

Supporting Information for “Uncovering Chemical Homology of Superheavy Elements: A Close Look at Astatine”

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S1 Hypothetical interpretation of Fig. 6 in ref. 38

The appearance of the AtOH molecule adsorbed on the Au(111) surface, as depicted in Fig. 6 of ref. 38, suggests that the OH group migrates to the edge of the supercell, while the At atom remains in the hollow-3 position. Furthermore, the values of $d(\text{At} - \text{O})_{\text{ads}} = 3.34 \text{ \AA}$ vs. $d(\text{At} - \text{O})_{\text{free}} = 2.15 \text{ \AA}$ in Table 6 suggest dissociative adsorption of the AtOH molecule.

We attempt to mimic this situation by putting the AtOH molecule in a “flat” position (the initial state in Fig. 1 here) on the Au₁₀ cluster, freezing the At (and Au) atoms, and allowing for the structure to relax.

In the initial state, the AtOH adsorption energy on Au₁₀ is *ca.* 106 kJ/mol, roughly the

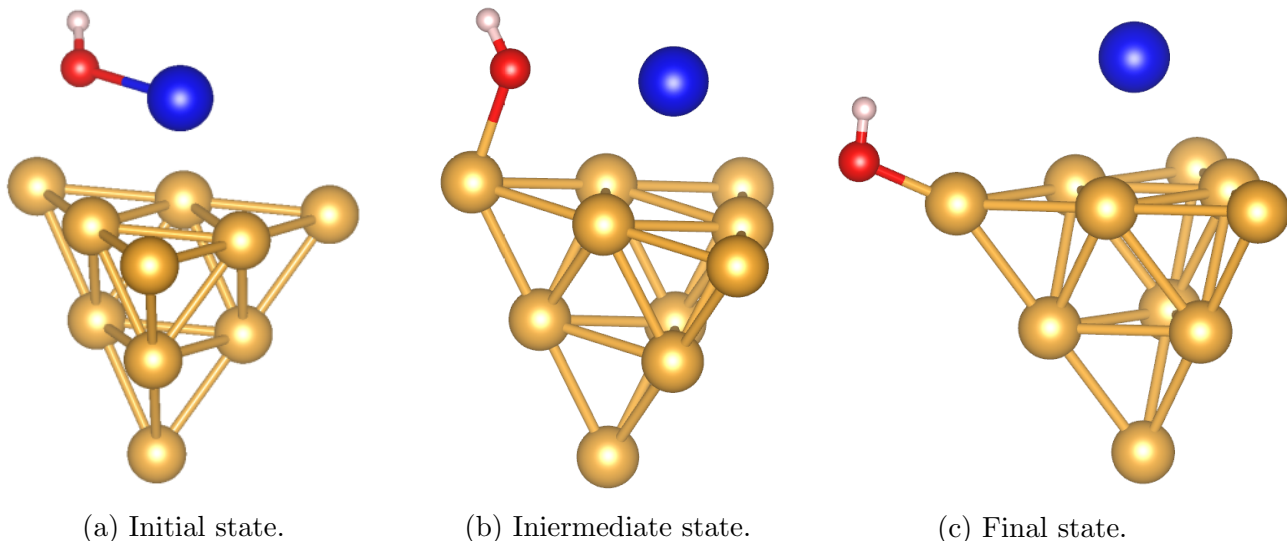


Figure S1: Structure of AtOH – Au₁₀ adsorption complex.

same as for the lateral position of the AtOH molecule with the same geometry (for larger clusters, as shown previously, the lateral position becomes preferred).

The final state (see Fig. 1 here) of this geometry optimisation (at the 2c-RDFT/PBE0-D4/RDFT (Au), PSO-Lc+g (At), aug-pcseg-2 (H, O) level) represents the complete dissociation of the At–O bond and the attachment of the OH group to the corner of the Au₁₀ cluster. Of course, this overly primitive simulation exaggerates the situation in ref. 38 through the stabilisation of this small cluster model as the OH group saturates the “free valences” of the corner atom. Still, it may point towards a similar driving force behind the migration of the OH to the edge of the supercell in ref. 38.

However, if we consider an “intermediate” state with the geometry reasonably close to that from Table 6 in ref. 38: $d(\text{At} - \text{O})_{\text{ads}} = 3.01 \text{ \AA}$ $d(\text{At} - \text{Au})_{\text{ads}} = 2.95 \text{ \AA}$ $d(\text{Au} - \text{O})_{\text{ads}} = 2.28 \text{ \AA}$ the resulting adsorption energy is 188 kJ/mol, which is close to the result in ref. 38. Thus, we find it possible to get a result similar to that in ref. 38 using the quasi-dissociated AtOH geometry. We hypothesise the attribution of this result to finite-size effects because, with the large cluster model used in our studies, the migration of OH to the edge does not happen, and AtOH adsorbs as a whole in the most stable lateral position, as demonstrated in this work.