

Supporting Information

The Bifurcation Point of the Oxygen Reduction Reaction at Au-Pd Nanoalloys

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EXPERIMENTAL

Details are similar to those previously described.^{a-c}

Chemicals.

Hydrolyzed poly(vinyl alcohol), 98%, average molecular weight of 16000 g/mol, was purchased from Acros Organics. Sodium borohydride (99.9%), hydrogen tetrachloroaurate(III) trihydrate (99.9%), palladium(II) chloride (99.9%) and redistilled HClO₄ (99.999%) 70% were supplied by Aldrich. Oxygen (99.95%) and Argon (99.997%) were obtained from BOC gases (UK). MilliQ[®] water (Millipore Inc.) was used in all experiments. XC-72R carbon black (Cabot Corporation) was used as electrocatalyst support and purified as described in References a-c and d.

Nanoalloy Synthesis.

Au_{1-x}Pd_x/C materials were prepared by a sequential reduction synthetic method.^{a,b} A 32 µg/ml Au aqueous solution containing poly(vinyl alcohol) (PVA) (Au:PVA in 2:1 weight ratio) was reduced by adding drop wise and with vigorous stirring a four-fold excess of 0.1 M NaBH₄. The Au colloidal solution was then added to a vigorously stirred aqueous suspension of acid treated carbon black^{c,d} (Vulcan XC72) in water prepared by dispersing carbon in 200 ml of water in an ultrasonic bath for 60 min. The dispersion was kept stirred for one hour and then the carbon supported catalyst was left to settle overnight. The solution was decanted, the solid collected, washed with water and centrifuged several times. The material obtained was first dried in air at 60 °C and then annealed for 6 hours under a stream of 10% H₂/90% Ar at 300 °C. The solid obtained was then re-dispersed in water in an ultrasonic bath (1 hour), PdCl₂ was added and the Pd(II) was reduced by bubbling H₂ through the suspension for 1 hour. As previously confirmed this procedure leads to the formation of an homogeneous Au-Pd catalyst.^a The materials obtained were separated by centrifugation, washed with water several times and finally dried in air at 60°C.

Characterisation.

Details on the characterisation of the electrode materials used can be found in Refs a-c.

Electrochemical experiments.

For the rotating ring-disk electrode (RRDE) experiments, a Pine Instrument Company glassy carbon (GC) / Pt disc–ring electrode of 0.247 cm² disc area was employed. Measurements were carried out in a three electrode cell using a long gold wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode. All potentials are reported with respect to this electrode. The ring potential was set at 1.0 V to ensure quantitative detection of the peroxide produced on the disc. A collection efficiency of 0.38 was determined from measurements of hexacyanoferrate(III) reduction. Aqueous 0.1 M HClO₄ was used as electrolyte for all the measurements and this solution was saturated with Ar or O₂. For the electrode preparation, 10 mg of carbon supported Au_(1-x)Pd_x particles, 2.25 ml of water and 0.25ml of 5% Nafion 117 solution (Fluka) were first mixed in an ultrasonic bath. 12 µl of this suspension were then placed on a previously polished GC disc and the suspension left to dry in air. All the RRDE measurements are reported on the positive going scan to ensure that the electrode surface was fully reduced thus avoiding possible interference from residuals surface oxides.

Electrode preparation.

The electrodes were prepared as previously described.^{a-c} Typically, 10 mg of carbon supported catalyst, 2.25 ml of water and 0.25ml of 5% Nafion 117 solution (Fluka) were mixed in an ultrasonic bath. The GC disc was polished to a mirror finish using increasingly finer aqueous alumina slurries (1.0, 0.3 and 0.05 µm, Buehler) prior to each experiment, followed by repeated sonication in water. The electrodes were prepared by placing 12 µl of the catalyst suspension on the glassy carbon electrode and then left to evaporate overnight. An electrocatalytic layer thickness of ~1 µm was calculated from the Au_{1-x}Pd_x/C and Nafion loadings and densities.^{a-c} The homogeneity of the layer was checked by observation with an optical microscope and electrochemically, from the reproducibility of the O₂ reduction experiments.

