Supporting Information

Platinum-Catalysed Selective Aerobic Oxidation of Methane to Formaldehyde in the Presence of Liquid Water

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Supplementary material to

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Section I: Catalyst synthesis and characterization

The catalysts were prepared by incipient wetness impregnation of platinic acid in deionized water on titanium dioxide (Sigma Aldrich; Rutile; \(S_{\text{BET}} = 44.5 \text{ m}^2/\text{g}\)), or alumina (\(\gamma-\text{Al}_2\text{O}_3\); Alfa Aesar, 3 Micron APD Powder, LOT: K27Y013, \(S_{\text{BET}} = 73.9 \text{ m}^2/\text{g}\)) as a support. The support was contacted with an aqueous solution of platinic acid (\(\text{H}_2\text{PtCl}_6\), Sigma Aldrich) to obtain 10 wt.-% platinum on the support. The solid was dried, calcined at 400°C (air flow rate: 48 ml/min/g) and subsequently reduced for 5 hrs at 400°C in flowing hydrogen (48 ml/min/g).

The elemental composition of the materials was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES). The nanoparticles were imaged using transmission electron microscopy (TEM; FEI Tecnai G2 T20 TEM, operating at 200 kV). Specimens for TEM analysis were prepared by casting one-drop of a colloidal suspension in acetone onto 3-mm carbon-coated copper grids. These were then air dried under ambient conditions. The particle size distribution and the average particle size of the nanosized particles representing platinum was determined by measuring between 400-550 nanoparticles using ImageJ® software.

The phase composition of the catalyst samples was determined using powder X-ray diffraction (XRD) on a Bruker D8 ADVANCE diffractometer (Co-K\(\alpha\) radiation: \(\lambda = 1.789 \text{ Å}, 35 \text{ kV}, 40\text{mA}\)). The spent catalysts were characterized using Fourier transform infrared spectroscopy (FTIR) on a Perkin Elmer Spectrum 100 FTIR Spectrometer in the range 650-4000 cm\(^{-1}\) with a resolution of 1 cm\(^{-1}\).

Table S.1: Metal loading and dispersion of Pt-based catalysts (values in brackets for the used catalyst)

| Sample                  | Pt/Al\(_2\)O\(_3\) | Pt/TiO\(_2\) (rutile) |
|-------------------------|--------------------|-----------------------|
| Pt-loading              | 10.2               | 10.3 (10.2)           |
| T\(_{\text{reduction}}\), °C | 400                | 400                   |
| t\(_{\text{reduction}}\), hrs | 5                  | 5                     |
| H\(_2\)-uptake, cm\(^3\)(STP)/g | 1.19               | 0.81 (0.90)           |
| Dispersion\(^a\)        | 20.6               | 14.3 (15.7)           |
| \(d_{\text{Pt}}\), nm   | 5.5                | 7.9 (7.2)             |
| \(d_{\text{Pt}}\), nm   | 3.2 ± 1.5 (3.6 ± 3.5) | 2.1 ± 0.9 (6.1 ± 4.5) |

\(^a\): based on H\(_2\)-chemisorption; \(^b\): estimated from \(d_{\text{Pt}} = \frac{113}{\text{Dispersion}(\%)}\); \(^c\): from TEM-measurement
Section II: Catalyst testing

Figure S.1 shows the process flow diagram of the trickle bed reactor, whilst Figure S.2 shows the cross-sectional schematic drawing of the reactor tube. The reactor consisted of a quartz tube (length:38 cm; I.D.=12 mm packed with ca. 1.5 g of the pelletized and sieved catalyst (100-150 µm) in its centre. The void space on top of the catalyst was packed with silicon carbide particles (dp ~300µm, obtained from Colbern Abrasives cc, Parow, South Africa). The catalyst and the silicon carbide were held in place with 2 small glass wool plugs on either end. The quartz tube was placed inside a 19.05 mm O.D. stainless steel tube. A quartz-sheathed thermocouple was placed at the centre of the catalyst bed for temperature measurement. The reactor is enclosed in an aluminium heating furnace controlled with multiple heating zones each controlled by thermocouples on the outside of the reactor. The isothermal zone in the reactor was ca. 10 cm. Argon flowed pressure-controlled through the annular space between the two tubes at the same pressure as inside the quartz tubing. The bottom of the reactor rested on a bed of silicon carbide (dp ~ 300 µm; bed length 15.5 cm) to ensure evaporation of the liquid dripping out of the catalyst bed (the argon flow rate was typically set at ca. 2-3 times the total flow rate, including steam, through the catalyst bed). The temperature of the bottom zone was adjusted depending on the water flow rate to achieve smooth operation.

The reactor effluent passed a heated expansion valve placed directly under the reactor to reduce the pressure to atmospheric pressure and was transferred to the on-line GC (T_transfer line = 180°C), where it was injected over a heated 6-way valve. The effluent passed a condenser (operating at room temperature) and was vented into the vent line of the walk-in fume hood.

The products were analysed on a GC-FID (Agilent 6890N) equipped with a two-step methanation reactor (PolyArc™, Activated Research Company) and an FID. The Polyarc™ reactor is designed to enable calibration free analysis of all carbon containing compounds via an FID by first oxidizing the organic samples eluting out of a GC column with air to carbon dioxide and then reducing the carbon dioxide with hydrogen to methane before passing it onto the FID [S1]. The products were separated on a HP-PLOT Q PT capillary column (0.32 mm diameter, 30 m length, 20 µm stationary phase film thickness polystyrene-divinylbenzene; Agilent Technologies).
Figure S.1: Process flow diagram of the trickle-bed reactor for the selective oxidation of methane
Figure S.2: Schematic cross-sectional representation of the trickle bed reactor for the selective oxidation of methane
Figure S.3: GC-trace obtained during the selective oxidation of methane under the gas-phase conditions

Figure S.4: Rate of methane oxidation over 10 wt.% Pt/TiO$_2$ (rutile) conducted in the gas phase reactor, with a (H$_2$O/CH$_4$)$_{feed}$ mol/mol ratio of 0 (a), 6 (b), 12 (c) and 50 (d) (CH$_4$=2 ml/min, P$_{total}$= 20 bar, O$_2$=16 ml/min. The He flow rate was modified to maintain constant inlet partial pressures of CH$_4$ and O$_2$.)
Figure S.5: Time-on-stream behavior in the oxidation of methane over 10% Pt/TiO$_2$ (top) and 10% Pt/Al$_2$O$_3$ (bottom) at 220°C, 30 bar and $F_{\text{CH}_4}/W = 3.2$ mmol/hr/g (inlet partial pressures $p_{\text{CH}_4} = 0.5$ bar; $p_{\text{O}_2} = 1.5$ bar; red/blue line indicating the water flow rate to the reactor with the blue line indicating flooding conditions in the reactor).
**Figure S6:** GC-trace obtained during the selective oxidation of methane under the trickle-bed conditions over 10% Pt/Al$_2$O$_3$
Figure S.7: Selectivity for the formation of CO$_2$ (+) and formaldehyde in the oxidation of methane over 10% Pt/TiO$_2$ (top) and 10% Pt/Al$_2$O$_3$ (bottom) at 220°C, 30 bar and F$_{\text{CH}_4}$/W = 3.2 mmol/hr/g (inlet partial pressures p$_{\text{CH}_4}$ = 0.5 bar; p$_{\text{O}_2}$ = 1.5 bar; red/blue line indicating the water flow rate to the reactor with the blue line indicating flooding conditions in the reactor).
**Figure S8:** Catalyst activity as a function of time on stream over Pt/TiO$_2$ (top) and Pt/Al$_2$O$_3$ (bottom) (220°C, 30 bar and F$_{\text{CH}_4}$/W = 3.2 mmol/hr/g; inlet partial pressures $p_{\text{CH}_4} = 0.5$ bar; $p_{\text{O}_2} = 1.5$ bar; inlet partial pressures $p_{\text{H}_2}\text{O}/\text{CH}_4$ feed = 0)
Section II: DFT Studies

Spin polarised quantum chemical calculations were performed using VASP [S2-S4] using the GGA-PBE functional [S5] with dispersion correction according to Grimme et al. with Becke-Jonson damping [S6,S7]. The PAW pseudopotentials were used to describe the electron-ion interaction [S3]. Smearing using 1st order Methfessel-Paxton method [S8] was applied with $\sigma=0.05$ eV for surface calculations. Brillouin zone was sampled using a $\Gamma$-centred Monkhorst-Pack grid [S9] with a plane wave cut-off energy of 500 eV (grid size $\sqrt{3}\times\sqrt{3}$: 12 x 12 x 1; (2x2): 10 x 10 x 1; (3x3): 7 x 7 x 1, respectively). The lattice parameter for bulk FCC platinum was evaluated to be 3.9246 Å with a bulk modulus of 301 GPa in good agreement with the experimental values of 3.9231 Å and 282.7 GPa, respectively [S10].

A five layer Pt(111) slab with a 15 Å vacuum layer was used in this study. For the geometry optimizations, all the atoms were allowed to relax except the bottom two layers of the slabs. Surface structures were optimized with a maximum force of 0.01 eV/Å applying dipole correction in the direction perpendicular to the surface (SCF < $10^{-5}$ eV). The optimized structures represent local minima on the potential energy surface confirmed by a vibrational analysis. The vibrational modes were obtained allowing only the atoms of the adsorbate to move by 0.015 Å.

