-2.18	2113	+0.25
$MoPt_3^+$	4	4	-2.36	2103	+0.25
Pt ₅ ⁺	4	4	-2.49	2093	+0.20
MoPt ₄ ⁺	4	4	-2.09	2099	+0.26
Pt ₆ ⁺	6	6	-2.34	2092	+0.18
MoPt ₅ ⁺	4	4	-2.25	2101	+0.25
Pt ₇ ⁺	4	4	-2.74	2091	+0.17
$MoPt_6^+$	4	2	-2.36	2094	+0.21

ure 4c. Consistent with the experimental data, the $v_{\rm CO}$ values for $Pt_n^+(CO)$ are found to decrease with increasing cluster size, and upon molybdenum doping $\nu_{\rm CO}$ is shifted downwards for n=3 and 4 and upwards for n=5-7 relative to the corresponding pure Pt clusters. Assuming that upon molybdenum doping the heat capacities of the clusters are affected only slightly, the CO dissociation rate constants $k_{\rm D}$ depend directly on E_{ads} ($E_{ads} = E_{cluster+CO} - E_{cluster} - E_{CO}$), that is, larger k_D values correspond to complexes with weaker-bound CO. A detailed description of the relation between $k_{\rm D}$ and $E_{\rm ads}$ is given in Ref. [28]. Based on the experimental results in Figure 2, one expects that molybdenum doping reduces the CO bonding for n = 5-7. The calculated results are in good agreement with these predictions: Molybdenum doping reduces the CO adsorption energy from -2.49 to -2.09 eV for n=5, from -2.34to -2.25 eV for n=6, and from -2.74 to -2.36 eV for n=7. In the case of n = 4, however, for which experimental dissociation rate constants were determined and DFT calculations are available, it is not possible to infer a tendency in E_{ads} upon doping due to the large uncertainty in the experiment.

Effect of electronic charge transfer

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 ν_{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 on the platinum binding site decreases monotonously with cluster size from +0.32*e* for Pt₃⁺ to +0.17*e* for Pt₇⁺. This decrease correlates with the redshift of ν_{CO} (Figure 4a) and confirms that the amount of back-donation, from the metal to CO, determines the redshift of ν_{CO} .

Molybdenum doping has an effect on the Löwdin charges at the reactive platinum atom. A comparison of the charge distributions in Pt_3^+ and $MoPt_2^+$ shows that transfer of electron density from molybdenum to platinum reduces the positive charge on the platinum binding site from +0.32e in Pt_3^+ to

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+0.22*e* in MoPt₂⁺. On the other hand, electron transfer from platinum to molybdenum is found for the larger cluster sizes (n=5-7), in which the platinum 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 molybdenum doping on the charge redistribution is visualized for n=3 and n=5 in Figure 6. In pure platinum clusters, the positive +1e charge of the cationic cluster is almost equally distributed over the atoms; thus each platinum in Pt₃⁺ has a more positive charge than each platinum in Pt₅⁺.



Figure 6. DFT-calculated minimum-energy structures of Pt_n^+ and $MOPt_{n-1}^+$ (n = 3, 5) clusters. The color code represents the atomic charge calculated by using the Löwdin scheme.

However, in MoPt₂⁺, molybdenum donates electron density to platinum, ending up with a positive charge of +0.60e, in contrast to MoPt₅⁺, in which electron density is transferred from platinum to molybdenum, leaving molybdenum with the smaller charge of +0.12e.