Electrochemical analyses

Calculation of k_3

The basic relationships of the RRDE electrode have been extensively discussed in the literature but for clarity in their application to the systems analysed here and differences with previous work in the interpretation of the parameters derived, these are described below. The classical calculation of k_3 considers that there is no cross talk between the intermediates generated during

O₂ reduction and the rate determining step of peroxide reduction. To avoid this uncertainty, k_3 was calculated employing the generalised approach described by Wroblowa et al.^e, The basic equation relating the disk and ring currents measured to the rate constants described in Scheme 1 is:

$$-\left(\frac{NI_D}{I_R}\right) = \left(1 + \frac{2k_1}{k_2}\right) + \frac{2k_3}{B_{H_2O_2}} \left(1 + \frac{k_1}{k_2}\right) \omega^{-\frac{1}{2}} \quad (\text{SI-1})$$

From the slope (Sl) and intercept (In) of the linear dependence of $-\left(\frac{NI_D}{I_R}\right)$ on $\omega^{-\frac{1}{2}}$, the potential dependence of k_3 can be calculated according to:

$$-Sl = \frac{2k_3}{B_{H_2O_2}} \left(1 + \frac{k_1}{k_2}\right) \quad (\text{SI-2})$$

$$-In = \left(1 + \frac{2k_1}{k_2}\right) \quad (\text{SI-3})$$

From (SI-3) and (SI-2),

$$k_3 = -\frac{Sl \times B_{H_2O_2}}{1 - In} \quad (\text{SI-4})$$

with $B_{H_2O_2}$ given by:

$$B_{H_2O_2} = 0.2006nFD_{H_2O_2}^{2/3} \nu^{-1/6} \quad (\text{SI-5})$$

Calculation of k_1 and k_2

Considering that $k_1 \neq 0$, Eqn. (10) in reference 18 becomes:

$$I_D = -4FAc_{O_2}^\sigma (k_1 + k_2) + I_R/N \quad (\text{SI-6})$$

From the mass balance condition for O₂:¹⁸

$$c_{O_2}^\sigma = \frac{c_{O_2}^b k_M(O_2)}{k_2 + k_M(O_2)} \quad (\text{SI-7})$$

From (SI-5) and (SI-6), we obtain after rearranging:

$$k_1 + k_2 = k_M(O_2) \frac{\left[\left(\frac{I_R}{AN} \right) - j_D \right]}{\left[j_D + 4Fc_{O_2}^b k_M(O_2) - \left(\frac{I_R}{AN} \right) \right]} = F(\omega) \quad (\text{SI-8})$$

Form (SI-3) and (SI-7) the values of k_1 and k_2 can be calculated from the experimental values of $F(\omega)$:

$$k_2 = \frac{2F(\omega)}{(-In + 1)} \quad (\text{SI-9})$$

and

$$k_1 = \frac{(-In - 1)F(\omega)}{(-In + 1)} \quad (\text{SI-10})$$

References

- a. J. S. Jirkovsky, M. Halasa and D. J. Schiffrin, *Phys. Chem. Chem. Phys.*, 2010, **12**, 8042-8052.
- b. J. S. Jirkovsky, I. Panas, E. Ahlberg, M. Halasa, S. Romani and D. J. Schiffrin, *J. Am. Chem. Soc.* 2011, **133**, 19432–19441.
- c. J.S. Jirkovsky, I. Panas, S. Romani, E. Ahlberg and D.J Schiffrin, *J. Phys. Chem. Lett.* 2012, **3**, 315-321.
- c. J. K. Edwards, B. Solsona, E. Ntainjua, A. F. Carley, A. A. Herzing, C. J. Kiely, G. J. Hutchings, *Science* 2009, **323**, 1037-1041
- e. H. S. Wroblowa, Y.-C. Pan and G. Razumney, *J. Electroanal. Chem.*, 1976, **69**, 195-201.