The obtained energies were referenced to that of the bare surface and the molecules CH₄, O₂, H₂, H, OH, H₂O, methanol, methanediol and formaldehyde, which were optimized by placing each molecule in a 15 Å x 16 Å x 17 Å box (plane wave cut-off energy: 1000 eV; Gaussian smearing, $\sigma=0.005$ eV; Gamma-centered k-point grid: 1x1x1; maximum allowable force: 0.01 eV/Å). The obtained bond distances and vibrational modes of the gas phase molecules were compared with experimentally determined values [S10-S12].

The adsorption energy as reported in Tables S3-S5 was determined relative to H₂O, O₂ and CH₄ in the gas phase and normalized with respect to the size of the unit cell taking the (2x2) unit cell as a basis:

$E_{ads} = \frac{E_{calHgO\gamma onPt(111)} - E_{Pt(111)-slab}}{N(\alpha \times \alpha)} - \frac{\alpha E_{CH_4}}{2} - \frac{\beta - 4\alpha x}{4} E_{H_2O(g)} - \frac{\gamma - 2\alpha x}{4} E_{O_2(g)}$

and $\Delta ZPE = \frac{ZPE_{calHgO\gamma onPt(111)} - ZPE_{Pt(111)-slab}}{N(\alpha \times \alpha)} - \frac{\alpha ZPE_{CH_4}}{2} - \frac{\beta - 4\alpha x}{4} ZPE_{H_2O(g)} - \frac{\gamma - 2\alpha x}{4} ZPE_{O_2(g)}$

with $N(\sqrt{3}\times\sqrt{3}) = \frac{3}{4} \times N(2\times2) = 1 \times N(3\times3) = \frac{9}{4}$

The most stable structure at a particular condition can be obtained by considering the Gibbs free energy of a particular structure at that condition. The Gibbs free energy associated with a structure was calculated as:

$G_{structure} = E_{structure} \cdot E_{bare\ slab} + h_{structure} \cdot s_{structure} \cdot T$

with $G_{structure}$: the Gibbs free energy associated with structure (slab + adsorbate)

$E_{structure}$: the electronic energy of the structure (slab + adsorbate)

$E_{bare\ slab}$: the electronic energy of the bare slab

$h_{structure}$: the enthalpy correction due to vibration of the adsorbate

$s_{structure}$: the entropy correction due to vibration of the adsorbate

After determining the Gibbs free energy of structures on the surface, surface phase diagrams of species on Pt(111) were determined in the presence of water and O₂ and in the presence of water, O₂, and CH₄. Numerous configurations can be obtained considering different species, vacant sites, and different adsorption geometries. Hence, only 63 configurations containing O, OH and H₂O were considered for the surface phase diagram on Pt(111) exposed to water and O₂ (see Table S.2). A much more limited additional set (10 different configurations) was considered when dealing with methyl and methoxy species on the surface was investigated to construct a surface phase diagram on Pt(111) exposed to water, O₂ and CH₄ (see Table S.3 and S.4).
The structure with the lowest Gibbs free energy at a given chemical potential of water, oxygen and methane (as determined by DFT) can be found by searching for the minimum value for:

\[
G = \min_i \left(G_{\text{structure},i} - \alpha \mu_{\text{CH}_4(g)} - \frac{\beta + \gamma}{4} \mu_{\text{H}_2\text{O}(g)} - \frac{2\gamma - \beta + \alpha}{4} \mu_{\text{O}_2(g)} \right)
\]

with

- \(G_{\text{structure},i}\): the Gibbs free energy associated with structure i (slab + adsorbate)
- \(\alpha\): the number of C-atoms in the adsorbate
- \(\beta\): the number of H-atoms in the adsorbate
- \(\gamma\): the number of O-atoms in the adsorbate
- \(N(a \times a)\): the number of surface Pt-atoms on one side of the unit cell

The prediction of the chemical potential of oxygen using DFT is improved significantly by relating the enthalpy/chemical potential of oxygen to the DFT-derived enthalpy/chemical potential of hydrogen and water\[S13,S14\] rather than using the enthalpy/chemical potential of oxygen derived from DFT-generated data:

\[
h_{\text{O}_2}^0 = 2 \cdot \left(h_{\text{H}_2\text{O}}^0 - h_{\text{H}_2}^0 - \Delta_f\text{H}_2\text{O}^0 \right), \quad \mu_{\text{O}_2}^0 = 2 \cdot \left(\mu_{\text{H}_2\text{O}}^0 - \mu_{\text{H}_2}^0 - \Delta_f\text{H}_2\text{O}^0 \right)
\]

Hence, the derived phase diagrams in this study refer use water and hydrogen as the reference state for gas phase oxygen.
Table S.2: Geometric characteristics, energetics, and normal modes of surface structures considered to determine the surface phase diagram of adsorbed O, OH and H₂O on Pt(111)

| Θ₀ | Θ₀ | Θ_H₂O | Θ_OH | \( E_{\text{ads}} \), eV | \( \Delta_{\text{ads}}ZPE \), eV |
|----|----|--------|------|-----------------|-----------------|
| 0.75 | 0.25 | - | - | -0.974 | 0.026 |
| d_Pt-O: 2.047, 2.047, 2.047 Å  
(O in fcc hollow on 2x2) | - | 470, 367, 366 cm⁻¹ |
| 0.75 | - | 0.25 | - | -0.464 | 0.073 |
| d_Pt-O(H): 2.410 Å  
d_Pt-O(H): 0.982, 0.982Å  
\( \angle_{\text{H-O-H}} \): 104.4°  
\( \angle_{\text{plane through H-O-H and surface}} \): 0.8°  
(H₂O in atop on 2x2) | 3658, 3563, 1551, 566, 508, 165, 151, 91, 84 cm⁻¹ |
| 0.67 | 0.33 | - | - | -1.049 | 0.011 |
| d_Pt-O: 2.070, 2.071, 2.071 Å  
(O in fcc hollow on √3x√3) | - | 448, 260, 259 cm⁻¹ |
| 0.67 | - | 0.33 | - | -0.630 | 0.081 |
| d_Pt-O(H): 2.447 Å  
d_Pt-O(H): 0.982, 0.983Å  
\( \angle_{\text{H-O-H}} \): 103.6°  
\( \angle_{\text{plane through H-O-H and surface}} \): 1.6°  
(H₂O in atop on √3x√3) | 3635, 3539, 1554, 584, 471, 150, 88, 75, 40 cm⁻¹ |
| 0.50 | 0.50 | - | - | -1.899 | 0.062 |
| d_Pt-O: 2.028, 2.028, 2.031, 2.031, 2.033, 2.033 Å  
(O in fcc hollow on 2x2) | - | 490, 471, 442, 413, 382, 371 cm⁻¹ |
Table S.2 (cont.)

| $\Theta^*$ | $\Theta_O$ | $\Theta_{H2O}$ | $\Theta_{OH}$ | $E_{ads}$, eV | $\Delta_{ads}ZPE$, eV |
|-----------|------------|----------------|---------------|----------------|---------------------|
| 0.50      | 0.25       | 0.25           | -             | -1.858         | 0.110               |
| $d_{Pt-O}$: 2.066, 2.085, 2.090 Å | $d_{Pt-OH}$: 2.380 Å | $d_{Pt-OH}$: 0.980, 0.982 Å | $\angle_{H-O-H}$: 105.2° | $\Delta_{plane through H-O-H and surface}$: 8.3° |
| (O in fcc hollow, $H_2O$ in atop on 2x2) | 3678, 3583, 1561, 624, 591, 437, 333, 311, 213, 183, 109, 74 cm$^{-1}$ |
| 0.50      | 0.25       | 0.25           | -             | -1.858         | 0.110               |
| $d_{Pt-O}$: 2.046, 2.046, 2.059 Å | $d_{Pt-OH}$: 1.989 Å | $d_{Pt-OH}$: 0.980 Å | $\angle_{Pt-O-H}$: 107.3° | (O in fcc hollow, OH in atop on 2x2) |
| 3650, 954, 521, 465, 370, 356, 170, 138, 110 cm$^{-1}$ |
| 0.50      | -          | 0.50           | -             | -1.335         | 0.167               |
| $d_{Pt-OH}$: 2.397 Å | $d_{Pt-HO}$: 2.489, 2.554, 2.711 Å | $d_{Pt-OH}$: 0.980, 1.001, 0.979, 0.996 Å | $\angle_{H-O-H}$: 106.1°, 102.5° | $\Delta_{plane through H-O-H and surface}$: 21.6°, 77.6° |
| (H$_2$O in atop and $H_2O$ above hcp hollow on 2x2) | 3674, 3638, 3296, 3192, 1604, 1547, 879, 634, 586, 525, 399, 249, 210, 165, 142, 71, 61 cm$^{-1}$ |
| 0.50      | -          | 0.25           | 0.25          | -1.664         | 0.117               |
| $d_{Pt-OH}$: 2.081 Å | $d_{Pt-NO}$: 2.186 Å | $d_{PtO-H}$: 0.977 Å | $\angle_{Pt-O-H}$: 106.2° | (OH in atop on 2x2) |
| 3690, 3690, 1853, 1539, 1269, 872, 738, 620, 422, 386, 307, 229, 164, 135, 109 cm$^{-1}$ |
| 0.33      | 0.67       | -              | -             | -2.047         | 0.082               |
| $d_{Pt-O}$: 2.038, 2.038, 2.038, 2.038, 2.038, 2.039 Å | (O in fcc hollow on $\sqrt{3}x\sqrt{3}$) |
| 503, 430, 428, 420, 388, 386 cm$^{-1}$ |
| 0.33      | 0.33       | 0.33           | -             | -              | -                   |

