SUPPORTING INFORMATION

Dopamine Adsorption on Rutile TiO$_2$(110):
Geometry, Thermodynamics, and Core-Level
Shifts from First Principles

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This Supporting Information contains:

- Geometries of gas-phase dopamine obtained with optB86b-vdW (Table S1)
- Adsorption energies for the dopamine-TiO$_2$(110) adsorption complex calculated within the optB88-vdW and PBE approaches (Table S2)
- Analysis of the presence of co-adsorbed hydrogen on the surface
- Core-level shift calculations within the initial state approximation for the most stable configuration
- Bader charge analysis for the “Bridging G” configuration

**Table S1.** Computed structural parameters for gas-phase dopamine predicted by the optB86b-vdW functional. For numbering, refer to Figure 1 in the main section.

| parameters       | Conformer G | Conformer A |
|------------------|-------------|-------------|
| $d$(O1–ring)     | 1.371 Å     | 1.385 Å     |
| $d$(O2–ring)     | 1.384 Å     | 1.371 Å     |
| $d$(C–C ring)    | ~1.398 Å    | ~1.398 Å    |
| $d$(C7–ring)     | 1.508 Å     | 1.509 Å     |
| $d$(C7–C8)       | 1.536 Å     | 1.533 Å     |
| $d$(C8–N)        | 1.467 Å     | 1.467 Å     |
| $d$(O–H)         | ~0.977 Å    | ~0.977 Å    |
| $d$(C–H)         | ~1.106 Å    | ~1.106 Å    |
| $d$(N–H)         | ~1.025 Å    | ~1.025 Å    |
| $d$(ring–H)      | ~1.095 Å    | ~1.095 Å    |
| $\angle$N–C8–C7 | 110°        | 110°        |
| $\angle$C8–C7–ring | 112°     | 113°        |
| $\angle$N–C8–C7–ring | 63°      | 178°        |
Table S2. Calculated adsorption energies in eV of dopamine adsorbed on the TiO$_2$(110) surface obtained with the other two correlation and exchange functionals considered in the present work.

| Configuration | optB88-vdW | PBE  |
|---------------|------------|------|
| Bridging G    | -2.83      | -1.95|
| Bridging A    | -2.80      | -1.92|
| Chelating G   | -1.38      | -0.67|
| Chelating A   | -1.34      | -0.66|

**Analysis of the Presence of Co-Adsorbed Hydrogen on the Surface**

To assess the effect of both dissociated hydrogen atoms on the dopamine-TiO$_2$(110) adsorption complex, test calculations for the most stable configuration were undertaken for two different locations relative to the adsorbed dopamine, which are labeled (1) and (2) in Figure S1. In location (1) the resulting surface hydroxyls were intentionally placed far away from the adsorption site to isolate the remaining dopamine, whereas in location (2) hydrogen interactions between both hydroxyl groups and enolate dopamine were promoted. It was found that a configuration resulting from placing both protons at location (2) is energetically more favorable than its counterpart by 0.29 eV. In this configuration the calculated tilt angles are $\alpha=68^\circ$ and $\beta=23^\circ$ (see Figure 4 in the main section). However, this adsorption geometry is not compatible with the values determined by angle-resolved NEXAFS spectra ($\alpha=78\pm5^\circ$ and $\beta=11\pm5^\circ$). Therefore, the dissociated hydrogen atoms from dopamine were placed as far as possible from the adsorption site in all configurations.