Rotation Rate Ring Disk Electrode results

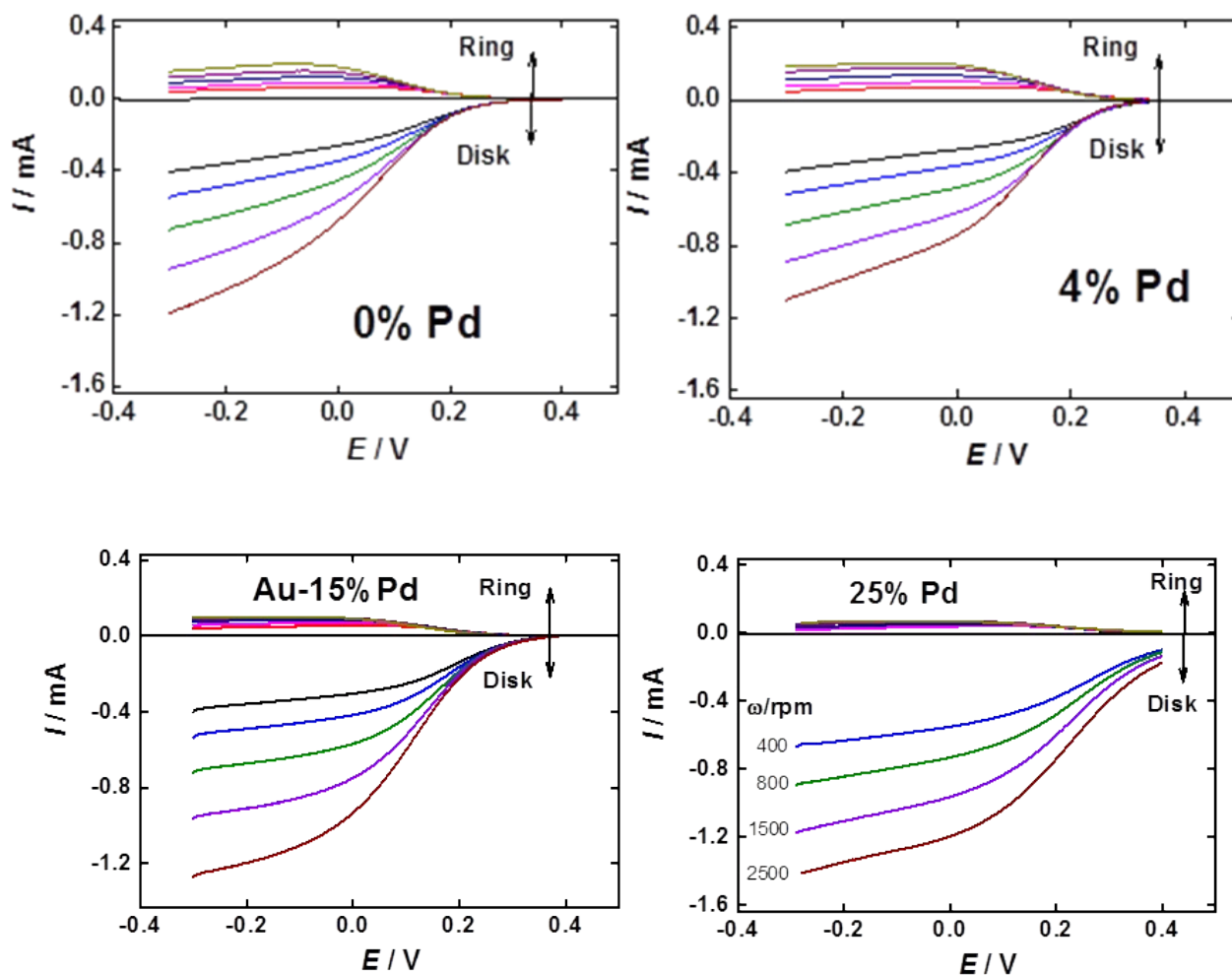


Figure SI-1 Summary of RRDE data for oxygen reduction in 0.1M HClO₄ on Au-Pd nanoparticle electrodes for different Pd concentrations. The concentration of Pd in the nanoalloys are given in the Figures. The rotation rates for 0, 4 and 15% were 200, 40, 800, 1500 and 2500 rpm. The values for the 25% nanoalloy are given in the Figure and the results for the 8% Pd nanoalloy are presented in the main text.