1 A structure containing $\Theta^*$ = 0.33, $\Theta_O$ = 0.33, $\Theta_{H2O}$ = 0.33 on ($\sqrt{3}x\sqrt{3}$)-Pt(111) optimises to a structure with $\Theta^*$ = 0.33, $\Theta_{OH}$ = 0.67.
| $\Theta$- | $\Theta$O | $\Theta$H2O | $\Theta$OH | $E_{\text{ads}}$, eV | $\Delta_{\text{adsZPE}}$, eV |
|---|---|---|---|---|---|
| 0.33 | 0.33 | - | 0.33 | -0.959 | 0.062 |
| $d_{\text{Pt}-O}$: 1.845 Å | $d_{\text{Pt}-O(H)}$: 1.957 Å | $d_{\text{Pt}-\text{H}}$: 1.003 Å | $\angle_{\text{Pt}-O-H}$: 105.6° | $\Delta_{\text{ads}}$, ZPE, eV | \( \text{H}_2\text{O} \) atop on $\sqrt{3} \times \sqrt{3}$ |
| 0.33 | 0.33 | - | 0.33 | -1.141 | 0.079 |
| $d_{\text{Pt}-O}$: 1.997, 2.004 Å | $d_{\text{Pt}-O(H)}$: 1.994 Å | $d_{\text{Pt}-\text{H}}$: 1.003 Å | $\angle_{\text{Pt}-O-H}$: 107.1° | (O in bridge and OH atop on $\sqrt{3} \times \sqrt{3}$) |
| 0.33 | - | 0.67 | - | -1.994 | 0.246 |
| $d_{\text{Pt}-O}$: 2.101 Å | $d_{\text{Pt}-O(H)}$: 2.201 Å | $d_{\text{Pt}-\text{H}}$: 1.017, 1.018 Å | $\angle_{\text{Pt}-O-H}$: 112.1° | (H$_2$O alternating in atop and perpendicular orientation on $\sqrt{3} \times \sqrt{3}$) |
| 0.33 | - | 0.33 | 0.33 | -2.831 | 0.225 |
| $d_{\text{Pt}-O}$: 2.101, 2.101, 2.101 Å | $d_{\text{Pt}-O(H)}$: 2.200, 2.200, 2.200 Å | $d_{\text{Pt}-\text{H}}$: 1.017, 1.017, 1.017 Å | $\angle_{\text{Pt}-O-H}$: 112° | (H$_2$O and OH in atop on $\sqrt{3} \times \sqrt{3}$) |
| 0.33 | - | 0.33 | 0.33 | -2.756 | 0.232 |
| $d_{\text{Pt}-O}$: 1.984, 1.984 Å | $d_{\text{Pt}-\text{H}}$: 1.008, 1.009 Å | $\angle_{\text{Pt}-O-H}$: 104.4°, 104.7° | (OH atop on $\sqrt{3} \times \sqrt{3}$) |
| 0.33 | - | 0.67 | - | -2.270 | 0.152 |
| $d_{\text{Pt}-O}$: 2.009, 2.119, 2.178 Å | $d_{\text{Pt}-\text{H}}$: 0.995, 1.037 Å | $\angle_{\text{Pt}-O-H}$: 103.7°, 104.2°, 105.9° | (bridging OH + OH atop on $\sqrt{3} \times \sqrt{3}$) |
| 0.33 | - | 0.67 | - | -2.155 | 0.137 |
| $d_{\text{Pt}-O}$: 2.009, 2.119, 2.178 Å | $d_{\text{Pt}-\text{H}}$: 0.995, 1.037 Å | $\angle_{\text{Pt}-O-H}$: 103.7°, 104.2°, 105.9° | (bridging OH + OH atop on $\sqrt{3} \times \sqrt{3}$) |

### Notes:
- Diameters in Å.
- Sums: $3 \times 3$ and $\sqrt{3} \times \sqrt{3}$.
- Two $\sqrt{3} \times \sqrt{3}$ adsorption structures.
- Pressure: 3000 bar.
- Temperature: 300 K.
- Adiabatic shifts.
- Vibrational frequencies in cm$^{-1}$.
Starting from a structure containing $\Theta^* = 0.25$, $\Theta_O = 0.25$, $\Theta_{H2O} = 0.25$ and $\Theta_{OH} = 0.25$ on (2x2)-Pt(111) optimises to a structure with $\Theta^* = 0.25$ and $\Theta_{OH} = 0.75$. 

| $\Theta^*$ | $\Theta_O$ | $\Theta_{H2O}$ | $\Theta_{OH}$ | $E_{ads}$, eV | $\Delta_{ads}$ZPE, eV |
|-----------|-----------|----------------|-------------|---------------|-------------------|
| 0.25      | 0.75      | -              | -           | -1.700        | 0.091             |
| $d_{Pt-O}$: 2.028, 2.028, 2.028, 2.029, 2.029, 2.034, 2.035 Å | 494, 469, 444, 444, 423, 422, 377, 377, 361 cm$^{-1}$ | |
| (O on fcc hollow on 2x2) | |
| 0.25 | 0.50 | 0.25 | - | -2.218 | 0.117 |
| $d_{Pt-O}$: 2.028, 2.032, 2.033, 2.045, 2.051, 2.052 Å | 3780, 3673, 1582, 488, 465, 446, 402, 399, 374, 370, 220, 189, 117, 56, 27 cm$^{-1}$ | |
| $d_{H-O-H}$: 0.973, 0.977 Å | |
| $\angle_{H-O-H}$: 104.8$^\circ$ | |
| $d_{plane}$ through H-O-H and surface: 48.4$^\circ$ | |
| (O on fcc hollow and H$_2$O atop on 2x2) | |
| 0.25 | 0.50 | 0.25 | 0.25 | -1.824 | 0.103 |
| $d_{Pt-O}$: 2.007, 2.011, 2.046, 2.049, 2.061, 2.072 Å | 3626, 1036, 527, 494, 467, 449, 416, 402, 353, 214, 127, 93 cm$^{-1}$ | |
| $d_{Pt-O}$: 0.982 Å | |
| $\angle_{Pt-O-H}$: 103.6$^\circ$ | |
| (O on fcc hollow and OH atop on 2x2) | |
| 0.25 | 0.25 | 0.50 | - | -2.627 | 0.220 |
| $d_{Pt-O}$: 2.069, 2.081, 2.121 Å | 3780, 3586, 3312, 2838, 1629, 1585, 1031, 768, 714, 575, 469, 406, 351, 343, 322, 280, 211, 169, 140, 105, 48 cm$^{-1}$ | |
| $d_{Pt-O}$: 1.979 Å | |
| $d_{Pt-O}$: 0.982 Å | |
| $d_{plane}$ through H-O-H and surface: 28.8$^\circ$, 47.6$^\circ$ | |
| (O on fcc hollow, H$_2$O atop on 2x2) | |
| 0.25 | 0.25 | 0.25 | 0.25 | 2 | |
| $d_{Pt-O}$: 1.984, 2.043, 2.066 Å | 3451, 3343, 1166, 1087, 571, 526, 517, 496, 423, 400, 374, 273, 194, 121, 64 cm$^{-1}$ | |
| $d_{Pt-O}$: 1.989, 2.005 Å | |
| $d_{Pt-O}$: 0.990, 0.993 Å | |
| $\angle_{Pt-O-H}$: 105.4$^\circ$, 106.2$^\circ$ | |
| (O on fcc hollow, OH atop on 2x2) | |
| 0.25 | 0.25 | - | 0.50 | -1.460 | 0.141 |
| $d_{OH}$: 2.314, 3.357 Å | 3627, 3611, 3477, 3354, 3222, 2777, 1673, 1602, 1574, 1097, 804, 677, 646, 625, 545, 515, 454, 389, 365, 257, 204, 172, 146, 122, 94, 68, 50 cm$^{-1}$ | |
| $d_{OH}$: 2.311 Å | |
| $d_{OH}$: 0.980, 0.982, 0.987, 0.993, 1.000, 1.023 Å | |
| $\angle_{OH}$: 103.8$^\circ$, 103.9$^\circ$, 105.8$^\circ$ | |
| $d_{plane}$ through H-O-H and surface: 23.8$^\circ$, 30.8$^\circ$, 78.1$^\circ$ | |
| (H$_2$O on/above atop on 2x2) | |

