

Platinum-hydrogen vibrations and low energy electronic excitations of 13-atom Pt nanoclusters

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Abstract

Two Pt–H vibrational bands at 1679 cm⁻¹ and 1392 cm⁻¹ observed with 13-atom Pt clusters supported in LTL zeolite by Fourier Transform Infrared (FTIR) spectroscopy confirms that H atoms bridge two Pt atoms across the edges of the metal cluster. An additional broad absorption band centred near 2200 cm⁻¹ which exhibits some substructure is assigned to low energy electronic excitations across the HOMO-LUMO gap of the developing band structure of the nanocluster.

Introduction

Small metal clusters are of fundamental scientific interest because they are intermediates between atoms and bulk solids. For example, the ionization energy varies from 9.0 eV for the isolated atom to the work function of the bulk metal, which is 5.3 eV. Thus, by tuning the size of particles the availability of electrons for redox reactions or to participate in chemical

bonds can be varied over a huge range compared with thermal energy which amounts to $RT = 26 \text{ meV}$ (2.5 kJ mol^{-1}) at 300 K .¹ This is the main origin of nanosize effects in chemistry.

Furthermore, the fraction of corner, edge and kink sites relative to the total number of surface sites is larger in nanoparticles. These lower coordinated sites often lead to stronger bonding, an effect that comes in addition to that of the position of electronic energy levels.¹

It has been demonstrated that it is possible to generate nearly monodisperse platinum nanoclusters with 13 ± 2 atoms.^{2,3} They are of close to icosahedral or cuboctahedral symmetry, but the exact structure varies to some extent as a function of the amount of chemisorbed hydrogen due in part to the open shell electronic structure.⁴ In contrast to bulk Pt which chemisorbs one hydrogen atom per surface Pt atom the nanoclusters adsorb up to 3 H per Pt.³ The adsorption isotherm was shown to saturate at this value already at a hydrogen pressure of ca. 70 mbar at room temperature.³ Up to 3 H atoms per Pt were also reported for small size ($\leq 1 \text{ nm}$) $\gamma\text{-Al}_2\text{O}_3$ -supported Pt nanoparticles, albeit at temperatures of 166-188 K.⁵ It is known that the H–Pt binding energy depends considerably on the type of support.⁶ Thus, the H_2 desorption energy from the Pt_{13} clusters amounts to 2.10 eV in LTL zeolite,⁶ 1.36 eV in Y zeolite,⁴ but only 0.8 eV from Pt(111) single crystal surfaces,⁷ and while the preferred binding site on the (111) surface is the three-fold hole the large number of adsorbed H per cluster suggests that H forms preferentially a bridging bond between two neighbouring atoms (edge site). In some cases, terminal bonding to single atoms has been observed (on-top site).

There have been numerous experimental studies of the vibrations of adsorbed hydrogen on bulk samples by infrared spectroscopy, neutron scattering, low-energy electron diffraction (LEED) or high resolution electron energy loss spectroscopy (HREELS). The observed features were often weak and their assignment remains somewhat controversial despite the help of theoretical work. First of all, there is general agreement that H bound on-top Pt leads

to IR absorption around 2100 cm^{-1} , dependent somewhat on the environment or support.^{8,9,10} Vibrations of terminal H were observed by IR absorption for the (110), (100), (111) and step-rich (111) surfaces of Pt electrodes near the hydrogen evolution potential.¹⁰ The discussion is more about the bridging edge and the three-fold or four-fold hole adsorption sites. Energy loss bands at 550 cm^{-1} and 1230 cm^{-1} at high hydrogen coverage on Pt(111) were assigned to a vibration perpendicular to the surface and the degenerate vibration parallel to the surface in a threefold hole, respectively.⁸ In many studies this is the accepted binding site for H on Pt(111). However, in contradiction to this, Yu et al.¹¹ predict the perpendicular vibration of this site at 894 cm^{-1} and the parallel vibration at 564 cm^{-1} . H in the four-fold hole on Pt(100) is calculated at 616 cm^{-1} while a 1266 cm^{-1} absorption on Pt(111) is assigned to a subsurface adsorption site.¹¹ Furthermore, the on-top site was predicted at 1500 cm^{-1} ,¹¹ significantly lower than by Baro et al.⁸ And the bridge-bonded H was said to be expected at 989 and 926 cm^{-1} on Pt(100) and at 947 cm^{-1} and 983 cm^{-1} on Pt(111).¹¹ A more recent combined experimental and theoretical study of an H monolayer on Pt(111) assigns the bands at 550 cm^{-1} and at 1233 cm^{-1} to the asymmetric and symmetric in-plane vibrations at the fcc three-fold hole site, while an additional mode at 910 cm^{-1} was attributed to a hybrid-type vibration.⁷

