IR Signature of Size–Selective CO_2 Activation on Small Platinum Cluster Anions, Pt_n^- (n = 4–7)

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Abstract: *Infrared multiple photon dissociation spectroscopy has been employed to determine the nature of CO_2 binding to size-selected platinum cluster anions, Pt_n^- (n = 4–7). Interpreted in conjunction with density functional theory simulations, the results illustrate that the degree of CO_2 activation can be controlled by the size of the metal cluster, with dissociative activation observed on all clusters $n \geq 5$. Of potential practical significance, in terms of the use of CO_2 as a useful C1 feedstock, CO_2 is observed molecularly-bound, but highly activated, on the Pt_4^- cluster. It is trapped behind a barrier on the reactive potential energy surface which prevents dissociation.*

The binding and activation of CO_2 at metal centers has attracted huge attention in recent years, not least for environmental reasons. Incompletely coordinated metal centers, either within metal complexes[1] or supported, for example, on extended surfaces[2] or metal oxide frameworks,[3] represent attractive systems for CO_2 capture and/or chemical reduction, which would make CO_2 a potentially attractive (i.e., cheap) C1 feedstock.[4]

The challenges associated with CO_2 activation, however, are considerable. It is highly thermodynamically stable and the large kinetic barriers involved in the necessary bond-breaking make it unreactive in the gas-phase.[5] Any practical application of CO_2 thus requires the use of some effective catalyst (usually metal-based) to fix the molecule and promote at least partial bond-breaking. Some of the most detailed mechanistic insight into metal–CO_2 interactions is provided by gas-phase studies of model systems which can capture the details of the key interactions without the complexity provided by solvents or catalytic supports.[6]

Amongst the simplest of all model systems are isolated metal–ligand complexes, $M^{+/0/-}(CO_2)_n$, which nevertheless provide useful information on the fundamental interactions involved. Infrared spectroscopy has been employed extensively to study $M^+(CO_2)_n$ complexes by the Duncan group,[7] and others.[8] Cationic complexes exhibit interesting structures and coordination shells but only weak CO_2 activation. This reflects the η^1O "end on" OCO–M^+ binding, arising from the charge–quadrupole interaction.

Effective CO_2 activation comes from partial electron transfer into the antibonding $2\pi_u$ LUMO orbitals. In addition to reducing the overall bond strength, this has the effect of bending the CO_2.[9] In a recent series of detailed spectroscopic studies, Weber and coworkers have shown that such activation is achieved efficiently by gas–phase complexation with atomic metal anions, M^-. Binding to different transition metal anions, in particular, results in variable CO_2 activation depending on the degree of electron transfer.[9-10] This leads to a range of motifs including simple η^1C coordination, bidentate η^2C,O binding, oxalate formation, as well as metal insertion structures (i.e., dissociative activation), which have all been identified from their characteristic infrared signatures.[10-11] In this way, isolated metal centers behave in an analogous manner to both extended metal[2b] and metal oxide surfaces. Furthermore, extensive work on both cationic and anionic metal–ligand complexes has illustrated the effect of solvent–driven activation, i.e. where multiple CO_2 ligands are involved.[7a, 12]

Here, we illustrate an alternative way in which control can be exerted over the degree of CO_2 activation. Instead of complexation of multiple ligands or with anions of different elements, the binding motif and the extent of electron donation into the LUMO of a single CO_2 is tuned by the size of the platinum cluster anion Pt_n^- on which the CO_2 is adsorbed. Size–effects in the physico-chemical properties of metal clusters, including reactivity with small molecules, are well documented,[13] if poorly understood.