2 Starting from a structure containing $\Theta^* = 0.25$, $\Theta_O = 0.25$, $\Theta_{H2O} = 0.25$ and $\Theta_{OH} = 0.25$ on (2x2)-Pt(111) optimises to a structure with $\Theta^* = 0.25$ and $\Theta_{OH} = 0.75$. 
| Θ* | ΘO | ΘH₂O | ΘOH | Eₐds, eV | ΔadsZPE, eV |
|-----|-----|-------|------|----------|-------------|
| 0.25 | -   | 0.50  | 0.25 | -2.591   | 0.253       |
| dₚₜ-OH: 2.149 Å |   |   |   | 3706, 3558, 3505, 2469, 2305, 1681, 1533, 1171, 1135, 868, 792, 722, 689, 630, 519, 393, 386, 337, 225, 196, 180, 147, 115, 113 cm⁻¹ |
| dₜ-OH: 2.323, 2.333 Å   |   |   |   |         |
| dₜ-OH: 0.983, 1.043 Å |   |   |   | 375, 67, 56, 45, 34, 23, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1 cm⁻¹ |
| dₜ-OH: 0.975 Å | 0.25 | 2.591 | 0.253 |
| ζₜ-H₂O: 107.9°, 107.9° | 107.9°|
| ζₜ-H₂O: 96.4° | 96.4°|
| ζₜ-plane through H-O-H and surface: 16.6°, 16.6° | 16.6°|
| 0.25 | -   | 0.50  | 0.25 | -2.873   | 0.210       |
| dₚₜ-OH: 2.034, 2.066 Å |   |   |   | 3670, 3019, 2942, 2114, 1589, 1272, 1166, 1097, 942, 876, 646, 492, 465, 451, 425, 324, 284, 206, 151, 134, 133 cm⁻¹ |
| dₜ-OH: 2.126 Å |   |   |   |         |
| dₜ-OH: 0.978, 1.004 Å |   |   |   | 3670, 3019, 2942, 2114, 1589, 1272, 1166, 1097, 942, 876, 646, 492, 465, 451, 425, 324, 284, 206, 151, 134, 133 cm⁻¹ |
| ζₜ-H₂O: 95.9° | 95.9°|
| ζₜ-plane through H-O-H and surface: 9.5° | 9.5°|
| 0.25 | -   | 0.75  | 0.50 | -2.635   | 0.165       |
| dₚₜ-OH: 1.980, 1.988, 1.985 Å |   |   |   | 3080, 3021, 2865, 1247, 1179, 1135, 933, 697, 605, 541, 519, 492, 358, 270, 245 cm⁻¹ |
| dₜ-OH: 1.007, 1.007, 1.015 Å |   |   |   |         |
| dₜ-OH: 103.4°, 103.7°, 104.6° | 103.4°|
| (OH atop on 2x2) | (OH atop on 2x2) |
| 0.25 | -   | 1.00  | 0.75 | -0.984   | 0.100       |
| dₚₜ-O: 2.041, 2.041, 2.041, 2.044, 2.044, 2.044, 2.044, 2.044, 2.044 Å |   |   |   | 496, 429, 428, 427, 419, 417, 416, 369, 368, 366, 310, 305 cm⁻¹ |
| (O on fcc-hollow on 2x2) | (O on fcc-hollow on 2x2) |
| 0.25 | -   | 0.75  | 0.25 | -1.818   | 0.171       |
| dₚₜ-O: 1.967, 1.968, 1.994, 1.998, 2.038, 2.046, 2.052, 2.059 Å |   |   |   | 3785, 3592, 1579, 577, 546, 510, 487, 455, 441, 425, 411, 379, 298, 272, 217, 118, 94, 79 cm⁻¹ |
| dₜ-OH: 3.265 Å |   |   |   |         |
| dₜ-OH: 0.973, 0.980 Å |   |   |   | 3785, 3592, 1579, 577, 546, 510, 487, 455, 441, 425, 411, 379, 298, 272, 217, 118, 94, 79 cm⁻¹ |
| ζₜ-H₂O: 105.3° | 105.3°|
| ζₜ-plane through H-O-H and surface: 14.8° | 14.8°|
| 0.25 | -   | 0.75  | 0.25 | -1.517   | 0.136       |
| dₚₜ-O: 2.013, 2.015, 2.021, 2.022, 2.036, 2.038, 2.044, 2.064, 2.072 Å |   |   |   | 3632, 1035, 520, 489, 477, 467, 450, 438, 435, 413, 381, 360, 188, 126, 106 cm⁻¹ |
| dₜ-OH: 1.982 Å |   |   |   |         |
| dₜ-OH: 0.982 Å |   |   |   | 3632, 1035, 520, 489, 477, 467, 450, 438, 435, 413, 381, 360, 188, 126, 106 cm⁻¹ |
| ζₜ-OH: 104.1° | 104.1°|
| (O on fcc-hollow; OH atop on 2x2) | (O on fcc-hollow; OH atop on 2x2) |
| $\Theta^*$ | $\Theta_O$ | $\Theta_{\text{H}_2\text{O}}$ | $\Theta_{\text{OH}}$ | $E_{\text{ads}}, \text{eV}$ | $\Delta_{\text{ads}}\text{ZPE}, \text{eV}$ |
|---------|----------|-----------------|----------------|-----------------|------------------|
| - | 0.67 | - | - | -1.683 | 0.141 |
| $d_{\text{Pt-O}}$: 2.032 Å | $d_{\text{O}_2}$: 1.344 Å | $d_{\text{H}_2\text{O}}$: 2.074 Å | $\angle_{\text{Pt-O}_2}$: 119.7° | $\Delta_{\text{ads}}\text{ZPE}$, eV | $d_{\text{H}_2\text{O}}$: 0.993, 1.090 Å |
| $d_{\text{O}_2}\text{H}_2$: 0.33 | - | -1.683 | $0.141$ | $d_{\text{Pt-O}}$: 2.015, 2.019, 2.027, 2.066, 2.067 Å |
| $d_{\text{H}_2\text{O}}$: 0.983 Å | $\angle_{\text{Pt-O}_2}$: 104.1° | (H,O and O2 atop on $\sqrt{3}\times\sqrt{3}$) | | $d_{\text{Pt-O}}$: 1.977 Å |
| 3606, 1068, 541, 522, 511, 473, 427, 402, 392, 260, 147, 137 cm$^{-1}$ | | | | $d_{\text{Pt-O}}$: 2.004, 2.042 Å |
| 3437, 1017, 801, 582, 562, 522, 417, 380, 286, 243, 165, 151 cm$^{-1}$ | | | | $d_{\text{Pt-O}}$: 2.032, 2.034, 2.045, 2.047, 2.050 Å |
| $d_{\text{Pt-O(H)}}$: 1.977 Å | $d_{\text{Pt-O}}$: 1.389 Å | $d_{\text{Pt-O}}$: 1.959 Å | $d_{\text{Pt-O}}$: 1.090°, 109.3° | $d_{\text{Pt-O}}$: 108.3° | (O$_2$ on bridge; OH atop on $\sqrt{3}\times\sqrt{3}$) |
| $d_{\text{Pt-O(H)}}$: 0.986 Å | $d_{\text{Pt-O}}$: 1.032, 1.043 Å | $d_{\text{Pt-O}}$: 103.3°, 104.5° | $d_{\text{Pt-O}}$: 28.2°, 40.7° | $d_{\text{Pt-O}}$: 0.50, 0.50, - | -3.174 | 0.247 |
| $d_{\text{Pt-O}}$: 1.966, 1.975, 2.022, 2.037, 2.050 Å | $d_{\text{Pt-O}}$: 1.090°, 109.3° | $d_{\text{Pt-O}}$: 108.3° | $d_{\text{Pt-O}}$: 104.1° | $d_{\text{Pt-O}}$: 1.090°, 109.3° | $d_{\text{Pt-O}}$: 108.3° | (O$_2$ on bridge; OH atop on $\sqrt{3}\times\sqrt{3}$) |
| $d_{\text{Pt-O(H)}}$: 1.977 Å | $d_{\text{Pt-O}}$: 1.090°, 109.3° | $d_{\text{Pt-O}}$: 108.3° | $d_{\text{Pt-O}}$: 104.1° | $d_{\text{Pt-O}}$: 1.090°, 109.3° | $d_{\text{Pt-O}}$: 108.3° | (O$_2$ on bridge; OH atop on $\sqrt{3}\times\sqrt{3}$) |
| $d_{\text{Pt-O}}$: 1.966, 1.975, 2.022, 2.037, 2.050 Å | $d_{\text{Pt-O}}$: 1.090°, 109.3° | $d_{\text{Pt-O}}$: 108.3° | $d_{\text{Pt-O}}$: 104.1° | $d_{\text{Pt-O}}$: 1.090°, 109.3° | $d_{\text{Pt-O}}$: 108.3° | (O$_2$ on bridge; OH atop on $\sqrt{3}\times\sqrt{3}$) |
| $d_{\text{Pt-O(H)}}$: 2.032, 2.034, 2.045, 2.047, 2.050 Å | $d_{\text{Pt-O}}$: 1.090°, 109.3° | $d_{\text{Pt-O}}$: 108.3° | $d_{\text{Pt-O}}$: 104.1° | $d_{\text{Pt-O}}$: 1.090°, 109.3° | $d_{\text{Pt-O}}$: 108.3° | (O$_2$ on bridge; OH atop on $\sqrt{3}\times\sqrt{3}$) |
| $d_{\text{Pt-O(H)}}$: 2.032, 2.034, 2.045, 2.047, 2.050 Å | $d_{\text{Pt-O}}$: 1.090°, 109.3° | $d_{\text{Pt-O}}$: 108.3° | $d_{\text{Pt-O}}$: 104.1° | $d_{\text{Pt-O}}$: 1.090°, 109.3° | $d_{\text{Pt-O}}$: 108.3° | (O$_2$ on bridge; OH atop on $\sqrt{3}\times\sqrt{3}$) |

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3 In this configuration molecularly adsorbed O$_2$ is on the surface rather than 2O
4 The same coverage with O in the fcc hollow site is more stable (E$_{\text{ads}}$ = -2.527 eV), but vibrational analysis resulted in a single imaginary frequency
Table S.2 (cont.)