Transfer coefficient results

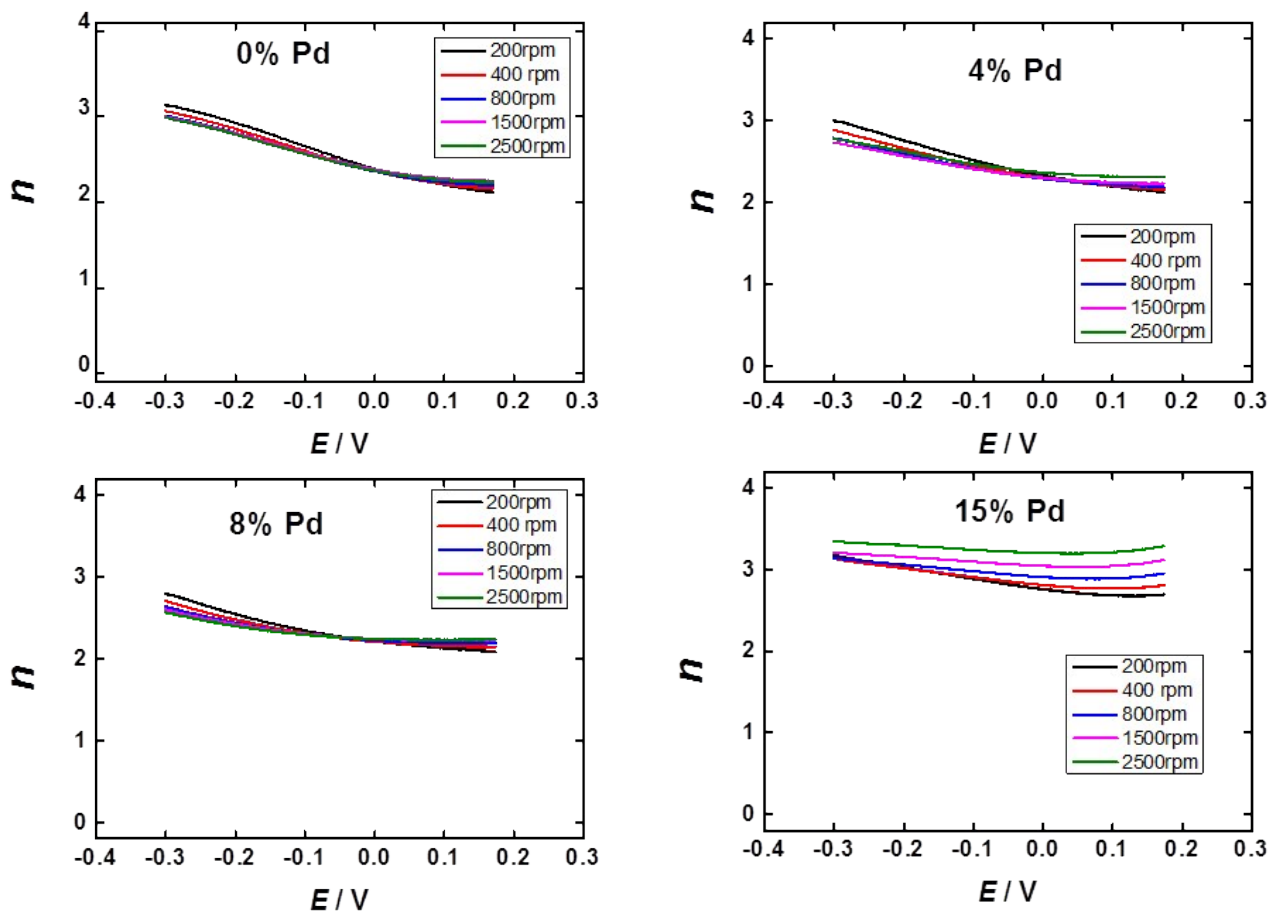


Figure SI-2 Dependence of the transfer coefficient on rotation rate for oxygen reduction in 0.1M HClO₄ on Au-Pd nanoparticle electrodes for different Pd concentrations. The concentration of Pd in the nanoalloys and the rotation rates are given in the Figures.

