Dissociative dynamics of O_2 on Ag(110)

Ivor Lončarić,[1, *] M. Alducin,[1, 2, †] and J.I. Juaristi[3, 1, 2, ‡]

[1] *Centro de Física de Materiales CFM/MPC (CSIC-UPV/EHU),
Paseo Manuel de Lardizabal 5, 20018 Donostia-San Sebastián, Spain*
[2] *Donostia International Physics Center DIPC, P. Manuel de Lardizabal 4, 20018 San Sebastián, Spain*
[3] *Departamento de Física de Materiales, Facultad de Químicas,
Universidad del País Vasco (UPV/EHU), Apartado 1072, 20080 San Sebastián, Spain*

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Electronic Supplementary Information

1. THREE DIMENSIONAL ATOMIC POTENTIAL ENERGY SURFACE

The interaction of the O atom with the frozen Ag(110) surface is described with a three-dimensional (3D) adiabatic potential energy surface (PES) that depends on the position $\mathbf{R}$ of the O atom over the surface. This 3D PES is simply used as an auxiliary utility to reduce the corrugation of the 6D O_2/Ag(110) PES. In this respect, it is important to keep the Ag(110) frozen, as done in the 6D PES.

The 3D PES $V^{3D}(\mathbf{R})$ is constructed by interpolating with the 3D corrugation reducing procedure (CRP) [1] the spin-polarized DFT energy grid described in Sec. II of the manuscript. In the 3D CRP, the function I^{3D} to be interpolated is calculated as

$$I^{3D}(\mathbf{R}) = V^{3D}(\mathbf{R}) - \sum_{i=1}^{n} V^{1D}(|\mathbf{R} - \mathbf{R}_i|). \tag{1}$$

where V^{1D} is a one-dimensional potential energy describing the interaction between the O atom and the *ith*-Ag atom that is located at $\mathbf{R_i}$. In our case, we use the potential energy of the O atom on the top site of Ag(110) for V^{1D}. The summation in Eq. (1) runs over first and second layer atoms that give a non zero contribution to V^{1D}. Compared to V^{3D}, the resulting I^{3D} is a less corrugated function that can be easily interpolated over X, Y and Z through a third order spline interpolation.

The dependence of the O/Ag(110) PES on the distance Z between the atom and the surface is shown in Fig. 1 for the top site, which is used to evaluate V^{1D}, and for other high-symmetry sites. In all cases the interaction of O with Ag(110) along the Z direction is characterized by a *well* followed by a repulsive wall. The systematic inspection of the (X, Y)-cuts of the 3D PES at fixed distances Z allows us to determine which sites are truly minima in 3D. From this analysis we confirm that there is a minimum at the long-bridge site with the O atom 0.56 Å above the surface and a well depth of 3.09 eV. However, the absolute minimum corresponds to the atom located at ($X = 1.41$ Å, $Y = 1.47$ Å, $Z = 0.78$ Å) with an adsorption energy of 3.13 eV. It is worthy to remark that surface relaxation may alter these results for O adsorption. Finally, we note that in common with the O_2/Ag(110) PES, none of the calculated sites show energy barriers in the entrance channel.

2. INTERPOLATION OF THE 6D O_2/Ag(110) PES

In this part of the Supplementary Information we describe in more detail the interpolation steps followed to obtain the value of the 6D PES at any point of the configurational space, i.e., $V^{6D}(X, Y, Z, r, \theta, \varphi)$.