We are not aware of any experimental studies of hydrogen vibrations on Pt clusters, however, as a B3LYP simulation of a Pt(100) surface a planar Pt_5 cluster with either one or five adsorbed hydrogen atoms added on-top gave frequencies all well above 2000 cm^{-1} .¹² In order to overcome the experimental deficit relating to H vibrations on Pt clusters, to support the binding geometry of hydrogen on the Pt_{13} and to set it in relation to the observations in macroscopic specimens we undertook an infrared spectroscopic study of hydrogen chemisorption on Pt_{13} clusters in LTL zeolite.

Experimental procedures

In short, Pt/KL samples with a Pt loading of 6% wt were prepared as follows: commercial KL zeolite (CU Chemie Uetikon, Switzerland) was stirred in an aqueous solution of $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ at 343 K. The product was filtered off, dried and calcined in a stream of O_2 using a heating rate of 0.5 K min^{-1} from room temperature up to 623 K where it was held for 5 h. It was then reduced in flowing H_2 at a heating rate of 4 K min^{-1} up to 507 K where it was kept for 1 h. Following this protocol, with full details given elsewhere,^{2-4,6} the 13-atom clusters are obtained reproducibly, which is verified best by EXAFS. The zeolite was then pressed to thin wavers and placed in the reaction chamber of a Magna 560 FT-IR spectrometer at a spectral resolution of 2 cm^{-1} . The sample was heated under vacuum at 573 K for 3 h for complete desorption of chemisorbed H atoms.^{3,6} Then the first spectrum is recorded and used as a background for the following difference spectra when the hydrogen pressure is stepped up in increments before measurement of the difference spectra. Hydrogen adsorption and measurement of spectra was conducted at room temperature. Spectra measured at hydrogen pressures above ca. 70 mbar should represent clusters with saturation coverage.³

Results and discussion

A set of spectra displayed in Figure 1 shows two bands which grow in simultaneously at 1679 cm^{-1} and 1392 cm^{-1} with increasing H_2 pressure, suggesting that they belong to the same species. No absorption bands are observed between 3000 cm^{-1} and 4000 cm^{-1} where the O–H stretching vibrations would be expected (see supporting information, Figure S2). Obviously, physisorbed water that was formed during reduction of PtO was completely desorbed during

and after reduction. The sharp drop near 1380 cm^{-1} is due to absorption by the zeolite lattice (see Figure S1). Unfortunately, this prevents spectroscopy at lower energies.

