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IR Signature of Size-Selective CO₂ Activation on Small Platinum Cluster Anions, Pt_n⁻ (n = 4–7)

Alice E. Green, Jasmin Justen, Wieland Schöllkopf, Alexander S. Gentleman, André Fielicke,* and Stuart R. Mackenzie*

Abstract: Infrared multiple photon dissociation spectroscopy (IR-MPD) has been employed to determine the nature of CO₂ 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 CO₂ activation can be controlled by the size of the metal cluster, with dissociative activation observed on all clusters n ≥ 5. Of potential practical significance, in terms of the use of CO₂ as a useful C1 feedstock, CO₂ is observed molecularly-bound, but highly activated, on the Pt₄⁻ cluster. It is trapped behind a barrier on the reactive potential energy surface which prevents dissociation.

The binding and activation of CO₂ 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 CO₂ capture and/or chemical reduction, which would make CO₂ a potentially attractive (i.e., cheap) C1 feedstock.^[4]

The challenges associated with CO₂ 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 CO₂ 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–CO₂ 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/-}(CO₂)_n, which nevertheless provide useful information on the fundamental interactions involved. Infrared spectroscopy has been employed extensively to study M⁺(CO₂)_n complexes by the Duncan group,^[7] and others.^[8] Cationic complexes exhibit interesting structures and coordination shells but only weak CO₂ activation. This reflects the η¹O “end on” OCO-M⁺ binding, arising from the charge-quadrupole interaction.

Effective CO₂ activation comes from partial electron transfer into the antibonding 2π_u LUMO orbitals. In addition to reducing the overall bond strength, this has the effect of bending the CO₂.^[9] In a recent series of detailed spectroscopic studies, Weber and co-workers 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 CO₂ activation depending on the degree of electron transfer.^[9,10] This leads to a range of motifs including simple η¹C coordination, bidentate η²C,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.^[12] Furthermore, extensive work on both cationic and anionic metal-ligand complexes has illustrated the effect of solvent-driven activation, that is, where multiple CO₂ ligands are involved.^[7a,12a]

Here, we illustrate an alternative way in which control can be exerted over the degree of CO₂ 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 CO₂ is tuned by the size of the platinum cluster anion Pt_n⁻ on which the CO₂ is adsorbed. Size-effects in the physico-chemical properties of metal clusters, including reactivity with small molecules, are well documented,^[13] if poorly understood.

CO₂ activation/reduction on Pt_n^{+0/-} clusters proceeds on the same reactive potential energy surface as the CO oxidation reaction (CO + 1/2 O₂). It has been studied experimentally on anionic,^[14] neutral^[15] and cationic platinum clusters.^[16] Hintz and Ervin studied the Pt_n⁻ + CO₂ reaction under single collision conditions and found that for small clusters (n < 7), the reaction proceeds by sequential addition of CO₂ 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 CO₂ adsorption in reaction with small Pt_n⁺ (n < 6) clusters,^[18] though these are effective in C–H

[*] A. E. Green, Dr. A. S. Gentleman, Prof. S. R. Mackenzie
Department of Chemistry, University of Oxford
Physical and Theoretical Chemistry Laboratory
South Parks Road, Oxford, OX1 3QZ (UK)
E-mail: stuart.mackenzie@chem.ox.ac.uk

J. Justen, Dr. A. Fielicke
Institute for Optics and Atomic Physics
Technische Universität Berlin
Hardenbergstrasse 36, 10623 Berlin (Germany)

Dr. W. Schöllkopf, Dr. A. Fielicke
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg, 4–6, 14195 Berlin (Germany)
E-mail: fielicke@fhi-berlin.mpg.de