CO_2 activation / reduction on $Pt_n^{+/0/-}$ clusters proceeds on the same reactive potential energy surface as the CO oxidation reaction (CO + ½O_2). It has been studied experimentally on anionic,[14] neutral[15] and cationic platinum clusters.[16] Hintz and Ervin studied the Pt_n^- + CO_2 reaction under single collision conditions and found that for small clusters (n < 7), the reaction proceeds by sequential addition of CO_2 without fragmentation and up to 100 times slower than collision rate.[17] They were unable to determine the nature of the adsorption in their mass spectrometric studies. Koszinowski *et al.* observed no CO_2 adsorption in reaction with small Pt_n^+ (n<6) clusters,[18] though these are effective in C–H activation.[19] Relevant to the studies here, CO_2 was found to adsorb only on cobalt cluster anions Co_n^- with n > 7, and a strong C=O stretching band around 1900 cm^{-1} signified dissociative binding.[20]

The instrument and IR source used in these studies have been described previously.[20-21] Briefly, platinum cluster anions were generated by pulsed laser ablation of a ^{194}Pt isotopically-enriched target. CO_2 was introduced to a reaction channel

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downstream at ~30 °C and the resulting anionic cluster distribution was probed by reflectron time-of-flight mass spectrometry. The experiment operates at 10 Hz and mass–resolved infrared multiple photon dissociation (IR-MPD) spectra were recorded by subjecting alternate pulses to the output of the FHI infrared free electron laser operating at 5 Hz in the spectral region 400 – 2100 cm^{-1}. Spectra were recorded as fractional (percentage) depletions in the intensity of parent ion signals, $[Pt_nCO_2]^-$, in the mass spectrum as a function of infrared wavenumber.

In order to help interpret the experimental spectra, a comprehensive DFT study of energetically low-lying structural isomers in different spin states was performed for Pt_4^-, Pt_5^- and their CO_2 complexes. A range of functionals and basis sets was employed (see Supporting Information) with comparisons shown below for the representative UB3P86-SDD functional-basis set combination. Scalar relativistic effects were included via the use of the Stuttgart/Dresden effective core potential. Use of the TPSS functional and the larger, Def2TZVP, basis set made no qualitative difference to the relative energy ordering of key structures. Calculated frequencies have been scaled by a factor of 1.0133 to match the known frequency of the free CO_2 antisymmetric stretch.[22] Calculations were performed using the Gaussian09 suite of programs[23] – the Supporting Information contains further details of the computational methods and results.

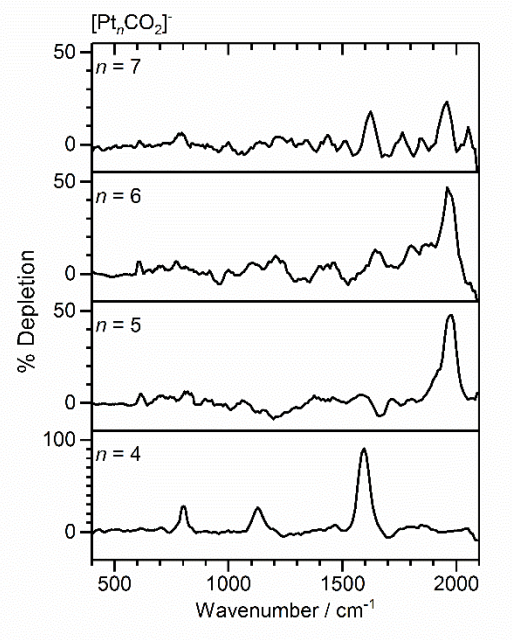

Figure 1. IR–MPD spectra of $[Pt_nCO_2]^-$ (n = 4–7) clusters illustrating the change from molecular adsorption (n = 4) to dissociative adsorption ($n \geq 5$).

Figure 1 shows the IR-MPD spectra of $[Pt_nCO_2]^-$ (n = 4–7) clusters in the spectral region 400 – 2100 cm^{-1}. A clear change in the nature of the CO_2 binding between n = 4 and n = 5 is apparent: The spectrum of the $[Pt_4(CO_2)]^-$ complex exhibits three intense, well–resolved infrared bands centered at 800 cm^{-1}, 1130 cm^{-1} and 1600 cm^{-1}. In marked contrast, these bands are essentially absent in the spectrum of the n = 5 cluster (making a very weak reappearance for n = 6, 7). Instead, for n > 4, an intense new band is observed in the region 1950 – 2000 cm^{-1}.