These charge distributions are correlated with the observed shifts in $\nu_{\rm CO}$ upon doping. If electron density is transferred from molybdenum to platinum, a larger back-donation occurs from platinum to the $2\pi^*$ antibonding orbital of CO, thereby decreasing the C-O bond strength and the CO stretching frequency. In contrast, when electron density is transferred from platinum to molybdenum, less back-donation is possible and $v_{\rm CO}$ increases. This close correlation between the atomic charge on the platinum binding site and v_{co} allows the charge transfer in the clusters to be predicted by using the measured $v_{\rm CO}$. Such empirical models have been used previously to understand trends in the measured $v_{\rm CO}$ values of CO adsorbed on different monometallic transition-metal clusters in different charge states: $(Rh,Co,Ni)_n^{-/0/+}CO,^{[18]} Co_n^{+}(H_2)_mCO,^{[21]}$ and $(Ni,Pd,Pt)_n^{-/0/+}CO.^{[19]}$ The main assumption of the model is that $v_{\rm CO}$ is mainly affected by the electron population at the $2\pi^*$ antibonding orbital of CO, P($2\pi^*$). Because this antibonding orbital is populated by back-donation of electron charge from the reactive site to the CO molecule, $P(2\pi^*)$ is proportional to the excess charge at this site. One can propose a model that assumes a linear dependence between $\nu_{\rm CO}$ and this excess charge. In an ideal metallic cluster, the charge is equally distributed over the surface atoms and one obtains Equation (4):

$$\nu_{\rm CO} = \nu_{\rm CO}^{\infty} + \Delta \nu_{\rm CO}^{\rm ES} + \frac{dz}{n_{\rm s}} \tag{4}$$

in which $\nu_{\rm CO}^{\infty}$ is the frequency in the limit of an infinite number of atoms on the cluster, $\Delta \nu_{\rm CO}^{\rm ES}$ 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* is the total charge on the cluster in *e*, *d* is a proportionality constant, and $n_{\rm s}$ is the number of surface atoms in the cluster (which, for the small sizes studied here, equals the number of atoms in the cluster, *n*). For $\Delta \nu_{\rm CO}^{\rm ES}$, Equation (5) can be applied:^[18]

$$\Delta v_{\rm CO}^{\rm ES} = 1395 \,\rm cm^{-1} (z/r^2) \tag{5}$$

in which *r* is the distance from the center of the cluster to the center of the CO molecule, with $r=r_{\rm CL}+r_{\rm C}+r_{\rm CO}/2$, in which $r_{\rm CL}$ is the radius of the cluster, which is assumed to be spherical $(r_{\rm CL} \approx r_{\rm M} n^{1/3})$, with $r_{\rm M}$ the radius of the atom obtained from the bulk density), $r_{\rm C}$ is the covalent radius of the carbon atom in a typical M–C bond $(r_{\rm C}=0.52$ Å), and $r_{\rm CO}$ is the C–O distance $(r_{\rm CO}=1.15$ Å). The pre-factor 1395 cm⁻¹ was obtained from DFT simulations.^[18] A fit of Equation (4) to the experimentally measured $\nu_{\rm CO}$ values is shown in Figure 7a and yields $\nu_{\rm CO}^{\infty}=2035\pm1$ cm⁻¹ and $d=146\pm7$ cm⁻¹.

Because this fit predicts the smooth evolution of v_{CO} with size, deviations between the fit and the measured values (Figure 7a) may be related to a non-uniform distribution of the charge. If this idea is correct, Equation (4) can again be used, but now to predict the local charges on the reactive platinum site. Therefore, the term z/n_s in Equation (4) is replaced by Q, the fractional charge at the reactive site, which can be calculated by using the fitted v_{CO}^{∞} and d values and the measured v_{CO}



Figure 7. a) Measured CO stretching frequencies, v_{CO} , for pure $Pt_n^+(CO)$ (n = 3-14) clusters (**a**) and fit to Equation (4) (——). b) Charge at the CO binding site for Pt_n^+ and $MOPt_{n-1}^+$ clusters, obtained from the empirical model and from DFT calculations.

