

CO adsorption on neutral iridium clusters

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Abstract. The adsorption of carbon monoxide on neutral iridium clusters in the size range of $n = 3$ to 21 atoms is investigated with infrared multiple photon dissociation spectroscopy. For each cluster size only a single $\nu(\text{CO})$ band is present with frequencies in the range between 1962 cm^{-1} ($n = 8$) and 1985 cm^{-1} ($n = 18$) which can be attributed to an atop binding geometry. This behaviour is compared to the CO binding geometries on clusters of other group 9 and 10 transition metals as well as to that on extended surfaces. The preference of Ir for atop binding is rationalized by relativistic effects on the electronic structure of the later $5d$ metals.

1 Introduction

The structure and chemical behaviour of small gas-phase transition metal (TM) clusters has been of great interest in the last decade due to their use as model systems for active sites in heterogeneous catalysis [1–4]. In particular the chemistry of carbon monoxide on transition metal clusters has been intensively studied [5–7] because of its relevance in a large number of catalytic processes. The chemical and physical properties of the clusters and their complexes can, in principle, be well characterized under isolated conditions in the gas phase. Thus they offer good benchmark systems for quantum chemical calculations, which become particularly challenging for the late $5d$ transition metals. The "CO on Pt(111) puzzle" is a well-known example for the difficulties in correctly predicting CO adsorption sites by density functional theory (DFT) [8,9]. The availability of structural information for cluster complexes is therefore vital for testing and improving theoretical methods.

Carbon monoxide is a ligand particularly suited for such investigations. The character of the M–CO bond is commonly described within the Blyholder model [10] of σ -donation and π -backdonation. The strength of the internal C–O bond and consequently the C–O stretching frequency is very sensitive to the degree of donation/backdonation and hence to the binding geometry and the electronic structure of the cluster. Infrared multiple photon dissociation (IR-MPD) spectroscopy allows the measurement of cluster size and composition specific IR-spectra of CO-complexes of transition metal clusters in the gas phase to determine, e.g., the CO binding geometries. Thereby it has been found that, in general, at low coverage CO binds to clusters of the $3d$ transition metals only in atop-configuration while for $4d$ and $5d$ transition metals bridging and face-capping CO ligands can also be present [7]. For instance, in a comparative study of the group 10 tran-

sition metals (Ni, Pd, Pt) it was found that Ni clusters bind CO only in atop positions while Pd clusters show a great variety of binding sites [11]. Pt clusters again show only atop binding, which was rationalised by the increasing role relativistic effects play in determining the electronic structure for heavier elements, leading to a direct influence of these effects on the chemical properties (see below). This direct influence has been observed previously for Pt(100) surfaces by Pacchioni *et al.* [12] using density functional theory calculations. Their results show a significant increase in the adsorption energies for both atop and bridge bound CO when relativistic effects were taken into account, with the effect being stronger for the atop bound CO. This leads to a change in the energy ordering of the binding geometries, with atop binding now being favoured over the bridge binding. The difference in the stabilization effect is related to the polarization of the CO 5σ lone pair. For the non-relativistic calculations the polarization towards the O atom is very strong for the bridge bound CO, thus reducing the strong Pauli repulsion with the substrate, but only moderate for the atop binding position. The inclusion of relativistic effects leads to a reduction of the kinetic energy repulsion due to mass-velocity corrections and a consequent shortening of the M–C bond length. This effect is large for the atop bound CO and the polarization of the CO 5σ lone pair towards the O atom increases significantly. On the other hand, the polarization for the bridge bound CO is only slightly increased compared to the non-relativistic case, leading to a smaller stabilisation effect compared to the atop binding configuration and only a minor contraction of the bond length [12]. Further details on the influence of relativistic effects on CO binding to late transition metals, especially the influence on the TM's $5d$ and $6d$ orbitals, can be found in reference [13].

A number of other DFT studies of the CO adsorption on Pt surfaces using Local Density Approximation (LDA)

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and General Gradient Approximation (GGA) failed to predict the correct absorption site on the Pt(111) surface, namely atop, in contrast to the calculated hollow site preference (see [8] and references therein). It has been shown that a better treatment of both relativistic effects and of the electronic structure, especially the exchange correlation, are important and can help to solve the puzzle [9, 14–16]. However, even with current DFT methods such calculations remain a challenging subject with the need for further benchmark data, preferably on elements which are strongly influenced by relativistic effects.