| Θ* | ΘO | ΘH2O | ΘOH | Eads, eV | ΔadZPE, eV |
|-----|----|-------|------|----------|------------|
| -   | 0.33 | 0.67 | -    | -        | -          |
| -   | 0.33 | 0.33 | 0.33 | -3.064   | 0.262      |
| df, O: | 1.840 Å |  |  |  |  |
| df, OOH: | 2.053 Å |  |  |  |  |
| df, OOH-H2: | 2.142 Å |  |  |  |  |
| df, OOH-H: | 0.987 Å |  |  |  |  |
| ZH2O: | 1.016, 1.017 Å |  |  |  |  |
| ZH, O: | 104° |  |  |  |  |
| ZH, O-H: | 110.7° |  |  |  |  |
| A plane through H-O-H and surface: 17.9° |  |  |  |  |  |
| (O, H2O and OH atop on √3x√3) |  |  |  |  |  |
| -   | 0.33 | - | 0.67 | -2.259 | 0.173 |
| df, O: | 1.831 Å |  |  |  |  |
| df, OOH: | 1.971, 1.971 Å |  |  |  |  |
| df, OOH-H2: | 1.005, 1.005 Å |  |  |  |  |
| df, OOH-H: | 0.975, 0.982, 0.985, 0.988, 1.011, 1.042 Å |  |  |  |  |
| ZH2O: | 103.3°, 105.4°, 105.0° |  |  |  |  |
| ZH, O: | 110.7° |  |  |  |  |
| ZH, O-H: | 110.7° |  |  |  |  |
| A plane through H-O-H and surface: 17.9° |  |  |  |  |  |
| (O and OH atop on √3x√3) |  |  |  |  |  |
| -   | 0.25 | 0.75 | - | -3.313 | 0.321 |
| df, O: | 2.058, 2.063, 2.083 Å |  |  |  |  |
| df, OOH: | 2.315, 3.399, 4.371 Å |  |  |  |  |
| df, OOH-H2: | 0.975, 0.982, 0.985, 0.988, 1.011, 1.042 Å |  |  |  |  |
| df, OOH-H: | 0.978, 1.018, 1.023, 1.052 Å |  |  |  |  |
| ZH2O: | 103.3°, 105.4°, 105.0° |  |  |  |  |
| ZH, O: | 105.4°, 105.4° |  |  |  |  |
| ZH, O-H: | 105.4°, 105.4° |  |  |  |  |
| A plane through H-O-H and surface: 23.0°, 60.7°, 45.2° |  |  |  |  |  |
| (O in fcc hollow; H2O atop on 2x2) |  |  |  |  |  |
| -   | 0.25 | 0.50 | 0.25 | -3.194 | 0.281 |
| df, O: | 2.025, 2.046, 2.082 Å |  |  |  |  |
| df, OOH: | 2.128Å |  |  |  |  |
| df, OOH-H2: | 2.138, 3.465 Å |  |  |  |  |
| df, OOH-H: | 0.975 Å |  |  |  |  |
| df, OOH-H: | 0.978, 1.018, 1.023, 1.052 Å |  |  |  |  |
| ZH2O: | 100.9° |  |  |  |  |
| ZH, O: | 97.4°, 102.4° |  |  |  |  |
| ZH, O-H: | 97.4°, 102.4° |  |  |  |  |
| A plane through H-O-H and surface: 26.9°, 35.4° |  |  |  |  |  |
| (O in fcc hollow; H2O, OH atop on 2x2) |  |  |  |  |  |
| -   | 0.25 | 0.25 | 0.50 | -2.373 | 0.216 |
| df, O: | 1.990, 2.006, 2.073 Å |  |  |  |  |
| df, OOH: | 2.068, 2.094, 2.159 Å |  |  |  |  |
| df, OOH-H2: | 1.015, 1.085 Å |  |  |  |  |
| df, OOH-H: | 0.973, 0.995 Å |  |  |  |  |
| df, OOH-H: | 100.5°, 104.8°, 105.9° |  |  |  |  |
| ZH2O: | 104.3° |  |  |  |  |
| ZH, O: | 97.4°, 102.4° |  |  |  |  |
| ZH, O-H: | 97.4°, 102.4° |  |  |  |  |
| A plane through H-O-H and surface: 45.9° |  |  |  |  |  |
| (O in fcc hollow; H2O atop, OH bridge on 2x2) |  |  |  |  |  |

5 A structure containing ΘO = 0.33, ΘH2O = 0.67 on (√3x√3)-Pt(111) optimises to a structure with ΘH2O = 0.33, ΘOH = 0.67.
Table S.2 (cont.)

| $\Theta^*$ | $\Theta_O$ | $\Theta_{H2O}$ | $\Theta_{OH}$ | $E_{ads}$, eV | $\Delta_{ads}ZPE$, eV |
|-------------|-------------|-----------------|--------------|--------------|---------------------|
| -           | 0.25        | 0.25            | 0.50         | -3.148       | 0.217               |
| $d_{Pt-O}$: | 1.861 Å     |                 |              |              |                     |
| $d_{Pt-OH}^i$: | 2.005, 2.006 Å |              |              |              |                     |
| $d_{Pt-OH}^2$: | 2.081 Å    |                  |              |              |                     |
| $d_{OH}^i$: | 0.994, 0.995 Å |              |              |              |                     |
| $d_{H(O,H)}$: | 1.030, 1.031 Å |              |              |              |                     |
| $\angle_{Pt-O-H}^i$: | 104.1°, 104.2° |              |              |              |                     |
| $\angle_{H-O-H}^i$: | 113.9° |              |              |              |                     |
| $\angle_{plane through H-O-H and surface}$: 18.8° | (O, H$_2$O and OH atop on 2x2) | | | | |
| -           | 0.25        | 0.25            | 0.50         | -3.179       | 0.234               |
| $d_{Pt-O}$: | 1.880 Å     |                 |              |              |                     |
| $d_{Pt-OH}^i$: | 1.990, 1.991 Å |              |              |              |                     |
| $d_{Pt-OH}^2$: | 2.098 Å    |                  |              |              |                     |
| $d_{OH}^i$: | 1.000, 1.005 Å |              |              |              |                     |
| $d_{H(O,H)}$: | 1.018, 1.020 Å |              |              |              |                     |
| $\angle_{Pt-O-H}^i$: | 103.9°, 104.3° |              |              |              |                     |
| $\angle_{H-O-H}^i$: | 111.1° |              |              |              |                     |
| $\angle_{plane through H-O-H and surface}$: 17.2° | (O, H$_2$O and OH atop on 2x2) | | | | |
| -           | 0.22        | 0.33            | 0.44         | -3.273       | 0.283               |
| $d_{Pt-O}$: | 1.843, 1.843 Å |              |              |              |                     |
| $d_{Pt-OH}^i$: | 1.954, 1.973, 2.074 Å | |              |              |                     |
| $d_{Pt-OH}^2$: | 0.982, 1.010, 1.013 Å | |              |              |                     |
| $d_{OH}^i$: | 1.000, 1.018, 1.018, 1.040, 1.042 Å | | | | |
| $\angle_{Pt-O-H}^i$: | 101.2°, 103.6°, 105.3° | | | | |
| $\angle_{H-O-H}^i$: | 81.1° | | | | |
| $\angle_{plane through H-O-H and surface}$: 15.3°, 15.4°, 18.5° | (O on fcc hollow, OH atop on 2x2) | | | | |
| -           | 0.11        | 0.44            | 0.44         | -3.273       | 0.283               |
| $d_{Pt-O}$: | 1.892, 1.843 Å |              |              |              |                     |
| $d_{Pt-OH}^i$: | 1.989, 2.052, 2.062, 2.062 Å | |              |              |                     |
| $d_{Pt-OH}^2$: | 2.134, 2.145, 2.148 Å | | | | |
| $d_{OH}^i$: | 0.999, 1.000, 1.018, 1.040, 1.042 Å | | | | |
| $\angle_{Pt-O-H}^i$: | 104.0°, 104.1°, 104.8°, 106.0° | | | | |
| $\angle_{H-O-H}^i$: | 103.4°, 104.8°, 108.0° | | | | |
| $\angle_{plane through H-O-H and surface}$: 15.3°, 15.4°, 18.5° | (O, H$_2$O, OH atop on 3x3) | | | | |

6 A structure containing $\theta_O = 0.11$, $\theta_{H2O} = 0.44$ and $\theta_{OH} = 0.44$ on (3x3)-Pt(111) optimises to a structure with $\theta_{H2O} = 0.33$, $\theta_{OH} = 0.67$
Table S.2 (cont.)