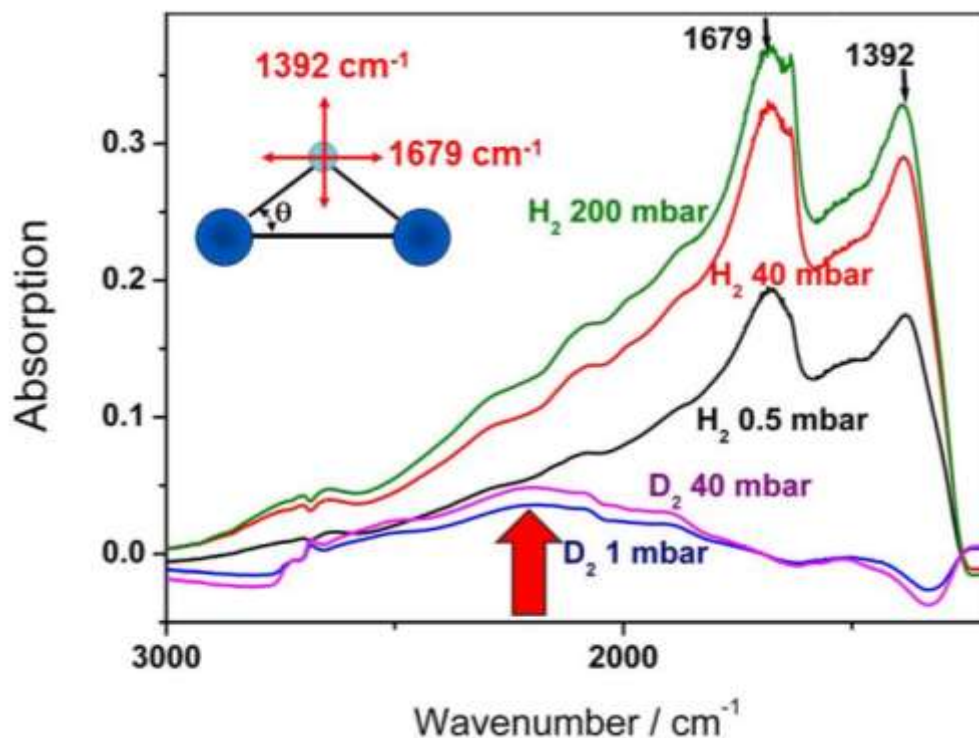


Figure 1: FT-IR difference spectra of a hydrogen desorbed Pt/KL sample recorded after equilibration at room temperature at the given pressures of H₂ or D₂. The inset shows the suggested assignment of the vibrations of H (grey) bonded over edge across a Pt–Pt fragment (blue balls).

Repeating the experiment with a fresh sample using D₂ in place of H₂ does not show these two bands, which proves that they both have to be ascribed to vibrations of adsorbed H. The corresponding D bands are expected to be shifted to lower energies by a factor of 1.4, but since they are masked by the zeolite absorption they are not observed. However, a broad but clear absorption grows in centred around 2200 cm^{-1} . It is also present in the H₂ loaded sample where it looks like a broad and strange extension towards higher energy relative to the 1679 cm^{-1} band. Since all spectra are flat above 3000 cm^{-1} the 2200 cm^{-1} absorption is not due to broad high frequency absorptions of the sample which are isotope-shifted to lower energy by

deuteration. The observed feature is thus an isotope-independent absorption which will be discussed further below.

The adsorption energy was calculated to be the largest for H on the bridge sites of icosahedral Pt₁₃, followed by the on-top and the hollow site.^{4,13} This is compatible with our own findings.⁶ However, the situation is complicated by a possible support-dependent structural transformation as H coverage increases.^{13,14} Figure 1 provides no evidence of such a phase transition for equilibrium hydrogen pressures between 0.5 mbar and 200 mbar. However, it should be noted that depending on the sample history⁶ the spectrum can be more complicated.

For the assumption that the two bands are due to an edge site (with a third band for H oscillating out of the paper plane expected to be at considerably lower frequencies) the ratio of the two absorption frequencies is determined solely by the triangular geometry (inset of Figure 1),¹⁵ since Pt is heavy and the effective mass of the motion is to a good approximation the hydrogen mass. There is a single stretching force constant k_0 for the Pt–H bond of nominal 50% bond order. It determines the effective force constants, k_{\parallel} and k_{\perp} , for the vibrations parallel and perpendicular to the bridged Pt–Pt bond. $k_{\parallel} / k_{\perp} = (v_{\parallel} / v_{\perp})^2$ equals $\cos \theta / \sin \theta$, where θ is the Pt–Pt–H angle. Assuming $v_{\parallel} = 1679 \text{ cm}^{-1}$ and $v_{\perp} = 1392 \text{ cm}^{-1}$ we obtain $\theta = 34.5^\circ$, and adopting the calculated Pt–Pt distance of 0.298 nm⁴ we obtain a Pt–H distance of 0.181 nm. This is in excellent agreement with prediction from DFT calculations⁴ and corroborates strongly the suggested assignment. 167 N m⁻¹ is obtained for k_{\parallel} , 115 N m⁻¹ for k_{\perp} , and 101 N m⁻¹ for k_0 , the force constant for the Pt–H stretching vibration in the triatomic fragment. There is of course an alternative, reverse assignment of the two bands, but this leads to a non-realistic Pt–H distance of 0.236 nm.

Assuming that the force constant for the terminal full Pt–H bond is approximately $2k_0$ this yields a predicted stretching vibration at 1867 cm^{-1} , somewhat lower than the literature values.^{8,9,10} Figure 1 (and also Figure 3 below) does not show a H dependent band in this range and therefore provides no evidence of terminally bound hydrogen. The curve at 200 mbar represents saturation coverage, which amounts to ca. 38 H per cluster,³ clearly more than can be accommodated at the 30 edge sites. This would mean that the additional atoms are probably bound in three-fold hole sites, as reported for the Pt(111) surface.^{7,8} As outlined in the introduction, vibrations of H atoms bound at these sites should be expected at wavenumbers well below 1300 cm^{-1} . Unfortunately this range is masked by the absorption of the zeolite. That hole sites are occupied before on-top sites contradicts predictions by DFT calculations,^{4,13} but these did not include zero-point energy corrections which could make the important difference in this delicate energy balance.⁷