The above calculations lead us to two conceptions. First, identification of adsorption geometry adopted by the dopamine onto TiO$_2$(110) surface cannot be done on the basis of adsorption energies alone; consequently, it is necessary to resort to a direct comparison with experiment. That was also the case for benzoate adsorption onto this surface, where a
combination of scanned-energy mode PhD and DFT calculations identified an upright/coplanar structure, even though theoretical modelling suggested that more tilted/twisted adsorption geometries were also possible.\textsuperscript{1} In this system, however, there is not a direct effect of co-adsorbed hydrogens in the tilted angles, which prefer to be adjacent to the adsorbed benzoate. And second, surface hydroxyls at location (2) might cause a rotational motion of the adsorbed dopamine across the surface. Upon adsorption, the fully dissociated dopamine donates its two hydrogen atoms to nearby $O_{be}$ atoms at the surface. Any of the two protons is prone to be back transferred from $O_{br}$ atoms, evidenced by a more twisted configuration resulting from scenario (2). When this happens, one $O_{dopamine}-Ti_{5f}$ bond is broken and the dopamine “lifts one leg” from the surface. After that, dopamine might rotate around the remaining $O_{dopamine}-Ti_{5f}$ bond. This dynamic process has been evidenced experimentally and theoretically for catechol on rutile-TiO$_2$(110) surface.\textsuperscript{2} The rotation of catechol on this surface consists of several intermediate states, with an energy barrier of 0.37 eV for the intermediate state with the highest energy. We believe that this might also be the case for the dopamine-TiO$_2$(110) system. However, the present investigation focuses on the immobile enolate dopamine only.

![Figure S1](image)

**Figure S1.** Representation of the two possible locations for both dissociated hydrogen atoms upon dopamine adsorption. Locations are relative to the adsorbed dopamine (represented with black spheres) and were selected to isolate the adsorbed dopamine (1), and to promote hydrogen interactions between both surface hydroxyl groups and enolate dopamine (2).
Core-Level Shift Calculations Within the Initial State Approximation for the Most Stable Configuration

Table S3. Core-level shift calculations within the initial state (IS) and final state (FS) approximations for the most stable configuration, Bridging G. Refer to Figure 1 in the main section for numbering.

|        | IS  | FS  | experiment^a |
|--------|-----|-----|--------------|
| ∆BE (C1) | 1.7 | 1.5 | 1.9          |
| ∆BE (C2) | 1.8 | 1.5 | 1.9          |
| ∆BE (C3) | 0.0 | 0.0 | 0.0          |
| ∆BE (C4) | 0.2 | 0.3 | 0.6          |
| ∆BE (C5) | 0.0 | 0.2 | 0.0          |
| ∆BE (C6) | 0.0 | 0.0 | 0.0          |
| ∆BE (C7) | -0.1 | 1.9 | 0.6          |
| ∆BE (C8) | 0.5 | 3.0 | 1.6          |

^a Ref. 3.

For the core-level shift calculations within the initial state approximation reported here, the chemical shift, ∆BE^{IS}_{CL}(A), is defined as the negative of the difference in core-level eigenvalue of specific core-electrons ε_{CL} between an atom A and a reference atom A_{ref}, as described in Ref. 4:

\[
\Delta BE^{IS}_{CL}(A) = -[\epsilon_{CL}(A) - \epsilon_{CL}(A_{ref})]
\]

Within this approximation, relaxation effects are completely neglected, i.e., only the state of the system before the photoionization process is considered.

According to Table S3, the calculated shifts in the C 1s BEs indicate that initial state effects dominate the relative chemical shifts in the benzene ring. On the other hand, such chemical shifts in the ethyl chain are directed by the so-called final state effects.
Bader Charge Analysis for the “Bridging G” Configuration

**Table S4.** Bader charge analysis for the most stable configuration, Bridging G. Positive (negative) values indicate electron charge depletion (gaining). For numbering, see Figure 1 in the main section.