| Θ= | ΘO | ΘH2O | ΘOH | Ebind, eV | ΔaZPE, eV |
|----|----|------|-----|----------|-----------|
| -  | 0.11 | 0.33 | 0.55 | -3.519  | 0.307     |
| df(O): 1.841 Å |  |  |  |  |  |
| df(OH): 1.998, 2.001, 2.060, 2.064, 2.072 Å |  |  |  |  |  |
| df(OH2): 2.135, 2.148, 2.151 Å |  |  |  |  |  |
| df(OH2H): 0.983, 0.983, 0.984, 0.984, 0.986 Å |  |  |  |  |  |
| df(OH2H2): 0.996, 0.996, 1.022, 1.027, 1.043, 1.046 Å |  |  |  |  |  |
| θ(OH): 104.5°, 104.7°, 104.8°, 105.9°, 106.3° |  |  |  |  |  |
| θ(H-O-H): 107.0°, 107.2°, 110.7° |  |  |  |  |  |
| L-plane through H-O-H and surface: 13.8°, 14.6°, 15.2° |  |  |  |  |  |
| (O, H2O, OH atop on 3x3) |  |  |  |  |  |
| -  | 1.00 | - | -2.733 | 0.389 |  |
| df(OH): 2.240 Å |  |  |  |  |  |
| df(OH2): 2.370, 2.377, 4.946 Å |  |  |  |  |  |
| df(OH2H): 1.036, 1.036 Å |  |  |  |  |  |
| df(OH2H2): 0.972, 0.988, 0.989, 0.990, 0.998, 1.007 Å |  |  |  |  |  |
| df(OH2H2H): 100.7°, 104.8°, 104.8°, 105.8° |  |  |  |  |  |
| L-plane through H-O-H and surface: 26.3°, 60.7°, 61.4°, 89.8° |  |  |  |  |  |
| (H2O, OH on/above atop on 2x2) |  |  |  |  |  |
| -  | 0.75 | 0.25 | -3.118 | 0.312 |  |
| df(OH): 2.071 Å |  |  |  |  |  |
| df(OH2): 2.145, 2.222, 4.268 Å |  |  |  |  |  |
| df(OH2H): 0.981 Å |  |  |  |  |  |
| df(OH2H2): 0.974, 0.991, 0.999, 1.014, 1.025, 1.094 Å |  |  |  |  |  |
| df(OH2H2H): 108.3° |  |  |  |  |  |
| L-plane through H-O-H and surface: 106.6°, 102.0°, 105.7° |  |  |  |  |  |
| (H2O, OH on/above atop on 2x2) |  |  |  |  |  |
| -  | 0.67 | 0.33 | -3.241 | 0.398 |  |
| df(OH): 2.186 Å |  |  |  |  |  |
| df(OH2): 2.340, 2.362 Å |  |  |  |  |  |
| df(OH2H): 0.983 Å |  |  |  |  |  |
| df(OH2H2): 0.991, 0.992, 0.996, 0.997 Å |  |  |  |  |  |
| df(OH2H2H): 105.2° |  |  |  |  |  |
| L-plane through H-O-H and surface: 106.4°, 106.3° |  |  |  |  |  |
| (H2O, OH on atop on √3x√3) |  |  |  |  |  |
| -  | 0.55 | 0.44 | -3.604 | 0.332 |  |
| df(OH): 2.100, 2.102, 2.121, 2.138 Å |  |  |  |  |  |
| df(OH2): 2.153, 2.161, 2.183, 2.211, 3.386 Å |  |  |  |  |  |
| df(OH2H): 0.972, 0.981, 0.982, 0.996 Å |  |  |  |  |  |
| df(OH2H2): 0.972, 0.990, 0.991, 0.998, 1.004, 1.010, 1.024, 1.029, 1.034, 1.042 Å |  |  |  |  |  |
| df(OH2H2H): 106.6°, 101.0°, 105.3°, 107.2° |  |  |  |  |  |
| L-plane through H-O-H and surface: 102.9°, 105.5°, 110.0°, 110.4°, 111.0° |  |  |  |  |  |
| (H2O, OH on atop on 3x3) |  |  |  |  |  |
| -  |  |  |  |  |  |
| df(OH): 3739, 3716, 3595, 3494, 3388, 3312, 3277, 3179, 3162, 2886, 2772, 2585, 2478, 2456, 1626, 1612, 1564, 1537, 1511, 1188, 1164, 1154, 1098, 1065, 1057, 1026, 1016, 1003, 956, 929, 922, 866, 857, 820, 804, 705, 689, 640, 569, 456, 423, 413, 402, 388, 384, 372, 348, 339, 328, 307, 299, 287, 277, 272, 253, 250, 239, 221, 217, 205, 191, 177, 140, 135, 127, 111, 88, 40 cm−1 |  |  |  |  |
| df(OH2): 3564, 2548, 3512, 2496, 2486, 3328, 3319, 2778, 2688, 2473, 2330, 1572, 1567, 1554, 1203, 1171, 1154, 1124, 1077, 1057, 1032, 1024, 1011, 1001, 988, 877, 720, 685, 651, 607, 555, 543, 506, 486, 473, 450, 433, 421, 414, 386, 380, 348, 332, 332, 317, 295, 293, 288, 277, 260, 256, 235, 228, 215, 203, 179, 151, 147, 144, 110 cm−1 |  |  |  |  |  |
|                | θ\{H\} | θ\{O\} | θ\{H\}_\{O\} | θ\{O\}_\{H\} | \(E_{\text{ads}}, \text{eV}\) | \(\Delta_{ZPE}, \text{eV}\) |
|----------------|---------|---------|-------------|-------------|----------------|----------------|
| \(d_{\text{Pt}-\text{O}}\) | 2.123 | 2.124 Å | 0.50        | 0.50        | -4.039         | 0.383          |
| \(d_{\text{Pt}-\text{OH}}\) | 2.173 | 2.174 Å |             |             |                 |                |
| \(d_{\text{Pt}-\text{OH}_2}\) | 0.983 | 0.983 Å |             |             |                 |                |
| \(\angle \text{H}_2\text{P}t\text{O}_2\) | 1.011 | 1.012, 1.012, 1.013 Å | | | | |
| \(\angle \text{H}_3\text{PtO}_3\) | 105.0°, 104.9° |             |             | | | |
| \(\angle \text{H}_4\text{PtO}_4\) | 109.7°, 109.7° |             |             | | | |
| \(\angle \text{plane through H}_2\text{O}-\text{H} \text{and surface}: 14.0°, 14.1° \text{(H}_2\text{O}, \text{OH on atop on 2x2)}\) | | | | | | |
| \(d_{\text{Pt}-\text{O}}\) | 2.060 | 2.069, 2.072, 2.077, 2.121 Å | 0.44 | 0.55 | -3.846 | 0.357 |
| \(d_{\text{Pt}-\text{OH}}\) | 2.144, 2.145, 2.157, 2.237 Å | | | | | |
| \(d_{\text{Pt}-\text{OH}_2}\) | 0.976, 0.981, 0.989, 0.990, 0.991 Å | | | | | |
| \(d_{\text{Pt}-\text{OH}_3}\) | 0.989, 0.993, 1.009, 1.014, 1.023, 1.031, 1.031, 1.043 Å | | | | | |
| \(\angle \text{Pt}-\text{OH}_4\) | 102.5°, 103.3°, 104.2°, 105.2°, 106.6° | | | | | |
| \(\angle \text{H}_2\text{PtO}_4\) | 108.2°, 108.8°, 109.4°, 109.5° | | | | | |
| \(\angle \text{plane through H}_2\text{PtO}_4 \text{and surface}: 14.2°, 14.2°, 15.8°, 17.4° \text{(H}_2\text{O}, \text{OH on atop on 3x3)}\) | | | | | | |
| \(d_{\text{Pt}-\text{O}}\) | 1.998 | 2.078 Å | 0.33 | 0.67 | -3.782 | 0.336 |
| \(d_{\text{Pt}-\text{OH}}\) | 2.155 Å | | | | | |
| \(d_{\text{Pt}-\text{OH}_2}\) | 0.981, 0.983 Å | | | | | |
| \(d_{\text{Pt}-\text{OH}_3}\) | 1.014, 1.015 Å | | | | | |
| \(\angle \text{Pt}-\text{OH}_4\) | 104.4°, 106.4° | | | | | |
| \(\angle \text{H}_2\text{PtO}_4\) | 106.4° | | | | | |
| \(\angle \text{plane through H}_2\text{PtO}_4 \text{and surface}: 13.9° \text{(H}_2\text{O}, \text{OH on atop on 3x3)}\) | | | | | | |
| \(d_{\text{Pt}-\text{O}}\) | 2.045, 2.045, 2.045, 2.046, 2.046, 2.046 Å | 0.33 | 0.67 | -4.049 | 0.330 |
| \(d_{\text{Pt}-\text{OH}}\) | 2.112, 2.112, 2.112 Å | | | | | |
| \(d_{\text{Pt}-\text{OH}_2}\) | 0.986, 0.986, 0.986, 0.987, 0.987, 0.987 Å | | | | | |
| \(d_{\text{Pt}-\text{OH}_3}\) | 1.030, 1.031, 1.031, 1.032, 1.032, 1.032 Å | | | | | |
| \(\angle \text{Pt}-\text{OH}_4\) | 104.2°, 104.2°, 104.2°, 104.3°, 104.3°, 104.3° | | | | | |
| \(\angle \text{H}_2\text{PtO}_4\) | 110.6°, 110.6°, 110.7° | | | | | |
| \(\angle \text{plane through H}_2\text{PtO}_4 \text{and surface}: 14.9°, 14.9°, 14.9° \text{(H}_2\text{O}, \text{OH on atop on 3x3)}\) | | | | | | |
| \(d_{\text{Pt}-\text{O}}\) | 2.008, 2.028, 2.036 Å | 0.25 | 0.75 | -3.927 | 0.304 |
| \(d_{\text{Pt}-\text{OH}}\) | 2.126 Å | | | | | |
| \(d_{\text{Pt}-\text{OH}_2}\) | 1.004, 1.005, 1.016 Å | | | | | |
| \(d_{\text{Pt}-\text{OH}_3}\) | 1.023, 1.033 Å | | | | | |
| \(\angle \text{Pt}-\text{OH}_4\) | 101.9°, 102.9° | | | | | |
| \(\angle \text{H}_2\text{PtO}_4\) | 97.6° | | | | | |
| \(\angle \text{plane through H}_2\text{PtO}_4 \text{and surface}: 9.9° \text{(H}_2\text{O}, \text{OH on atop on 2x2)}\) | | | | | | |
|                | $\Theta^*$ | $\Theta_O$ | $\Theta_{H2O}$ | $\Theta_{OH}$ | $E_{ads}$, eV | $\Delta_{ads}ZPE$, eV |
|----------------|-----------|-----------|----------------|--------------|---------------|----------------------|
| $d_{Pt-O(H)}$: | 1.982, 2.005, 2.008, 2.024, 2.024, 2.025, 2.026 Å | 0.22 | 0.77 | -3.800 | 0.291 |
| $d_{Pt-O(H)}$: | 2.079, 2.146 Å | - | - | 3.369 | 0.250 |
| $d_{Pt-O(H)}$: | 0.987, 0.990, 0.991, 0.996, 0.997, 0.997 Å | - | - | 3.369 | 0.250 |
| $d_{H10-O-H}$: | 1.021, 1.021, 1.047, 1.051 Å | - | - | 3.369 | 0.250 |
| $\angle_{Pt-O-H}$: | 102.7°, 102.9°, 103.1°, 103.4°, 104.3°, 104.4°, 107.1° | - | - | 3.369 | 0.250 |
| $\angle_{H-O-H}$: | 109.1°, 112.0° | - | - | 3.369 | 0.250 |
| $\angle_{plane through H-O-H and surface}$: | 9.7°, 15.3° | - | - | 3.369 | 0.250 |