The broad absorption centred about 2200 cm^{-1} (heavy red arrow in Figure 1) is obviously not due to hydrogen since it is isotope independent. Any vibrations involving Pt vibrations are expected at far lower energies, and they should also be eliminated in the difference spectrum. We suggest that this absorption is due to an electronic excitation within the band structure evolving from the Pt 5d valence orbitals into Pt_{13} cluster molecular orbitals. The situation is illustrated schematically in Figure 2, where the left side shows the energy levels near the Fermi energy (HOMO-LUMO gap) as calculated by Watari and Ohnishi for icosahedral geometry.¹⁶ The blue shaded area indicates the maximum range of levels which can be excited at 3000 cm^{-1} (370 meV). This prediction would give rise to a relatively sharp band at 240 meV (1930 cm^{-1}) if the transition were not forbidden because all involved states have g symmetry in this highly symmetric superatom-like cluster. However, the icosahedral symmetry can be broken for several reasons. Firstly, open shell systems tend to undergo

Jahn-Teller distortion. Secondly, spin-orbit coupling plays an important role in heavy elements and has been predicted to garble the energy levels of these systems.¹⁷ Furthermore, any impact of the environment such as remaining alkali cations or framework aluminium centres in the neighbourhood will distort the symmetry. Finally, adsorption of hydrogen titrates out the electrons near the Fermi level by pinning one electron to form a bond to each H atom. The 1s levels of atomic H come in at -13.6 eV, significantly below the 5d derived valence orbitals of the cluster, rendering H hydride-like, and the new orbitals are far below the HOMO-LUMO gap, but the symmetry and the energy of the states near the Fermi level changes for every new hydrogen that is bound. The predicted density of states around the Fermi level amounts to about 6-8 levels per 1 eV for Pt₁₃ and Pt₁₃H₂₀. Since for any given nominal Pt₁₃H_x stoichiometry there is a distribution of actual H coverages in the sample this is expected to lead mostly to broad and structure-less features, in accord with the observation shown in Figure 1.

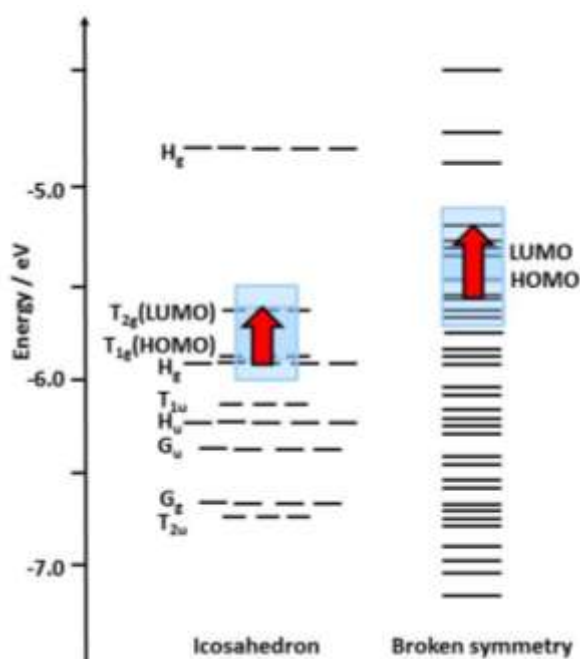


Figure 2: Calculated energy level diagram of Pt₁₃ clusters of icosahedral symmetry (left, based on data in Ref. 15), and schematic representation of the same levels under broken symmetry (right).

Figure 3 displays spectra at partial H₂ and D₂ coverage after complete hydrogen desorption. It reveals somewhat better resolution. In particular the band near 1400 cm⁻¹ shows distinct substructure, suggesting the presence of H bound across slightly inequivalent Pt–Pt edges, as expected in open-shell Pt₁₃ clusters,⁴ or also as a consequence of incomplete restructuring on adsorption after desorption.⁶ We also note that a nominal hydrogen coverage often represents an average over clusters with slightly different coverages,⁶ and the resolution will depend on the details of contributing states. The two main peaks seen at 1392 cm⁻¹ and 1679 cm⁻¹ in Figure 1 are basically present for H₂ but not for D₂ adsorption, which is ascribed to the isotopic shift to lower energies for the deuterium case.