The differences in the IR-MPD spectra for different clusters are readily interpreted as a qualitative change in the nature of the CO_2 binding to Pt_n^- clusters as a function of cluster size. The three infrared bands in the spectrum of $[Pt_4(CO_2)]^-$ signify the presence of strongly activated, but molecularly–adsorbed, CO_2. The absence of these bands on the $[Pt_5(CO_2)]^-$ cluster, and the new 1950 – 2000 cm^{-1} band, characteristic of the carbonyl, C=O, stretch,[24] indicate complete, dissociative activation of CO_2.

Minor dips in the $[Pt_4CO_2]^-$ spectrum at 1700 ± 20, 1500 ± 20, 1220 ± 20 and 750 ± 20 cm^{-1}, match well with peaks in the depletion spectrum of the larger $[Pt_4(CO_2)_2]^-$ complex which fragments into this species by CO_2 loss. Similar weak enhancements arise for depletion of $[Pt_5(CO_2)_2]^-$ into $[Pt_5(CO_2)]^-$ (see Supporting Information).

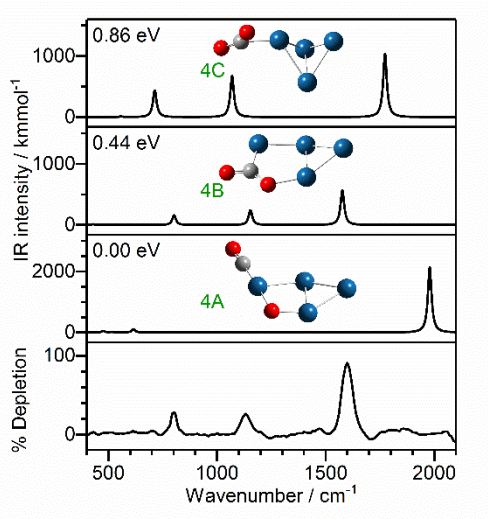

Figure 2. Comparison of the IR–MPD spectrum of $[Pt_4CO_2]^-$ with simulated IR spectra for energetically low-lying isomers, all with a quartet spin state. The absence of a CO absorption band around 2000 cm^{-1} indicates molecular adsorption and the simulated spectrum from the lowest energy molecularly-adsorbed isomer (E = 0.44 eV) represents an excellent match with the experimental data. All energies are relative to the global minimum and are zero-point corrected.

Figure 2 shows the spectrum of the $[Pt_4(CO_2)]^-$ cluster together with calculated IR spectra for the three lowest energy isomers computed. For ease of visual comparison, the simulated spectra have had a 20 cm^{-1} linewidth function applied. DFT calculations predict a global minimum $[OCPt_nO]^-$ structure with CO_2 dissociated on the cluster surface. The experimental spectrum, however, shows no evidence for such a structure – the expected carbonyl band is absent. Instead, the spectrum matches well with that simulated for the lowest energy isomer with molecularly–adsorbed CO_2, (structure 4B), which lies 0.44 eV above the putative global minimum. In this structure, the CO_2 moiety is strongly bent and bound in a side-on fashion bridging two adjacent platinum atoms (see Figure 3a). At 1.26 Å and 1.32 Å, both bonds are markedly longer than in free CO_2 (calculated at 1.19 Å), reflecting significant activation. Both the lengths of the activated bonds and the calculated OĈO bond angle, at 127°, are closer to their respective values in the $CO_2^{\bullet-}$ radical anion (calculated at 1.28 Å and 134°) than to corresponding values in CO_2. Natural population analysis of structure 4B (see Supporting Information) indicates a partial charge on the CO_2 moiety of –0.6e, *i.e.*, near complete electron transfer from the Pt_4^- cluster.