One of these elements is iridium, as it is adjacent to platinum in the $5d$ metals. Here we present our recent findings on the binding geometry of CO adsorbed on neutral Ir clusters in the size range of 3 to 21 atoms, thus complementing our previous studies on the group 9 transition metals Co and Rh [17].

2 Experimental Techniques

IR-MPD spectra are obtained by irradiating a molecular beam containing Ir_nCO complexes with intense IR radiation and measuring the changes induced in the mass distribution. At a vibrational resonance, a cluster complex can absorb (multiple) IR photons and, if the absorbed energy is sufficient, dissociation can be induced. IR spectra are constructed by analyzing the intensity changes as a function of the IR wavelength.

All experiments reported here are performed at the Free Electron Laser for Infrared eXperiments (FELIX) facility [18] in the Netherlands, and the details of the experiments have been reported elsewhere [19, 20]. Briefly described, iridium clusters are generated by laser ablation of a rotating Ir rod. A continuous stream of He serves as carrier gas, while a mixture of 1 % CO in He is introduced 60 mm downstream the ablation in a flow reactor [21]. The level of CO is adjusted such that the clusters adsorb at most a single CO molecule. The cluster beam expands into vacuum where it is irradiated by the counterpropagating FELIX beam. The charged particles are deflected from the molecular beam while the neutral clusters continue to propagate until they are ionized by 7.9 eV photons from an F_2 excimer laser in the acceleration region of a reflectron time-of-flight mass spectrometer. The molecular beam experiment runs at 10 Hz with a repetition rate of FELIX of 5 Hz so that mass spectra with and without FELIX radiation are recorded alternately, accounting for changes in cluster intensity. The IR region covered is 1580 cm^{-1} to 2040 cm^{-1} corresponding to the typical frequencies of the C–O stretches for the different binding geometries.

3 Results and Discussion

The depletion spectra of the Ir_nCO complexes for $n = 6$ to 13 are shown in figure 1. Similar spectra have been measured for the range from $n = 3$ to 21 and the dependence of the frequencies on the cluster size is shown in figure 2.

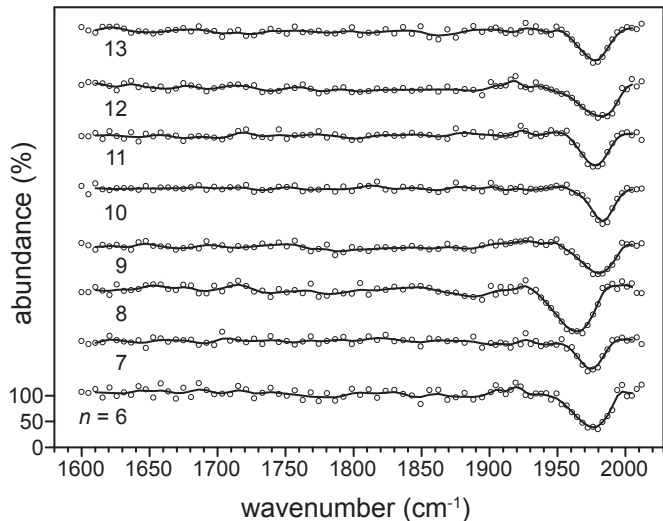


Fig. 1. IR-MPD spectra of CO adsorbed on neutral Ir clusters of different size n . The dots are the actual data points, the line is a binomially weighted five point average.

The peak positions of the $\nu(\text{CO})$ bands are determined by a least-squares fit to a Gaussian line shape function. In the $1580\text{--}2040\text{ cm}^{-1}$ range only a single band is present, which can be attributed to the internal $\nu(\text{CO})$ stretch of an atop, μ^1 , bound CO molecule as discussed below. The band position varies smoothly with cluster size, with the exception of $n = 8$. The reason for the shift in the frequency of more than 10 cm^{-1} compared to the values for $n = 7$ and $n = 9$ is unclear, but may be related to a change in geometry, as binding to lower coordinated metal atoms is expected to lead to a red-shift of the $\nu(\text{CO})$ stretching frequency (*vide infra*). Such a shift in frequency is unusual for other transition metal clusters [11, 17, 20], where in general the variations are smooth. However, there are exceptions. Platinum, for example, shows a step in the frequency dependence at $n = 11$ for both the neutral and the anionic clusters but not for the cations. For Ni cations and neutrals an increased value of $\nu(\text{CO})$ is observed for $n = 6$. In the case of Rh neutral clusters a negative shift in frequency occurs for $n = 6$, which is not present in both the cations and the anions. Though probably related to structural effects, the detailed reasons for these shifts remain unclear.