|       | Bader net atomic charge | chemical shifts |
|-------|-------------------------|-----------------|
|       | gas-phase dopamine      | adsorbed dopamine | charge redistribution | theory | experiment<sup>a</sup> |
| O1    | -1.14                   | -1.04           | 0.10              | 0.0    | 0.0                  |
| O2    | -1.16                   | -1.05           | 0.12              | 0.0    | 0.0                  |
| C1    | 0.49                    | 0.49            | 0.01              | 1.5    | 1.9                  |
| C2    | 0.38                    | 0.59            | 0.21              | 1.5    | 1.9                  |
| C3    | -0.04                   | -0.01           | 0.03              | 0.0    | 0.0                  |
| C4    | 0.05                    | -0.04           | -0.08             | 0.3    | 0.6                  |
| C5    | -0.10                   | -0.07           | 0.03              | 0.2    | 0.0                  |
| C6    | 0.02                    | 0.05            | 0.03              | 0.0    | 0.0                  |
| C7    | 0.02                    | 0.02            | -0.01             | 1.9    | 0.6                  |
| C8    | 0.28                    | 0.29            | 0.01              | 3.0    | 1.6                  |
| N     | -1.12                   | -1.13           | -0.01             | -      | -                    |
| H–O<sub>br</sub> | 0.62 | 0.62 | 0.00 | - | - |
| H–O<sub>br</sub> | 0.63 | 0.63 | -0.01 | - | - |
| H–C3  | 0.06                    | 0.08            | 0.02              | -      | -                    |
| H–C5  | 0.06                    | 0.06            | 0.00              | -      | -                    |
| H–C6  | 0.06                    | 0.07            | 0.01              | -      | -                    |
| H–C7  | 0.03                    | 0.01            | -0.01             | -      | -                    |
| H–C7  | 0.03                    | 0.03            | 0.00              | -      | -                    |
| H–C8  | 0.04                    | 0.05            | 0.01              | -      | -                    |
| H–C8  | 0.01                    | 0.02            | 0.01              | -      | -                    |
| H–N   | 0.40                    | 0.39            | -0.01             | -      | -                    |
| H–N   | 0.39                    | 0.39            | 0.00              | -      | -                    |
| 1<sup>st</sup> tri-layer | - | - | -0.50 | - | - |

<sup>a</sup>Ref. 3.
We have calculated the effective atomic charges using the Bader methodology, where an atom is defined as a region of real space delimited by surfaces through which the flux of the density gradient is zero. For our Bader analysis we employed the implementation by Henkelman et al. 6-8

Bader charge analysis shows that a net charge of 0.45 $e$ is transferred to the TiO$_2$(110) surface. The amount of transferred charge is practically accounted by the benzene ring and the oxygens in the adsorbate which causes a charge redistribution among these atoms. Such a redistribution is not seen in C7 and C8.

REFERENCES

(1) Busayaporn, W.; Duncan, D. A.; Allegretti, F.; Wander, A.; Bech, M.; Møller, P. J.; Doyle, B. P.; Harrison, N. M.; Lipsky, B. R. Structure of a Model Dye/Titania Interface: Geometry of Benzoate on Rutile-TiO$_2$ (110)(1 × 1). J. Phys. Chem. C 2016, 120 (27), 14690–14698.

(2) Li, S. C.; Chu, L. N.; Gong, X. Q.; Diebold, U. Hydrogen Bonding Controls the Dynamics of Catechol Adsorbed on a TiO$_2$(110) Surface. Science 2010, 328 (5980), 882–884.

(3) Jackman, M. J.; Syres, K. L.; Cant, D. J. H.; Hardman, S. J. O.; Thomas, A. G. Adsorption of Dopamine on Rutile TiO$_2$ (110): A Photoemission and near-Edge x-Ray Absorption Fine Structure Study. Langmuir 2014, 30 (29), 8761–8769.

(4) Lizzit, S.; Baraldi, A.; Groso, A.; Reuter, K.; Ganduglia-Pirovano, M.; Stampfl, C.; Scheffler, M.; Stichler, M.; Keller, C.; Wurth, W.; Menzel, D. Surface Core-Level Shifts of Clean and Oxygen-Covered Ru(0001). Phys. Rev. B 2001, 63 (20), 205419.
(5) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press, Oxford (UK), 1990.

(6) Henkelman, G.; Arnaldsson, A.; Jónsson, H. A Fast and Robust Algorithm for Bader Decomposition of Charge Density. *Comput. Mater. Sci.* 2006, 36 (3), 354–360.

(7) Sanville, E.; Kenny, S. D.; Smith, R.; Henkelman, G. Improved Grid-Based Algorithm for Bader Charge Allocation. *J. Comput. Chem.* 2007, 28 (5), 899–908.

(8) Tang, W.; Sanville, E.; Henkelman, G. A Grid-Based Bader Analysis Algorithm without Lattice Bias. *J. Phys. Condens. Matter* 2009, 21 (8), 084204.