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activation.^[19] Relevant to the studies here, CO₂ 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 ¹⁹⁴Pt isotopically-enriched target. CO₂ was introduced to a reaction channel downstream at ca. 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_nCO₂]⁻, 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 Pt₄⁻, Pt₅⁻, and their CO₂ 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 CO₂ 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 shows the IR-MPD spectra of [Pt_nCO₂]⁻ ($n = 4$ –7) clusters in the spectral region 400–2100 cm⁻¹. A clear change in the nature of the CO₂ binding between $n = 4$ and $n = 5$ is apparent: The spectrum of the [Pt₄(CO₂)]⁻ 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 CO₂ binding to Pt_n⁻ clusters as a function of cluster size. The three infrared bands in the spectrum of [Pt₄(CO₂)]⁻ signify the presence of strongly activated, but molecularly-adsorbed, CO₂. The absence of these bands on the [Pt₅(CO₂)]⁻ cluster, and the new 1950–2000 cm⁻¹ band, characteristic of the carbonyl, C=O, stretch,^[24] indicate complete, dissociative activation of CO₂.

Minor dips in the [Pt₄CO₂]⁻ spectrum at 1700 ± 20, 1500 ± 20, 1220 ± 20 and 750 ± 20 cm⁻¹, match well with peaks in the depletion spectrum of the larger [Pt₄(CO₂)₂]⁻ complex which fragments into this species by CO₂ loss. Similar weak enhancements arise for depletion of [Pt₅(CO₂)₂]⁻ into [Pt₅(CO₂)]⁻ (see Supporting Information).

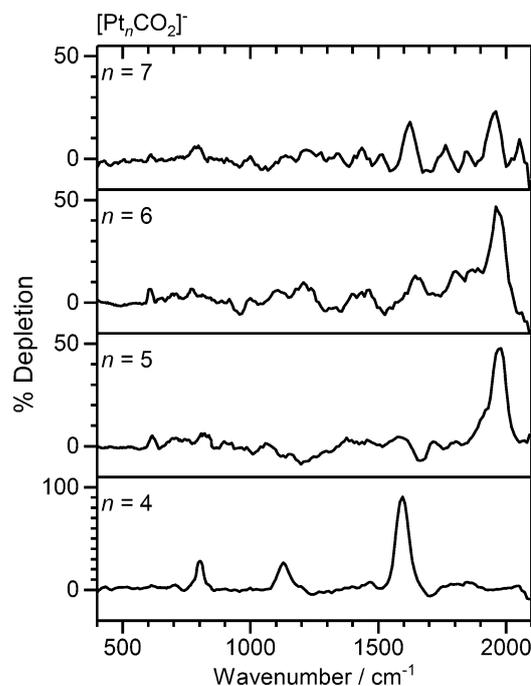


Figure 1. IR-MPD spectra of [Pt_nCO₂]⁻ ($n = 4$ –7) clusters illustrating the change from molecular adsorption ($n = 4$) to dissociative adsorption ($n \geq 5$).

Figure 2 shows the spectrum of the [Pt₄(CO₂)]⁻ 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 CO₂ dissociated on the cluster

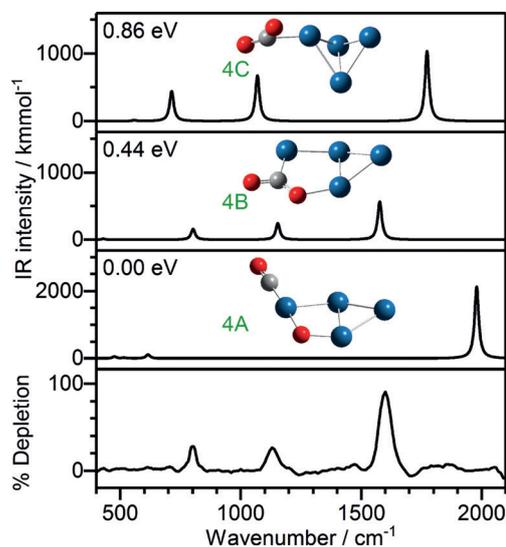


Figure 2. Comparison of the IR-MPD spectrum of [Pt₄CO₂]⁻ with simulated IR spectra for energetically low-lying isomers, all with a quartet spin state. The absence of a CO absorption band around 2000 cm⁻¹ indicates molecular adsorption and the simulated spectrum from the lowest energy molecularly-adsorbed isomer (4B, $E = 0.44$ eV) represents an excellent match with the experimental data. All energies are relative to the global minimum and are zero-point corrected.