This degree of activation is reflected in the vibrational frequencies associated with the CO_2 moiety. Figure 3b shows a comparison of the IR–MPD spectrum with the calculated spectra of free CO_2 and $CO_2^{\bullet-}$. The strong ν_3 at 1600 cm^{-1} is red-shifted by *ca.* 750 cm^{-1} relative to the free CO_2 equivalent, and all three bands lie much closer to the $CO_2^{\bullet-}$ values. Weber has correlated the red-shifts observed in CO_2 stretching frequencies with the degree of electron transfer in $[MCO_2]^-$ complexes and a 750 cm^{-1} red-shift corresponds to full electron transfer.[9] Note, however, that these are not directly comparable as the bridged binding observed here affects the effective reduced mass as well as the force constant for the vibrational mode.

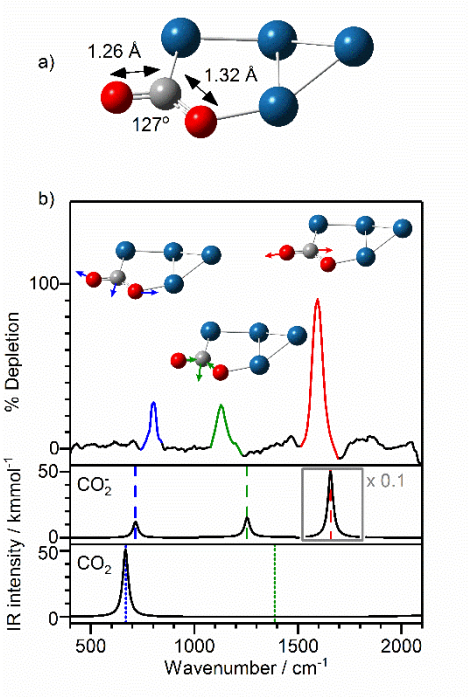

Figure 3. a) The calculated structure, and b) vibrational modes of the lowest energy isomer of $[Pt_4CO_2]^-$ identified with molecularly-adsorbed CO_2 (E = 0.44 eV). The dotted lines indicate the wavenumbers of the bend (667 cm^{-1}) and infrared inactive symmetric stretch (1388 cm^{-1}) vibrations in free CO_2 (the asymmetric stretch lies at 2349 cm^{-1}).[22] The dashed lines indicate the wavenumbers of the bend (714 cm^{-1}), symmetric stretch (1254 cm^{-1}), and asymmetric stretch (1658 cm^{-1}) vibrations in free CO_2^-.[25]

Figure 4 shows a truncated reaction potential energy surface for the Pt_4^- + CO_2 reaction (see Supporting Information for an extended version). The fluxional nature of the Pt_4^- cluster itself is a complicating factor in these calculations with many very similar structures obtained. Where these are pertinent, they are identified in Figure 4 as different levels in the same potential well. A C-bound η^1 starting structure leads *via* a submerged barrier to Structure 4B, which is clearly an entrance–channel complex. The fact that the percentage depletion observed for the 1600 cm^{-1} band exceeds 90% (Figure 2) indicates a remarkably pure isomeric distribution: >90% of $[Pt_4(CO_2)]^-$ complexes in the cluster beam exhibit this spectral feature. In turn, this suggests that the vast majority of clusters become kinetically trapped in this minimum (structure 4B), behind a significant barrier which prevents access to the global minimum, fully-dissociated, structure (4A). The transition state is similar to that for the reverse, CO oxidation reaction, on Pt and other clusters. [16b, 26]