Peroxide yield results

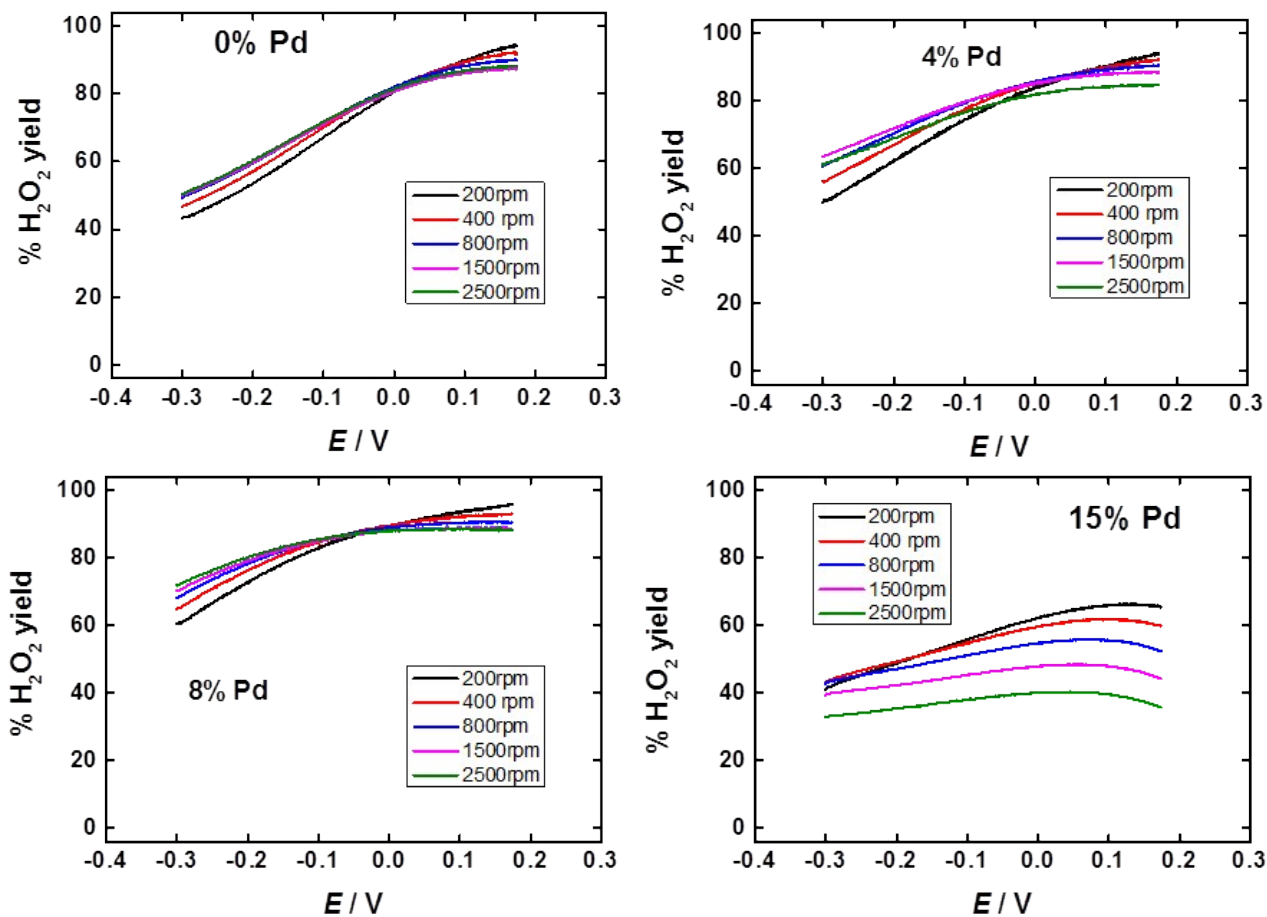


Figure SI-3 Dependence of the peroxide yield on rotation rate for oxygen reduction in 0.1M HClO₄ on Au-Pd nanoparticle electrodes for different Pd concentrations. The concentration of Pd in the nanoalloys and the rotation rates are given in the Figures.