Once the (r_i, Z_i)-cuts of the 34 configurations $(X_0, Y_0, \theta_0, \varphi_0)$ that conform the DFT energy grid described in Sec. II of the manuscript are calculated, we start obtaining the corresponding (r_i, Z_i)-cuts of the interpolation function I^{6D} for each of these configurations. This consists in subtracting the 3D potential V^{3D} as indicated in Eq. (1) of the manuscript. Next, a conventional 2D cubic spline algorithm (as in Ref. [1]) is used to interpolate the (r_i, Z_i)-cuts of each $I^{6D}(X_0, Y_0, \theta_0, \varphi_0)$ for the requested values (r, Z). The latter are then interpolated over φ and θ with Fourier expansions that take into account the symmetry of every site (X_0, Y_0). In particular, the Fourier functions used are as follows:
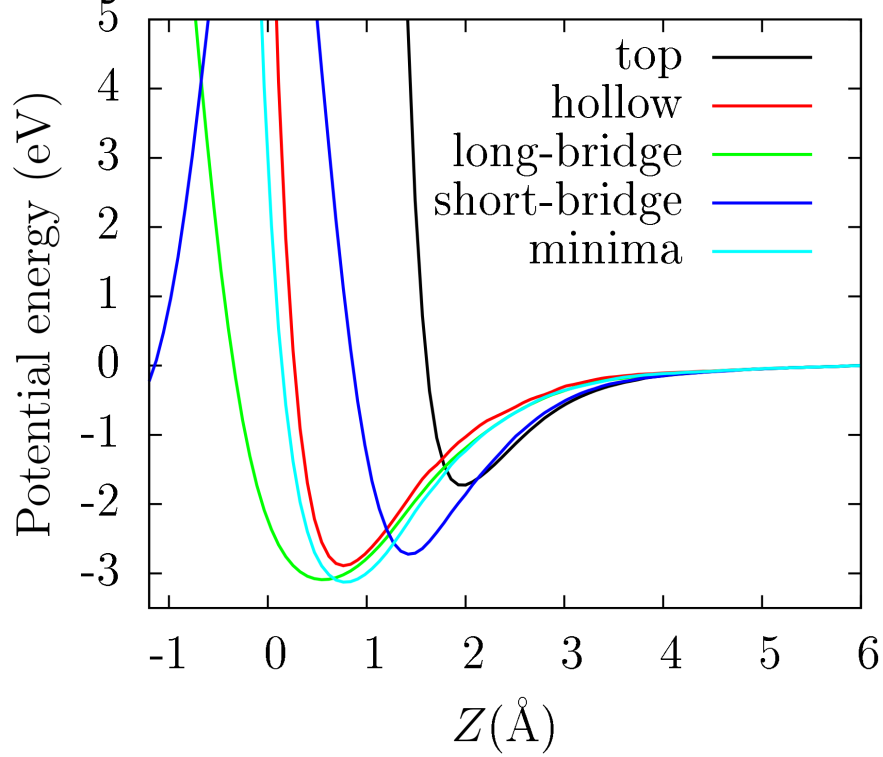
FIG. 1. Dependence of 3D atomic PES on distance Z of the oxygen atom from the Ag(110) for most symmetric sites on the surface and for the site where the absolute minima of the 3D PES is located (see text).

a) The configurations calculated on top site ($X = 0, Y = 0$) and hollow site ($X = a/2, Y = a/(2\sqrt{2})$) (both sites have the same symmetry) are: (1) $\theta = 0°$; (2) $\theta = 45°$ and $\varphi = 0°$; (3) $\theta = 45°$ and $\varphi = 35.26°$; (4) $\theta = 45°$ and $\varphi = 90°$; (5) $\theta = 90°$ and $\varphi = 0°$; (6) $\theta = 90°$ and $\varphi = 35.26°$; (7) $\theta = 90°$ and $\varphi = 90°$. In the following the notation $I(j)$ refers to the value of the interpolation function I^{6D} at the orientation conditions of item (j) above. Then, the Fourier functions $I_\theta(\varphi)$ for φ interpolation on top and hollow sites and $\theta = 0°, 45°, 90°$ are:

$$I_0(\varphi) = I(1) \tag{2}$$

$$I_{45}(\varphi) = \frac{1}{16}\left(2I(2) + 9I(3) + 5I(4) + 8(I(2) - I(4))\cos 2\varphi + (6I(2) - 9I(3) + 3I(4))\cos 4\varphi\right) \tag{3}$$

$$I_{90}(\varphi) = \frac{1}{16}\left(2I(5) + 9I(6) + 5I(7) + 8(I(5) - I(7))\cos 2\varphi + (6I(5) - 9I(6) + 3I(7))\cos 4\varphi\right) \tag{4}$$

The Fourier function for θ interpolation on top (T) and hollow (H) sites is:

$$I_{T,H}(\theta, \varphi) = \frac{1}{4}\left((I_0(\varphi) + 2I_{45}(\varphi) + I_{90}(\varphi) + 2(I_0(\varphi) - I_{90}(\varphi))\cos 2\theta + (I_0(\varphi) - 2I_{45}(\varphi) + I_{90}(\varphi))\cos 4\theta\right) \tag{5}$$

b) The configurations calculated on long-bridge site ($X = a/2, Y = 0$) and short-bridge site ($X = 0, Y = a/(2\sqrt{2})$) (both sites have the same symmetry) are: (1) $\theta = 0°$; (2) $\theta = 45°$ and $\varphi = 0°$; (3) $\theta = 45°$ and $\varphi = 90°$; (4) $\theta = 90°$ and $\varphi = 0°$; (5) $\theta = 90°$ and $\varphi = 90°$. The Fourier functions of φ interpolation on long-bridge and short-bridge sites are:

$$I_0(\varphi) = I(1) \tag{6}$$

$$I_{45}(\varphi) = \frac{1}{2}(I(2) + I(3)) + \frac{1}{2}(I(2) - I(3))\cos 2\varphi \tag{7}$$

$$I_{90}(\varphi) = \frac{1}{2}(I(4) + I(5)) + \frac{1}{2}(I(4) - I(5))\cos 2\varphi \tag{8}$$