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 CO₂, (structure 4B), which lies 0.44 eV above the putative global minimum. In this structure, the CO₂ moiety is strongly bent and bound in a side-on fashion bridging two adjacent platinum atoms (see Figure 3a). At 1.26 Å and

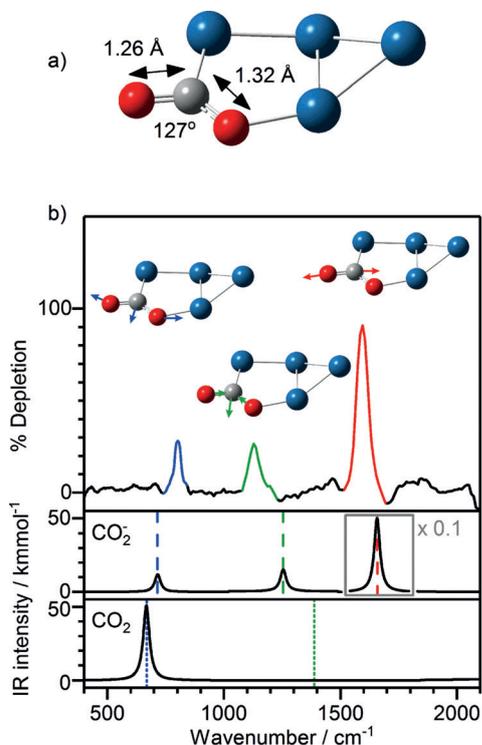


Figure 3. a) The calculated structure, and b) vibrational modes of the lowest energy isomer of [Pt₄CO₂]⁻ identified with molecularly-adsorbed CO₂ (4B, *E* = 0.44 eV). The dotted lines indicate the wavenumbers of the bend (667 cm⁻¹) and infrared inactive symmetric stretch (1388 cm⁻¹) vibrations in free CO₂ (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 CO₂⁻.^[25]

1.32 Å, both bonds are markedly longer than in free CO₂ (calculated at 1.19 Å), reflecting significant activation. Both the lengths of the activated bonds and the calculated O–C–O bond angle, at 127°, are closer to their respective values in the CO₂⁻ radical anion (calculated at 1.28 Å and 134°) than to corresponding values in CO₂. Natural population analysis of structure 4B (see Supporting Information) indicates a partial charge on the CO₂ moiety of -0.6e, i.e., near complete electron transfer from the Pt₄⁻ cluster.

This degree of activation is reflected in the vibrational frequencies associated with the CO₂ moiety. Figure 3b shows a comparison of the IR-MPD spectrum with the calculated spectra of free CO₂ and CO₂⁻. The strong ν₃ band at 1600 cm⁻¹ is red-shifted by ca. 750 cm⁻¹ relative to the free CO₂ equivalent, and all three bands lie much closer to the CO₂⁻ values. Weber has correlated the red-shifts observed in

CO₂ stretching frequencies with the degree of electron transfer in [MCO₂]⁻ 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 4 shows a truncated reaction potential energy surface for the Pt₄⁻ + CO₂ reaction (see Supporting Information for an extended version). The fluxional nature of the Pt₄⁻ 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.