| $d_{Pt-O(H)}$: | 1.975, 1.976, 1.976 Å | - | - | -3.369 | 0.250 |
| $d_{Pt-O(H)}$: | 1.003, 1.003, 1.003, 1.004 Å | 1.00 | - | -3.369 | 0.250 |
| $\angle_{Pt-O-H}$: | 104.4°, 104.4°, 104.4°, 104.4° | 1.00 | - | -3.369 | 0.250 |

(H$_2$O, OH on atop on 3x3)
### Table S.3: Geometric characteristics, energetics, and normal modes of surface structures of proposed intermediates in the aerobic oxidation of methane on Pt(111)

| Structure          | Geometric Characteristics | E\text{ads}, eV | ΔE\text{ads}, ZPE, eV | Normal Modes (cm⁻¹) |
|--------------------|---------------------------|----------------|-----------------------|---------------------|
| Methoxy            |                           |                |                       |                     |
| d_{Pt-O-C}         | 1.990 Å                   |                |                       |                     |
| d_{Pt-O-H}         | 1.404 Å                   | -2.154         | 0.084                 |                     |
| d_{O-H}            | 1.104 Å, 1.112 Å, 1.114 Å|                |                       |                     |
| ΔE\text{ads}, ZPE | 116.5°                    |                |                       |                     |
| θ_{O-C-H}          | 106.8°, 112.3°, 112.3°    |                |                       |                     |
| Methanol           |                           | -1.702         | 0.185                 |                     |
| d_{Pt-O}           | 2.290 Å                   |                |                       |                     |
| d_{O-H}            | 0.982 Å                   |                |                       |                     |
| d_{O-C}            | 1.452 Å                   |                |                       |                     |
| d_{C-H}            | 0.9595, 1.099, 1.110 Å    |                |                       |                     |
| ΔE\text{ads}, ZPE | 96.1°                     |                |                       |                     |
| θ_{Pt-O-C}         | 117.3°                    |                |                       |                     |
| θ_{H-O-C}          | 109.3°                    |                |                       |                     |
| θ_{O-C-H}          | 106.2°, 108.9°, 110.9°    |                |                       |                     |
| Hydroxy-methoxy    |                           | -4.388         | 0.197                 |                     |
| d_{Pt-O-C}         | 2.048 Å                   |                |                       |                     |
| d_{Pt-O-H}         | 2.238 Å                   |                |                       |                     |
| d_{C-O}            | 1.499 Å                   |                |                       |                     |
| d_{C-H}            | 1.351 Å                   |                |                       |                     |
| d_{H-O}            | 1.105 Å, 1.114 Å          |                |                       |                     |
| d_{C-O}            | 111.7°                    |                |                       |                     |
| d_{O-H}            | 115.9°                    |                |                       |                     |
| d_{H-O-C}          | 101.1°                    |                |                       |                     |
| d_{O-C-H}          | 113.9°                    |                |                       |                     |
| θ_{C-H-O}          | 101.6°, 105.7°, 110.8°    |                |                       |                     |
| Methanediol        |                           | -3.967         | 0.250                 |                     |
| d_{Pt-O-C}         | 2.264 Å                   |                |                       |                     |
| d_{Pt-H-O-C}       | 1.475 Å                   |                |                       |                     |
| d_{H-O-C}          | 1.379 Å                   |                |                       |                     |
| d_{H-O}            | 0.981 Å                   |                |                       |                     |
| d_{H-C}            | 0.996 Å                   |                |                       |                     |
| d_{O-H}            | 1.099 Å, 1.104 Å          |                |                       |                     |
| ΔE\text{ads}, ZPE | 119.3°                    |                |                       |                     |
| θ_{Pt-O-H-C}       | 104.4°                    |                |                       |                     |
| θ_{Pt-O-C}         | 112.9°                    |                |                       |                     |
| θ_{O-C-H}          | 103.3°, 106.6°, 108.8°    |                |                       |                     |
| Normal Modes (cm⁻¹)| 3602, 2958, 2790, 1401, 1329, 1248, 1172, 1106, 987, 742, 603, 487, 408, 303, 248, 138, 104, 84 | | | |
Table S.4: Geometric characteristics, energetics, and normal modes of surface structures of proposed intermediates in the aerobic oxidation of methane on Pt(111) covered with O, OH and H₂O.

| Initial structure | Final structure | \(d_{\text{Pt-O}}\): 2.043, 2.052, 2.058 Å | \(d_{\text{Pt-OH}}\): 2.007 Å | \(d_{\text{O-H}}\): 0.978 Å | \(d_{\text{Pt-CH}_3}\): 2.005 Å | \(d_{\text{C-H}}\): 1.093, 1.093, 1.094 Å | \(\angle_{\text{Pt-O-C}}\): 105.9° | \(\angle_{\text{Pt-C-H}}\): 102.7°, 108.3°, 108.4° | \(\Delta_{\text{ads}}\), eV | -1.551 |
|-------------------|----------------|--------------------------------------|--------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| \(\Theta_{\text{CH}_3} = 0.25\) | \(\Theta_{\text{CH}_3} = 0.25\) | \(\Theta_{\text{O}} = 0.25\) | \(\Theta_{\text{O}} = 0.25\) | \(\Theta_{\text{OH}} = 0.25\) | \(\Theta_{\text{OH}} = 0.25\) | \(\Theta_{\text{OCH}_2} = 0.50°\) | \(\Theta_{\text{H}_2\text{O}} = 0.25\) | \(\Delta_{\text{ads}}\), eV | -3.100 |
| \(\Delta_{\text{ZPE}}\), eV | 0.171 |
| \(E_{\text{ads}}\), eV | 3.761 |
| \(\Delta_{\text{ZPE}}\), eV | 0.411 |
| \(\Delta_{\text{ads}}\), eV | 3.076, 3058, 3008, 2949, 2827, 2698, 2676, 2499, 1610, 1474, 1445, 1440, 1424, 1256, 1235, 1181, 1157, 1136, 1126, 1102, 1023, 931, 838, 693, 487, 459, 438, 384, 341, 317, 277, 231, 207, 169, 148, 110, 90, 78, 68 cm⁻¹ |

\(\Theta_{\text{OCH}_3} = 0.25\) | \(\Theta_{\text{OH}} = 0.25\) | \(\Theta_{\text{H}_2\text{O}} = 0.25\) | \(\Theta_{\text{OCH}_2} = 0.50°\) | \(\Theta_{\text{H}_2\text{O}} = 0.25\) | \(\Theta_{\text{OH}} = 0.25\) | \(\Theta_{\text{OCH}_2} = 0.50°\) | \(\Theta_{\text{H}_2\text{O}} = 0.25\) | \(\Theta_{\text{OH}} = 0.25\) | \(\Delta_{\text{ads}}\), eV | -1.551 |
| \(\Delta_{\text{ads}}\), eV | 3.761 |
| \(\Delta_{\text{ads}}\), eV | 3.076, 3058, 3008, 2949, 2827, 2698, 2676, 2499, 1610, 1474, 1445, 1440, 1424, 1256, 1235, 1181, 1157, 1136, 1126, 1102, 1023, 931, 838, 693, 487, 459, 438, 384, 341, 317, 277, 231, 207, 169, 148, 110, 90, 78, 68 cm⁻¹ |