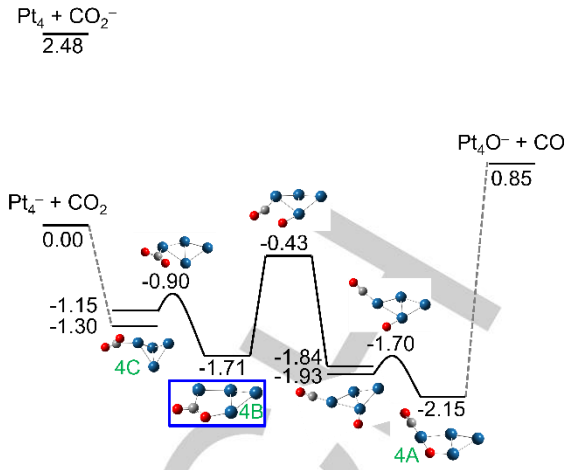

Figure 4. A truncated potential energy surface for the adsorption and dissociation of CO_2 on Pt_4^- ($2S$+1= 4) calculated at the B3P86/SDD level of theory (relative energies represent zero-point corrected vales in eV). Despite a global minimum structure with dissociatively-adsorbed CO_2 (i.e., structure 4A), the experimental spectra are consistent with a strongly activated, but molecularly-adsorbed, structure 4B, lying 1.71 eV below the CO_2 + Pt_4^- asymptote. An extended pathway is included in the Supporting Information.

Figure 5 shows a comparison of the experimental IR–MPD spectrum of $[Pt_5CO_2]^-$ with the simulated spectra for a range of low energy structures. From the absence of the molecular $CO_2/CO_2^{\bullet-}$ vibrations, it is clear that the molecule is dissociatively–adsorbed. The lowest energy molecularly–bound structure, 5D, lies 0.27 eV above the putative ground state but there is no evidence for it in the spectrum, which is well–reproduced by that of the global minimum structure. The 1980 cm^{-1} band observed is assigned to a η^1– (*i.e.*, atop–) bound carbonyl group. Bands corresponding to η^2–(5C) and η^3–bound structures (5E) are more red–shifted. This is consistent with previous studies of CO adsorption on clusters[24] and extended surfaces.[27] The CO stretch itself is not particularly diagnostic of the structure of the Pt_5O substrate and does not permit the unambiguous determination of the full structure, though the weak feature at 600 cm^{-1} may signify bridging O-atoms.[16b, 28] The assignment of the spectrum to dissociatively–adsorbed CO_2 indicates a reduced barrier to dissociation on the Pt_5^- + CO_2 potential energy surface compared with that for Pt_4^- + CO_2.

The carbonyl stretch is also the dominant feature in the spectra of the $[Pt_nCO_2]^-$ (n = 6, 7) (see Figure 1), but there is also weak evidence for the co-existence of isomers with molecularly-adsorbed CO_2. The IR–MPD spectrum is particularly weak for the n = 7 cluster despite the efficient production of the parent ion in the cluster beam (see Supporting Information) with even the carbonyl peak limited to *ca.* 20% depletion.

Present technology for making practical use of CO_2 is most advanced for the reverse water gas-shift reaction, which suffers from extensive side reactions, and syngas synthesis from dry reforming.[29] Both processes are highly endothermic. This usage is unlikely to change in the near future but the type of clean control over the degree of CO_2 activation demonstrated here in $[Pt_4CO_2]^-$ could lead to different and more interesting reactivity. In many ways, this direct partial activation of CO_2, if it could be implemented practically, may offer significant advantages as the CO_2 dissociation step, rather than CO / O atom transport and desorption, often provides the rate limiting step in reactions involving metal nanoparticles including platinum.[29]