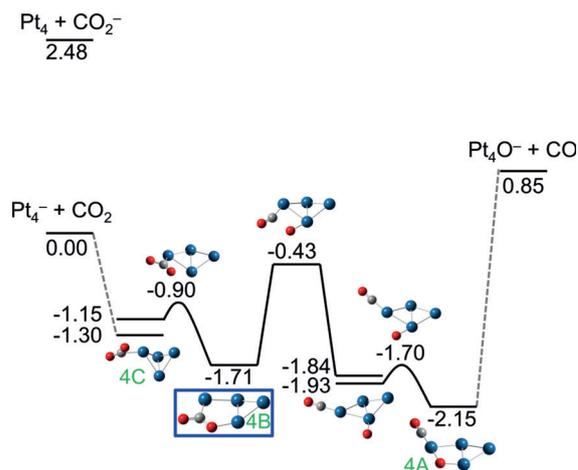


Figure 4. A truncated potential energy surface for the adsorption and dissociation of CO₂ on Pt₄⁻ (2S + 1 = 4) calculated at the B3P86/SDD level of theory (relative energies represent zero-point corrected values in eV). Despite a global minimum structure with dissociatively-adsorbed CO₂ (i.e., structure 4A), the experimental spectra are consistent with a strongly activated, but molecularly-adsorbed, structure 4B, lying 1.71 eV below the CO₂ + Pt₄⁻ asymptote. An extended pathway is included in the Supporting Information.

A C-bound η¹ 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 [Pt₄(CO₂)]⁻ 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 5 shows a comparison of the experimental IR-MPD spectrum of [Pt₅CO₂]⁻ with the simulated spectra for a range of low energy structures. From the absence of the molecular CO₂/CO₂⁻ 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

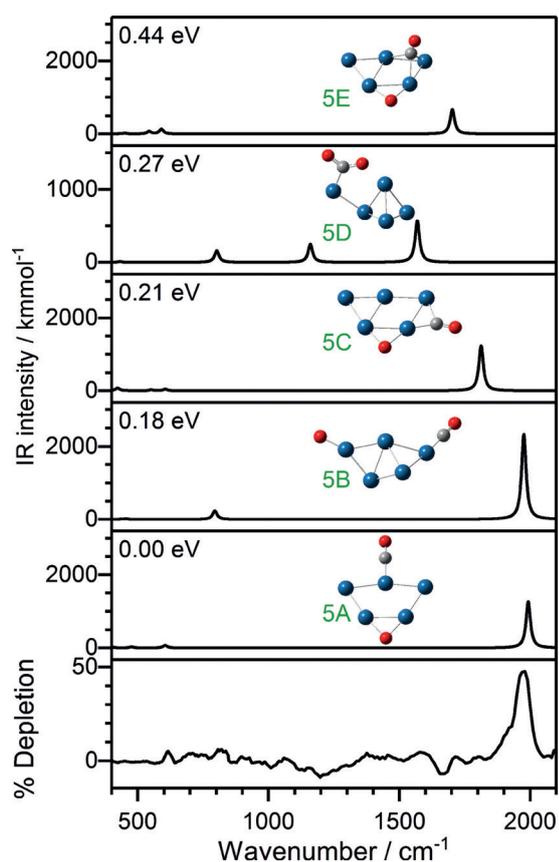


Figure 5. Comparison of the IR-MPD spectrum of $[\text{Pt}_5\text{CO}_2]^-$ with simulated IR spectra for energetically low-lying isomers. Only quartet spin states are shown. Similar structural motifs are predicted for sextet states (see Supporting Information). The band at 1980 cm^{-1} is a clear signature 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.

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 $\text{Pt}_5^- + \text{CO}_2$ potential energy surface compared with that for $\text{Pt}_4^- + \text{CO}_2$.

The carbonyl stretch is also the dominant feature in the spectra of the $[\text{Pt}_n\text{CO}_2]^-$ ($n=6, 7$) (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 $[\text{Pt}_4\text{CO}_2]^-$ 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. The CO_2 dissociation step, rather than CO or O atom transport and desorption, often provides the rate limiting step in reactions involving metal nanoparticles including platinum.^[29]

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.

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Conflict of interest

The authors declare no conflict of interest.

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