The Fourier function for θ interpolation on long-bridge (LB) and short-bridge (SB) sites is:

$$I_{LB,SB}(\theta,\varphi) = \frac{1}{4}\left((I_0(\varphi) + 2I_{45}(\varphi) + I_{90}(\varphi) + 2(I_0(\varphi) - I_{90}(\varphi))\cos 2\theta + (I_0(\varphi) - 2I_{45}(\varphi) + I_{90}(\varphi))\cos 4\theta\right) \tag{9}$$

c) The configurations calculated on the non-symmetrical top-hollow site ($X = a/4, Y = a/(4\sqrt{2})$) are: (1) $\theta = 0°$; (2) $\theta = 45°$ and $\varphi = 35.26$; (3) $\theta = 45°$ and $\varphi = 90°$; (4) $\theta = 45°$ and $\varphi = 144.74°$; (5) $\theta = 45°$ and $\varphi = 215.26°$; (6) $\theta = 45°$ and $\varphi = 270°$; (7) $\theta = 45°$ and $\varphi = 324.74°$; (8) $\theta = 90°$ and $\varphi = 35.26°$; (9) $\theta = 90°$ and $\varphi = 90°$; (10) $\theta = 90°$ and $\varphi = 144.74°$. The Fourier functions of φ interpolation on the top-hollow site are:

$$I_0(\varphi) = I(1) \tag{10}$$

$$a_0 = \frac{1}{16}(3(I(2) + I(4) + I(5) + I(7)) + 2(I(3) + I(6)))$$

$$a_1 = \frac{\sqrt{6}}{8}(I(2) - I(4) - I(5) + I(7))$$

$$a_2 = \frac{3}{16}(I(2) + I(4) + I(5) + I(7) - 2(I(3) + I(6)))$$

$$b_1 = \frac{1}{32\sqrt{3}}(9(I(2) + I(4) - I(5) - I(7)) + 10\sqrt{3}(I(3) - I(6)))$$

$$b_2 = \frac{3\sqrt{2}}{16}(I(2) - I(4) + I(5) - I(7))$$

$$b_3 = \frac{3}{32}(\sqrt{3}(I(2) + I(4) - I(5) - I(7)) + 2(I(6) - I(3)))$$

$$I_{45}(\varphi) = a_0 + a_1\cos\varphi + a_2\cos 2\varphi + b_1\sin\varphi + b_2\sin 2\varphi + b_3\sin 3\varphi \tag{11}$$

$$I_{135}(\varphi) = a_0 - a_1\cos\varphi + a_2\cos 2\varphi - b_1\sin\varphi + b_2\sin 2\varphi - b_3\sin 3\varphi \tag{12}$$

$$I_{90}(\varphi) = \frac{1}{8}(3I(8) + 3I(10) + 2I(9) + 3\sqrt{2}(I(8) - I(10))\sin 2\varphi + 3(I(8) + I(10) - 2I(9))\cos 2\varphi) \tag{13}$$

The Fourier function for θ interpolation on the top-hollow (T-H) site is:

$$I_{T-H}(\theta,\varphi) = \frac{1}{4}\left((I_0(\varphi) + I_{45}(\varphi) + I_{90}(\varphi) + I_{135}(\varphi)) + (I_0(\varphi) - I_{45}(\varphi) + I_{90}(\varphi) - I_{135}(\varphi))\cos 4\theta\right)$$
$$+ \frac{1}{2}\left((I_0(\varphi) - I_{90}(\varphi))\cos 2\theta + (I_{45}(\varphi) - I_{135}(\varphi))\sin 2\theta\right) \tag{14}$$

Once the (r, Z, θ, φ) interpolation is performed, one is left with one I^{6D} value for each of the five sites that conform the DFT energy grid: top I_T, hollow I_H, long-bridge I_{LB}, short-bridge I_{SB} and top-hollow I_{T-H}. Then, we use the 2D scattered cubic spline interpolation from Ref. [2] to get values in between each of top, hollow, long bridge and short bridge sites giving us a rectangular grid of nine values. On this grid we use a 2D periodic cubic spline as in Ref. 3 to get the final value $I^{6D}(X, Y, Z, r, \varphi, \theta)$ from which we finally get the intended $V^{6D}(X, Y, Z, r, \varphi, \theta)$ by adding the corresponding V^{3D} values.

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* ivor.loncaric@gmail.com
† wapalocm@ehu.es
‡ josebainaki.juaristi@ehu.es

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