The assignment of the $\nu(\text{CO})$ bands to an atop binding geometry is made by comparison with previous measurements of CO molecules bound to TM surfaces [22, 23] and clusters [17, 20]. For the neutral Ir clusters being discussed here, the frequencies of $\nu(\text{CO})$ are at minimum 1962 cm^{-1} and at maximum 1985 cm^{-1} . This corresponds to a red-shift of about $40\text{--}60\text{ cm}^{-1}$ compared to the values reported for atop bound CO on Ir(100) and Ir(111) surfaces for low coverage, 2026 cm^{-1} and 2030 cm^{-1} , respectively [22, 23]. Such a shift is consistent with results for other transition metal clusters [11, 17, 20]. For example, the red-shift for atop bound CO on Pt clusters compared to different Pt surfaces is about $50\text{--}80\text{ cm}^{-1}$ [11], representing the general finding of a red-shift of the CO stretching frequen-

cies for all neutral (and anionic) transition metal clusters compared to the extended surface values. The stronger C–O bond activation on the cluster can be explained by the lower coordination of the metal atoms, similar to the effect that has been shown both experimentally [24] and theoretically [25,26] for CO adsorption on different Pt surfaces, where lower coordination numbers for the Pt atom binding the CO molecule lead to larger red shifts of the C–O stretching frequency. A possible explanation is related to the π -backdonation occurring from the interaction of the filled metal d -orbitals with the CO π^* -orbital. This effect is expected to be stronger for the lower coordinated clusters atoms. However, Curulla *et al.* calculate a similar contribution for both the σ -donation and π -backdonation regardless of the coordination number, suggesting a different reason, e.g. differences in substrate polarization or differences in Pauli repulsion [26].

CO binds to extended Ir surfaces only in atop positions, even at higher coverages [23,27,28]. Gajdoš *et al.* calculated frequencies for higher coordinated CO binding sites to be in a range from *ca.* 1730 to 1825 cm^{-1} [29], while also calculating $\nu(\text{CO})$ to be 2041 cm^{-1} for the atop binding geometry. There is a difference of between 240 and 150 cm^{-1} for the $\nu(\text{CO})$ stretching frequency for these higher coordinated sites, compared to our values. In contrast, the difference for the atop binding geometry is only about 65 cm^{-1} , supporting our assignment, even without taking into account the red-shift of the $\nu(\text{CO})$ bands for TM clusters compared to extended surfaces.

Higher coordinated CO ligands are present, however, in the saturated cluster carbonyl $\text{Ir}_6(\text{CO})_{16}$ that exists in two isomers, a black one with four μ^2 -CO ligands and a red one with four μ^3 -CO ligands. The $\nu(\text{CO})$ frequencies for their vibrations are *ca.* 1840 and 1760 cm^{-1} , respectively, significantly lower than our observations [30].

Zhou *et al.* measured CO stretching frequencies for IrCO in neon matrices [31]. Their value of 2024.5 cm^{-1} is about 50 cm^{-1} higher in energy compared to our mean value of 1976 cm^{-1} . The same trend is true when comparing their results for CoCO and RhCO with our earlier measurements on Co_nCO and Rh_nCO . The CO stretching frequencies in the neon matrices for Co and Rh are about 44 and 62 cm^{-1} higher in energy, respectively [17,31]. It is possible that these differences can be attributed to matrix effects since even the choice of the matrix element can change the frequency significantly (e.g. for RhCO from 2022.5 cm^{-1} in neon to 2007.6 cm^{-1} in argon).

The assignment to atop bound CO is also consistent with DFT calculations (UB3LYP) on Ir_{13} clusters with CO adsorbed by Okumura *et al.* [32]. They include scalar relativistic effects to calculate the interaction of Ir_{13} with CO and other small ligands, assuming a cuboctahedral geometry for the cluster. As they calculate a C–O stretching frequency of 2190 cm^{-1} for gas phase C–O, while the real value is 2143 cm^{-1} , their results need to be scaled for a comparison. This leads to a vibrational frequency of 1978 cm^{-1} for atop bound CO (unscaled 2021 cm^{-1}) which is in good agreement with our experimental value of 1976 cm^{-1} .