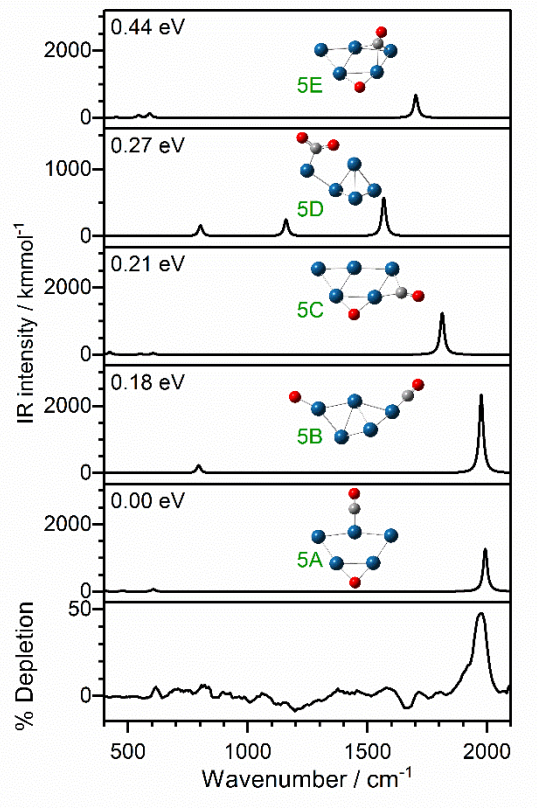

Figure 5. Comparison of the IR–MPD spectrum of $[Pt_5CO_2]^-$ with simulated IR spectra for energetically low-lying isomers. Only quartet spin states are shown. Similar structural motifs are predicted for sextet states (see Supporting Information). The band at 1980 cm^{-1} is a clear signature of atop-bound (η^1) CO indicating dissociative adsorption of CO_2. The weak feature around 600 cm^{-1} may indicate O-atoms bound at 2-atom bridge sites. All energies are relative to the global minimum and are zero-point corrected.

In any practical application it will almost certainly be necessary to deposit active size-selected clusters on a suitable electron donating (*e.g.*, metal oxide, or carbon) support. Preserving upon deposition the very features of the cluster which make it chemically interesting will present a substantial challenge. However, this work has identified a potentially useful system to target as well as the key features which make it interesting to aim for – the negative charge transfer driving the CO_2 activation and the energetic barrier behind which the activated species remains trapped. It remains to be seen if it proves possible to maintain these features upon deposition on a suitable support.

In summary, IR action spectroscopy has revealed clear size–dependence in the nature of CO_2 adsorption on small Pt_n^- clusters. CO_2 is highly activated but remains molecularly–adsorbed on Pt_4^-. Larger clusters show conclusive evidence for dissociative adsorption. In all cases, the IR–MPD spectra are very well–reproduced by simulated spectra of energetically low-lying structures from quantum chemical calculations. It is likely that these differing degrees of activation will lead to different and interesting chemistry in reactions with other small molecules.

Acknowledgements

This work is funded by EPSRC under Programme Grant EP/L005913 and SCG Chemicals Co. via the Oxford Centre of Excellence Innovation Fund. The Oxford authors would like to acknowledge the use of the University of Oxford Advanced Research Computing (ARC) facility in carrying out this work. http://dx.doi.org/10.5281/zenodo.22558. AEG thanks Magdalen College, Oxford for her graduate studentship. AF thanks the Deutsche Forschungsgemeinschaft for a Heisenberg grant (FI 893/5).

Keywords: CO_2 activation • platinum anion clusters • IR-MPD • heterogeneous catalysis • ab initio calculations

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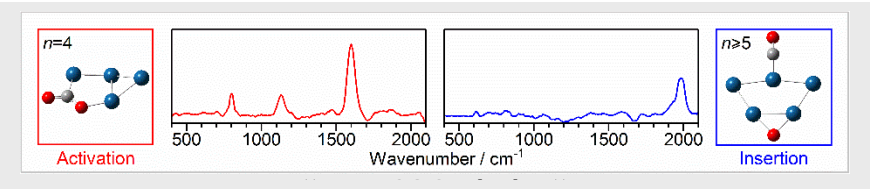

Dial-up-activation: Small gas-phase platinum cluster anions show size-dependence in their ability to activate carbon dioxide. On Pt_4^-, CO_2 is highly activated but remains molecularly intact despite a dissociative global minimum structure. This is likely to be highly reactive towards other small molecules as a first step towards converting CO_2 to more useful products.

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IR Signature of Size–Selective CO_2 Activation on Small Platinum Cluster Anions, Pt_n^- (*n* = 4–7)

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