Further substructure is observed near 2000 cm⁻¹, dominated by a dispersion-like feature near 2060 cm⁻¹ which is shifted by less than 10 wavenumbers when the H isotope is replaced by D. The fully hydrogen desorbed cluster spectrum reveals a clear band at 2045 cm⁻¹ (not shown) which shifts to higher values by ca. 40 cm⁻¹ on hydrogen adsorption, leading to the dispersion-like feature. In context with this shift and the loss of substructure with increasing coverage we remind of the fact that the number of available valence electrons in the cluster decreases with each additional hydrogen atom that binds to its surface (compare Figure 2). Concomitantly, the Pt–Pt bond strength decreases,⁴ and also the Pt–H bond strength and the cluster symmetry change. A given nominal coverage may represent a distribution of coverages and simultaneously a distribution of slightly different structures of the Pt₁₃ body. We also remind that the hysteresis behaviour as a function of coverage observed for EPR active clusters and in SQUID experiments⁶ may further influence resolution and reproducibility.

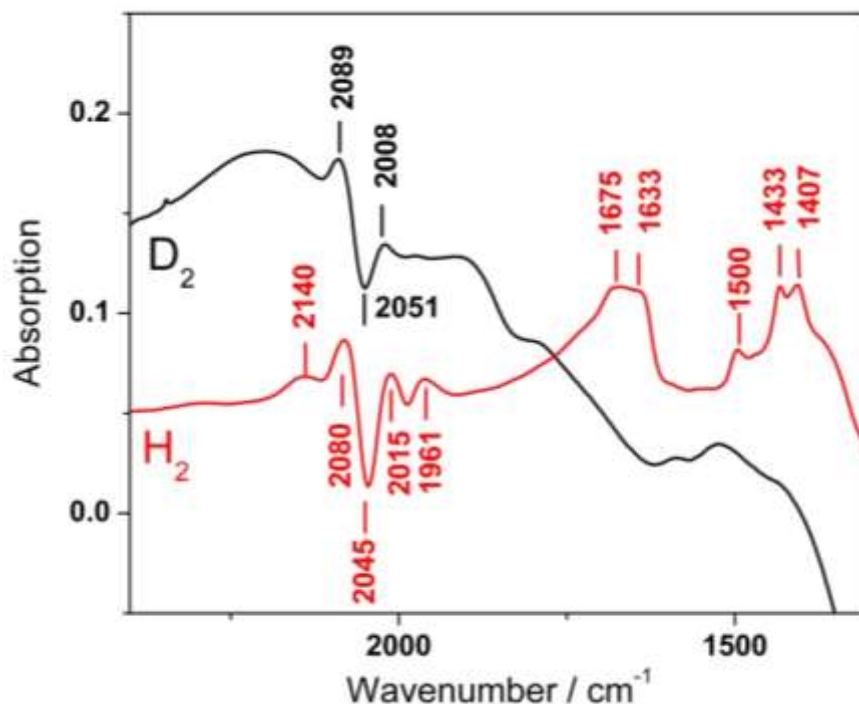


Figure 3: Difference spectra of H₂ and D₂ adsorption at 350 mbar relative to those of fully desorbed Pt₁₃ with band positions given in cm⁻¹.

Conclusions

High quality infrared spectra were observed upon chemisorption of H and D on Pt₁₃ clusters. We conclude that the two absorption bands at 1679 and 1392 cm⁻¹ represent H adsorbed on Pt₁₃ clusters at edge bridging positions. Terminal (or on-top) Pt–H adsorption near 2100 cm⁻¹ was not observed. Low frequency vibrations as expected for adsorption in three-fold hole sites are not in the observable range since they are masked by the absorption of the zeolite lattice modes, but saturation of adsorption with *ca.* 38 H per cluster would require that all H atoms exceeding the number of edges (30 for icosahedral Pt₁₃) are probably bound at these sites.

Furthermore, an interesting low-energy electronic excitation within the Pt₁₃ and the Pt₁₃H_x clusters was observed in the infrared. This signature represents a characteristic nanosize

effect and reflects the evolving band structure between the atomic energy levels and the full band structure of a bulk metal. The distinct substructure of both types of transitions is attributed to the structural changes as a function of hydrogen coverage which are partly dependent on sample history.⁶

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Supporting electronic information:

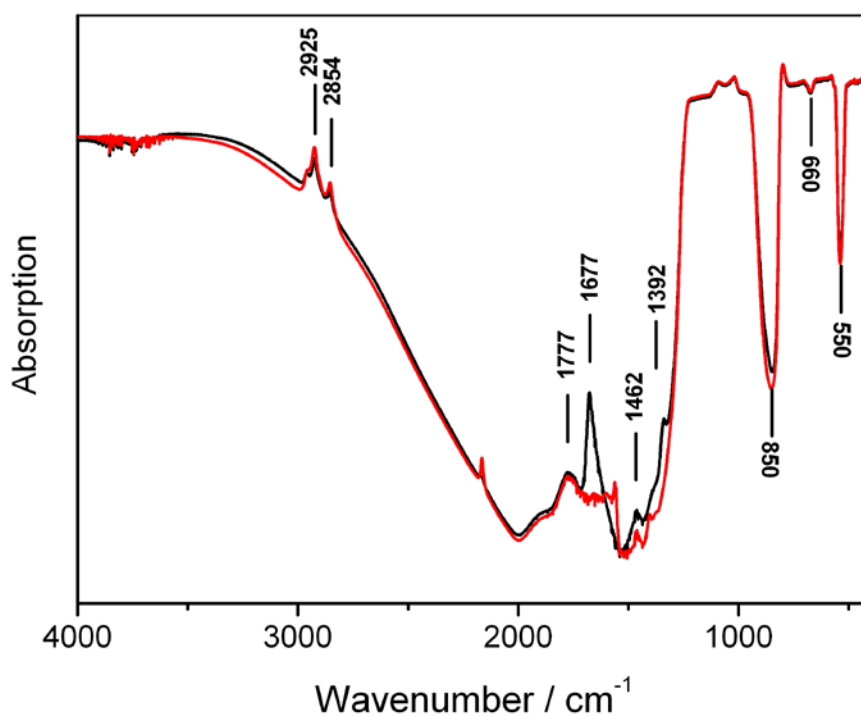


Figure S1: Raw spectra of the Pt/KL sample after initial hydrogen (H_2) reduction (black) and after hydrogen desorption at 573 K (red), measured as difference against the empty cell. Such spectra are taken as the background which is subtracted by the instrument software from all spectra of the subsequent series of measurements. It is seen that the zeolite blocks IR radiation below ca. 1380 cm^{-1} except at two narrow windows at 850 and 550 cm^{-1} . The noise-like features near 3700 cm^{-1} belong to water vapour in the beam (likely outside the cell) and the bands at 2925 and 2854 cm^{-1} are C–H stretching vibrations of organic condensates, perhaps on the cell window.

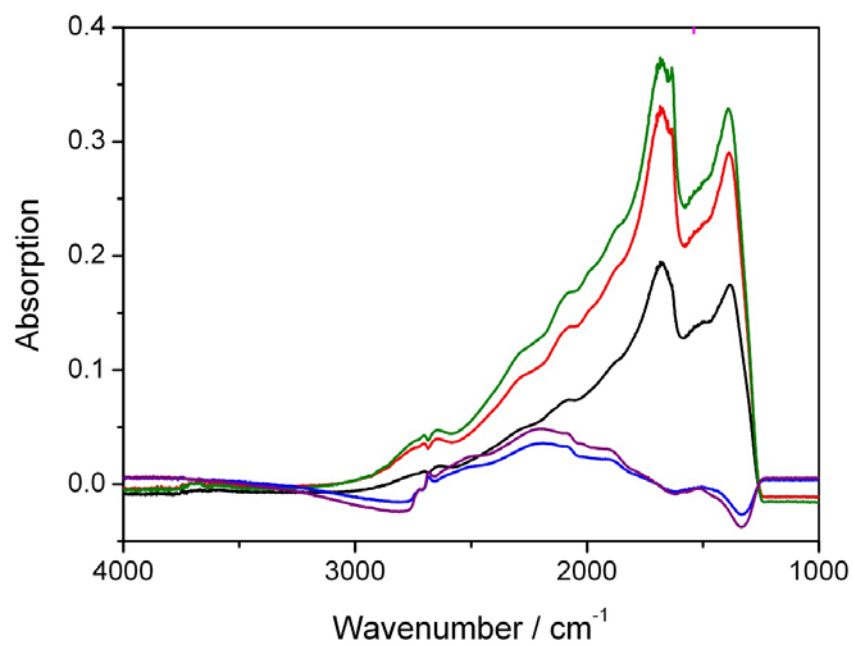


Figure S2: Extended range of IR difference spectra shown in Figure 1 to illustrate the absence of significant absorption due to the Pt clusters above ca. 3100 cm^{-1} (From top to bottom: H₂ 200 mbar (green), H₂ 40 mbar (red), H₂ 0.5 mbar (black), D₂ 40 mbar (purple), D₂ 1 mbar (blue)).