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for the pure Pt_n^+ and doped $MoPt_{n-1}^+$ clusters. The resulting Q values are shown in Figure 7b for n=3-14, together with the excess charges, as obtained from DFT calculations for n=3-7. Error bars on the modelled Q values are propagated from the uncertainties on the fitted values of $\nu_{\rm CO}{}^\infty$ and d and the measured ν values using Equation (4). For cluster 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 of electron density can be estimated for the larger sizes by using the measured $\nu_{\rm CO}$. In particular, for n = 14, v_{CO} is redshifted upon molybdenum doping (see Figure 4a). This suggests that the CO-binding platinum site in $MoPt_{13}^{+}$ is less positively charged than that in Pt_{14}^{+} and indicates an electron transfer from molybdenum to platinum. This was also seen in the DFT calculations on the larger Pt₁₉⁺CO and MoPt₁₈⁺CO clusters.^[28] The empirical model yields local charges of +0.08e and +0.02e on the reactive sites in Pt₁₄⁺CO and MoPt₁₃⁺CO, respectively. Bader charge analysis, used in Ref. [28] for Pt_{19}^+CO and $MoPt_{18}^+CO$, gave local charges of +0.08e and +0.01e, respectively.

Finally, we discuss the correlation between the transfer of electron density and CO binding energies. In the Blyholder interpretation, bonding between CO and platinum is attributed to electron donation from the 5σ MO of CO to empty d orbitals of platinum as well as the back-donation process. Thus, molybdenum-dopant-induced electron redistribution in the cluster may affect both interactions in opposite ways and therefore requires 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_s⁺ CO and MoPt₄⁺ projected on to carbon, oxygen, and the platinum d states. As a reference, the energies of the MOs of free CO are indicated by vertical dashed lines. A first observation from Figure 8 is the strong stabilization of the 4σ and 5σ MOs,



Figure 8. Top: Partial density of states (PDOS) of Pt₅⁺CO and MoPt₄⁺CO. The states projected onto carbon, oxygen, and platinum (d states) are shown in red, blue, and gray, respectively. Fermi energies, *E*_F, are shown by a dotted line and the MOs of free CO by dashed lines. Bottom: Wavefunctions of two selected MOs of Pt₅⁺CO corresponding to the 4 σ (right) and 5 σ (left) MOs of free CO.

which, under the interaction with platinum, are located at energies of around -19 and -16.5 eV, respectively. The wavefunctions 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 platinum. It is important to note that the 5σ stabilization is stronger in MoPt₄⁺ than in Pt₅⁺. This is a consequence of the electronic charge transfer from platinum to molybdenum in this size of cluster, which leads to a larger density of unoccupied platinum d states available to interact with CO. The enhanced stabilization of 5σ seems to contradict the result that upon molybdenum doping the CO adsorption energy for this size cluster is reduced. However, this effect is over-compensated by the back-donation from the occupied d states of platinum to the antibonding $2\pi^{\ast}$ MO of CO. Located between -14 eV and the Fermi level, $E_{\rm F}$ several hybridized states of $2\pi^*$ character are found in the PDOS spectra.^[28] Because this MO is empty in free CO, these hybridized states are ascribed to the back-donation of electron density from platinum to CO. These hybridized states are antibonding for the C-O interaction, but bonding for the Pt-C bond.^[8,11] An inspection of Figure 8 shows that the density of these states is larger in $\mathrm{Pt}_{\mathrm{5}}^{\,+}$ than in MoPt₄⁺, especially near $E_{\rm F}$ due to the lower population of platinum d states below the Fermi energy in the doped cluster, as a consequence of the platinum-to-molybdenum electron transfer. An integration of the density of states of carbon and oxygen 1 eV below $E_{\rm F}$ gives around a 50% larger population in Pt_5^+ than in MoPt₄⁺. So we can conclude that for Pt_5^+ the effect of charge redistribution upon molybdenum doping has a stronger influence on the back-donation than on the $5\sigma{\rightarrow}d$ transfer, thereby reducing the CO binding energy. A similar influence of molybdenum doping, that is, a reduction of the CO adsorption energy, was observed previously for the Pt19+ cluster.^[28] However, in that case, a transfer of electron density from molybdenum to platinum was observed and the 5σ stabilization was more important than the $2\pi^*$ hybridization.