Microsolvation effects

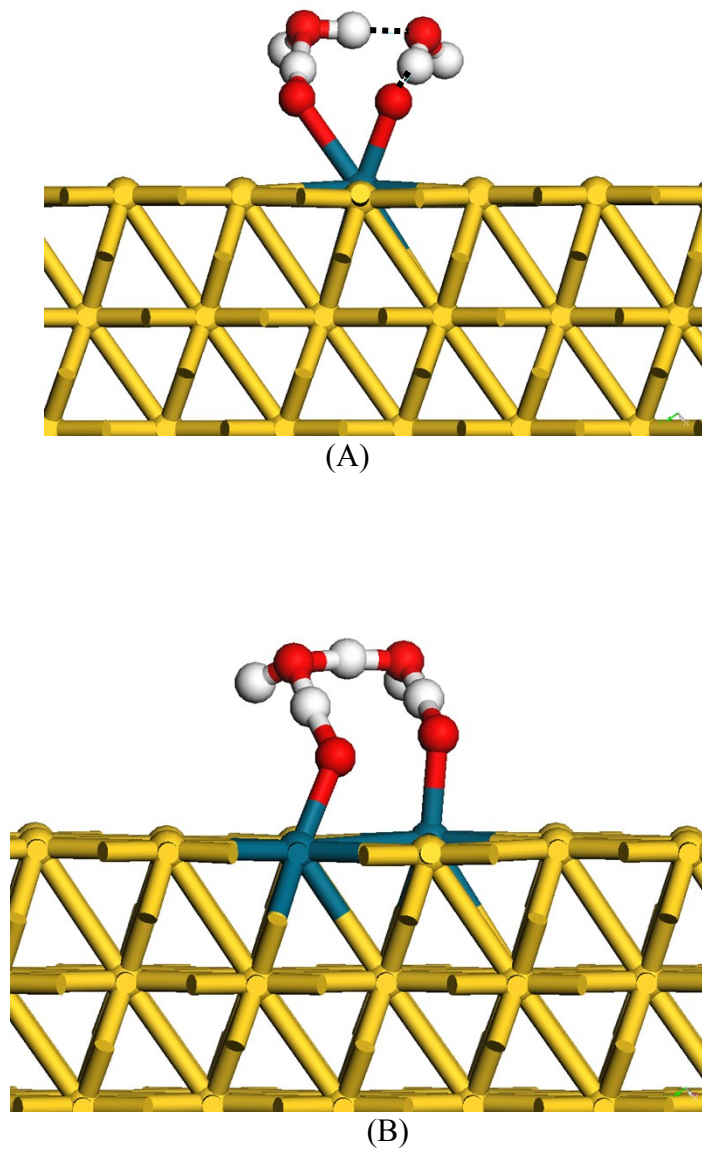


Figure SI-4. Solvation effect on the transition states. (A) Microsolvated OOH(ads) transition state (TS) with proton transfer on Pd monomer (Pd@Au) and (B) Pd dimer sites (Pd₂@Au). Both panels depict TS with simultaneous proton transfer (entries 9,10 in Table 2); in A the proton transfer occurs before the splitting of the O-O bond and in B both processes happen simultaneously. Pd is dark blue, Au yellow, oxygen red and hydrogen white.

Microsolvation effects

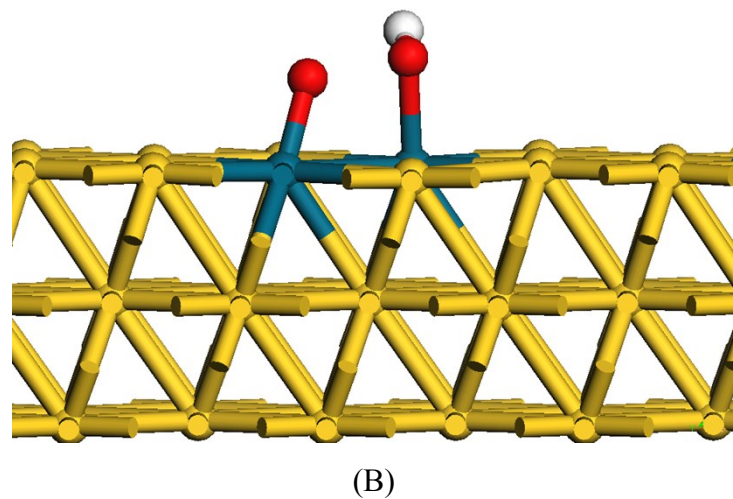
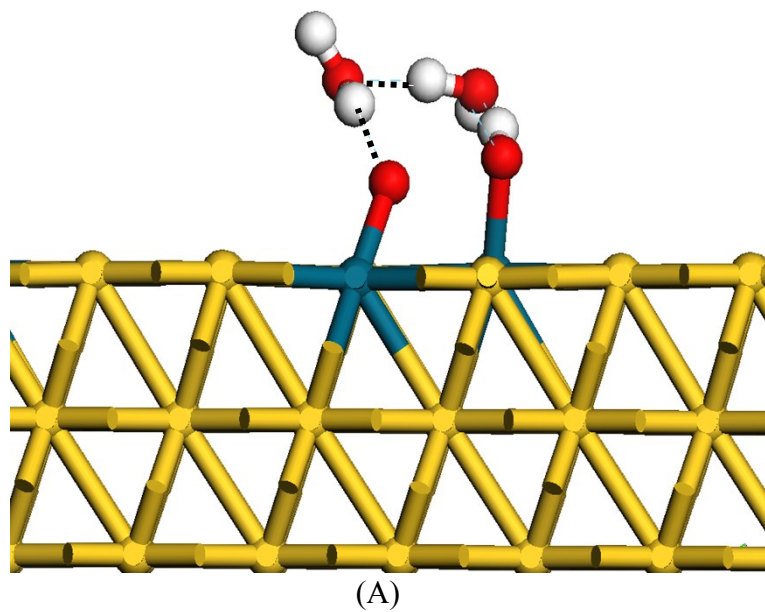


Figure SI-5. Transition state at the diatomic site Pd₂@Au without simultaneous proton transfer: (A) with microsolvation (Entry 11 in Table 2) and (B) without microsolvation (Entry 5 in Table 2). Pd is dark blue, Au yellow, oxygen red and hydrogen white.