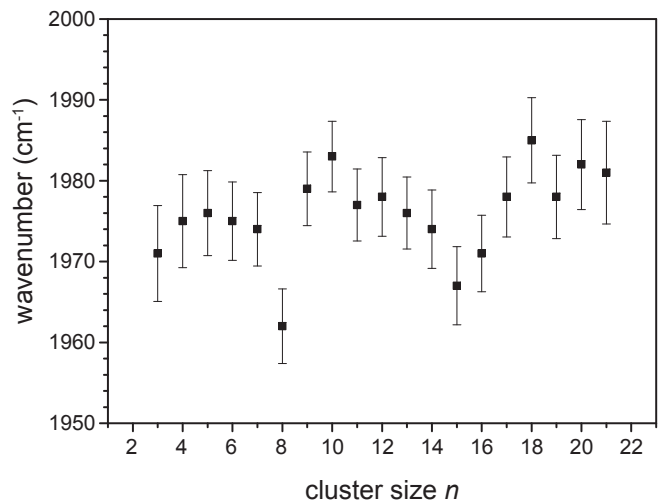


Fig. 2. Peak position of the $\nu(\text{CO})$ band for different cluster sizes n . The error stems from two parts: an uncertainty in the wavelength calibration of about 0.2 % that equally applies to all values (thus not changing relative peak positions) and the standard deviation of the least square fit to a Gaussian line shape function used to determine the peak positions ($\leq 2.5 \text{ cm}^{-1}$).

As mentioned above, to our knowledge, CO is bound to Ir surfaces only in atop positions [23,27,28]. In contrast to the case of Pt, previous DFT calculations have consistently predicted the experimentally observed binding site (see [33] and references therein). However, there exists no direct comparison of calculations with and without inclusion of relativistic effects as is the case for Pt. As the group 9 metal clusters show a very similar behaviour compared to the group 10 metal clusters, namely atop binding for the $3d$ metals, various binding sites for $4d$ metals and again atop binding for the $5d$ metals, a common reason for the change in CO adsorption geometry seems plausible. That is, that relativistic effects lead to a contraction and decrease in energy for the s - and p -orbitals while d - and f -orbitals increase in energy due to a radial expansion, with the effect being biggest for the $5d$ metals, moderate for the $4d$ metals and almost negligible for the $3d$ metals. This results in an ordering of the M–CO bond length for the group 10 metals that is $\text{Ni} < \text{Pt} < \text{Pd}$ whereas without relativistic influences the Pt–CO bond length would be the largest. As this decrease in bond length is large for atop binding but almost nonexistent for bridge binding, the former is strongly stabilized, leading to an unusual preference for this binding site for the late $5d$ metals [12]. It is interesting to compare this to the case of tungsten and rhenium. Both are $5d$ metals but, in contrast to Pt and Ir, their clusters bind CO in both atop positions and higher coordination sites [20]. This behaviour was rationalized by a smaller relative stabilization of the atop site compared to the late $5d$ TMs due to the spatially more extended $5d$ orbitals.

4 Conclusion

The adsorption of CO on neutral Ir clusters in the size range of 3 to 21 atoms has been investigated with IR-MPD spectroscopy. The vibrational spectra reveal that the only CO-binding geometry present is atop binding with $\nu(\text{CO})$ frequencies between 1962 cm^{-1} and 1985 cm^{-1} . These results complement earlier studies on the other group 9 and 10 TM clusters showing a similar behaviour for both groups with respect to the observed CO-binding geometries. The $3d$ metals bind CO only in atop position, the $4d$ metals have various (size dependent) binding sites and the $5d$ metals again show only atop binding. The behaviour of the $5d$ metals can be explained by the increased influence of relativistic effects on their electronic structure. Interestingly, the earlier $5d$ TMs tungsten and rhenium do not show the preference of platinum and iridium because of their spatially more extended $5d$ orbitals and the consequently smaller stabilisation of the atop binding. With our measurements we provide further benchmark data on a system that is strongly affected by relativistic effects, thus aiding in testing and developing appropriate theoretical models for the challenging calculations on TM clusters.

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