Di-\(\pi\) surface species
Table S.4 (cont.):

| Initial structure | Final structure | $d_{\text{P-O-C}}$, Å | $d_{\text{P-O-H}}$, Å | $d_{\text{O-H}}$, Å | $\angle_{\text{P-O-C}}$ | $\angle_{\text{P-O-H}}$ | $\angle_{\text{O-H}}$ | $\Delta_{\text{ZPE}}$, eV | $E_{\text{ads}}$, eV |
|------------------|-----------------|-----------------------|-----------------------|---------------------|------------------|------------------|------------------|------------------|------------------|
| $\Theta_{\text{HOCCH}_3} = 0.25$ | $\Theta_{\text{HOCCH}_3} = 0.25$ | 3.185 | 1.430 | 1.025 | 137.7$^\circ$ | 108.0$^\circ$, 110.0$^\circ$, 110.9$^\circ$ | 99.9$^\circ$, 110.4$^\circ$ | 0.406 | -3.804 |
| $\Theta_{\text{H}_2\text{O}} = 0.25$ | $\Theta_{\text{H}_2\text{O}} = 0.25$ | | | 1.098, 1.099, 1.102 Å | | | | | |
| $\Theta_{\text{OH}} = 0.50$ | $\Theta_{\text{OH}} = 0.50$ | | | | | | | | |
| $\Theta_{\text{OCH}_2\text{OH}} = 0.22^\circ$ | $\Theta_{\text{OCH}_2\text{OH}} = 0.22^\circ$ | 2.039 | 2.180 | 1.371 | 124.8$^\circ$ | 116.1$^\circ$ | 102.2$^\circ$ | 0.320 | -4.740 |
| $\Theta_{\text{OH}} = 0.88$ | $\Theta_{\text{OH}} = 0.88$ | | | 1.471 | | | | | |
| $\Theta_{\text{H}_2\text{O}} = 0.11$ | $\Theta_{\text{H}_2\text{O}} = 0.11$ | | | 1.098, 1.104 Å | | | | | |
| $\Theta_{\text{OH}} = 0.66$ | $\Theta_{\text{OH}} = 0.66$ | | | | | | | | |
| $\Theta_{\text{OCH}_2\text{OH}} = 0.22^\circ$ | $\Theta_{\text{OCH}_2\text{OH}} = 0.22^\circ$ | 2.078 | 2.184 | 1.382 | 126.5$^\circ$ | 119.4$^\circ$ | 102.8$^\circ$ | 0.355 | -4.866 |
| $\Theta_{\text{OH}} = 0.77$ | $\Theta_{\text{OH}} = 0.77$ | | | 1.474 | | | | | |
| $\Theta_{\text{H}_2\text{O}} = 0.11$ | $\Theta_{\text{H}_2\text{O}} = 0.11$ | | | 1.094, 1.101 Å | | | | | |
| $\Theta_{\text{OH}} = 0.55$ | $\Theta_{\text{OH}} = 0.55$ | | | | | | | | |
| $\angle_{\text{plane through H-O-H and surface}} = 14.4^\circ$ | | | | | | | | | |
| $\angle_{\text{plane through H-O-H and surface}} = 19.5^\circ$ | | | | | | | | | |
Table S.4 (cont.)

| Initial structure | Final structure | \[d_{\text{O}-\text{C}}\]: 2.133 Å | \[d_{\text{N}-\text{C}}\]: 1.431 Å | \[d_{\text{C}-\text{H}}\]: 1.011, 1.01, 1.103 Å | \[\angle_{\text{N}-\text{C}-\text{H}}\]: 132.3° | \[\angle_{\text{N}-\text{C}=\text{O}}\]: 108.0°, 110.1°, 110.4° | \[d_{\text{P}-\text{O}}\]: 1.973, 2.040, 2.056 Å | \[d_{\text{P}-\text{O}}\]: 2.075, 2.077 Å | \[\angle_{\text{P}-\text{O}-\text{C}}\]: 90.0° | \[\angle_{\text{P}-\text{O}-\text{H}}\]: 90.0°, 99.0°, 99.0° | \[\angle_{\text{P}-\text{O}-\text{H}}\]: 103.6° | \[\angle_{\text{P}-\text{O}-\text{H}}\]: 101.5°, 101.0°, 101.3° | \[\angle_{\text{H}_{\text{O}-\text{H}}-\text{O}-\text{H}}\]: 102.6°, 103.6° | \[\angle_{\text{H}_{\text{O}-\text{H}}-\text{O}-\text{H}}\]: 111.4°, 111.7°, 112.4° | \[\angle_{\text{plane through }\text{H}-\text{O}-\text{H}}\]: 17.0°, 17.2°, 25.9° |
|-------------------|-----------------|---------------------|---------------------|---------------------|------------------|------------------|---------------------|---------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| \[\Theta_{\text{OCH3}}\] = 0.11 | \[\Theta_{\text{OCH3}}\] = 0.11 | \[\Theta_{\text{H}_{\text{O}-\text{H}}}\] = 0.33 | \[\Theta_{\text{OH}}\] = 0.55 | \[\Theta_{\text{OCH3}}\] = 0.11 | \[\Theta_{\text{OCH3}}\] = 0.11 | \[\Theta_{\text{H}_{\text{O}-\text{H}}}\] = 0.33 | \[\Theta_{\text{OH}}\] = 0.55 |

\[
E_{\text{ads}}, \, \text{eV} = -4.198
\]

\[
\Delta_{\text{ads}}ZPE, \, \text{eV} = 0.586
\]

| Initial structure | Final structure | \[d_{\text{P}-\text{O}}\]: 2.969 Å | \[d_{\text{P}-\text{O}}\]: 1.432 Å | \[d_{\text{O}-\text{H}}\]: 1.017 Å | \[d_{\text{C}-\text{H}}\]: 1.097, 1.100, 1.102 Å | \[d_{\text{P}-\text{O}}\]: 2.050, 2.059, 2.068 Å | \[d_{\text{P}-\text{O}}\]: 2.071, 2.082 Å | \[d_{\text{P}-\text{H}_{\text{O}}\text{H}}\]: 2.089, 2.137, 2.163 Å | \[d_{\text{P}-\text{H}_{\text{O}}\text{H}}\]: 0.985, 0.990, 0.990 Å | \[d_{\text{P}-\text{H}_{\text{O}}\text{H}}\]: 0.998, 1.01 Å | \[\angle_{\text{P}-\text{H}_{\text{O}}\text{H}}\]: 101.6°, 102.0°, 102.2° | \[\angle_{\text{P}-\text{H}_{\text{O}}\text{H}}\]: 102.3°, 104.0° | \[\angle_{\text{H}_{\text{O}-\text{H}}-\text{O}-\text{H}}\]: 97.6°, 107.5°, 111.3° | \[\angle_{\text{plane through }\text{H}-\text{O}-\text{H}}\]: 9.6°, 14.5°, 26.9° |
|-------------------|-----------------|---------------------|---------------------|---------------------|------------------|------------------|---------------------|---------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| \[\Theta_{\text{OCH3}}\] = 0.11 | \[\Theta_{\text{OCH3}}\] = 0.11 | \[\Theta_{\text{H}_{\text{O}-\text{H}}}\] = 0.33 | \[\Theta_{\text{OH}}\] = 0.55 | \[\Theta_{\text{OCH3}}\] = 0.11 | \[\Theta_{\text{OCH3}}\] = 0.11 | \[\Theta_{\text{H}_{\text{O}-\text{H}}}\] = 0.33 | \[\Theta_{\text{OH}}\] = 0.55 |

\[
E_{\text{ads}}, \, \text{eV} = -4.407
\]

\[
\Delta_{\text{ads}}ZPE, \, \text{eV} = 0.381
\]

| Initial structure | Final structure | \[d_{\text{P}-\text{O}}\]: 2.078 Å | \[d_{\text{P}-\text{O}}\]: 2.184 Å | \[d_{\text{P}-\text{C}}\]: 1.382 Å | \[d_{\text{P}-\text{O}}\]: 1.474 Å | \[d_{\text{P}-\text{O}}\]: 1.013 Å | \[d_{\text{C}-\text{H}}\]: 1.094, 1.101 Å | \[\angle_{\text{P}-\text{O}}\]: 126.5° | \[\angle_{\text{P}-\text{O}}\]: 119.4° | \[\angle_{\text{P}-\text{O}}\]: 102.8° | \[\angle_{\text{O}-\text{C}-\text{O}}\]: 115.3° | \[d_{\text{P}-\text{O}}\]: 1.992, 2.036, 2.043 Å | \[\angle_{\text{P}-\text{O}}\]: 101.1°, 101.1°, 101.3° | \[\angle_{\text{P}-\text{O}}\]: 101.8°, 102.1°, 103.8° | \[\angle_{\text{P}-\text{O}}\]: 101.8°, 106.9° | \[\angle_{\text{plane through }\text{H}-\text{O}-\text{H}}\]: 12.8°, 15.7° |
|-------------------|-----------------|---------------------|---------------------|---------------------|------------------|------------------|---------------------|---------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| \[\Theta_{\text{H}_{\text{O}-\text{H}}\text{OH}}\] = 0.22° | \[\Theta_{\text{H}_{\text{O}-\text{H}}\text{OH}}\] = 0.22° | \[\Theta_{\text{H}_{\text{O}-\text{H}}}\] = 0.22 | \[\Theta_{\text{OH}}\] = 0.55 | \[\Theta_{\text{H}_{\text{O}-\text{H}}}\] = 0.22 | \[\Theta_{\text{H}_{\text{O}-\text{H}}}\] = 0.22 | \[\Theta_{\text{OH}}\] = 0.55 |

\[
E_{\text{ads}}, \, \text{eV} = -4.866
\]

\[
\Delta_{\text{ads}}ZPE, \, \text{eV} = 0.355^8
\]

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\[^8\] Not determined as structure is identical to structure starting from \[\Theta_{\text{OCH3}}\] = 0.11, \[\Theta_{\text{H}_{\text{O}-\text{H}}}\] = 0.11 and \[\Theta_{\text{OH}}\] = 0.77
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