Conclusions

In this work, the effect of a single molybdenum 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 DFT calculations to investigate the reactivity of the clusters. Theory and experiment are well in agreement, showing that, upon doping, CO binding energies are reduced, in particular, for Pt₅⁺, Pt₆⁺, and Pt₇⁺. In addition, electronic charge transfer induced by molybdenum doping was characterized by IR spectroscopic measurements of the CO stretching frequencies and charge population analysis calculations. Electron transfer was 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 on the platinum 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 $2\pi^*$ back-donation are responsible for the Pt–CO bonding.

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However, these two mechanisms are affected oppositely by the charge at the atomic platinum binding site. This work has shown that in very small molybdenum-doped platinum clusters the effect of reduced $2\pi^*$ back-donation affects the CO binding more strongly than enhanced 5σ donation, thereby 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 of sensitively controlling the donation and back-donation effects in the Pt– CO interaction by doping and cluster size.

Experimental Section

CO reactivity measurements

The reactivity of the clusters towards CO was studied in a low-pressure collision cell,^[29,30] installed in a molecular beam set-up with a laser ablation cluster source and a time-of-flight mass spectrometer.^[31] Rectangular molybdenum and platinum targets were ablated by two independent Nd:YAG lasers (532 nm, 10 Hz). Before ablation, helium gas was introduced into the source by using a pulsed valve (7 bar, 10 Hz) to trigger cluster formation. In this study, the source was either maintained at room temperature or cooled 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 0–0.2 Pa. The intensities of the clusters and their CO complexes were analyzed by timeof-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 in the Supporting Information.

IR spectroscopy measurements

IR spectroscopy experiments were carried out in a dual-target dual-laser cluster set-up connected to a beamline of the Infrared Free Electron Laser at the Fritz Haber Institute of the Max Planck Society in Berlin (FHI FEL).^[32, 33] A detailed description of the cluster source is available in Ref. [34] and the principle of operation is similar to the source used for the CO reactivity measurements. The main difference is that for the IR spectroscopy experiments the CO gas was introduced through 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 $MoPt_{n-1}^{+}$ 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. At the position of the aperture, the 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 reflectron 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).^[19] An average pulse energy of 25 mJ and a step size of 2 cm^{-1} were used for the measurements. The bandwidth of the IR radiation was $10-15 \text{ cm}^{-1}$ (full-width at half-maximum).

Density functional theory calculations

DFT calculations on the bare clusters, Pt_n^+ and $MoPt_{n-1}^+$, and their corresponding CO complexes, $Pt_n^+(CO)$ and $MoPt_{n-1}^+(CO)$ (n=3-7), were carried out by using the TPSS exchange-correlation functional as implemented in the ORCA 3.0.3 software package.^[35] For the platinum and molybdenum atoms, 18 and 14 electrons were included in the valence, respectively, whereas the other electrons were described by the Stuttgart-Dresden ECP(def2-TZVP) pseudopotentials.^[36] All electrons of the carbon and oxygen atoms were treated explicitly with the aug-cc-pVDZ basis set. $\ensuremath{^{[37]}}$ The selection of this computational level was motivated by the results presented in 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. The first minimum-energy structures of the bare clusters ${\rm Pt}_n^+$ and ${\rm MoPt}_{n-1}^+$ (n=3–7) were searched, followed by an independent search of the corresponding CO complexes. This search was carried out by using the hybrid B3PW91 functional $^{\left[39,40\right] }$ in conjunction with the aug-cc-pVTZ (for carbon and oxygen) and aug-cc-pVTZ-pp (for platinum and molybdenum, pp represents a set of pseudopotential) 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 in the Supporting Information. Löwdin populations were calculated to study the atomic electronic charge distributions of the bare clusters and their CO complexes.

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Keywords: carbon monoxide · charge transfer · doping · IR spectroscopy · molybdenum · platinum

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