

# Electronic Supplementary Information

## Ground and excited electronic states of AuH<sub>2</sub> via detachment energies on AuH<sub>2</sub><sup>-</sup> using state-of-the-art relativistic calculations

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## Theoretical insights on the Pseudo Jahn-Teller Effect (PJTE)

It has been previously reported in literature how, the distortion of linear centrosymmetric molecules is more likely a symmetry breaking (SB) consequence of the pseudo Jahn-Teller effect (PJTE), where a strong vibronic coupling is present in near-degenerate states. Here, we are going to shortly review the main points of the theory that may be useful to discuss our results. For further insights into PJTE theory, the reader may consult Refs. 1-4 .

The PJTE formalism allows to express the energy of the two coupled states as follows:

$$\varepsilon_{\pm}(Q) = \frac{1}{2} K_0 Q^2 \pm [\Delta^2 + F^2 Q^2]^{1/2} \quad [1]$$

where “ $\varepsilon$ ” is the energy of the two near-degenerate states, “ $Q$ ” is the nuclear displacement, “ $K_0$ ” the force constant in absence of vibronic coupling which in the model is assumed to be the same for the two electronic states, “ $\Delta$ ” is the electronic coupling parameter and “ $F$ ” is the vibronic coupling constant.

There are some conditions for which the PJTE has an impact on the APESs of potentially coupled states. First of all, there is a symmetry constraint: PJTE takes place (i.e.  $F \neq 0$ ) only when the symmetry of the two states is compatible with the symmetry of the displacement, as follows:

$$\check{\Gamma} = \Gamma \times \Gamma' \quad [2]$$

where  $\check{\Gamma}$  is the irreducible representation of the nuclear displacement and  $\Gamma$  and  $\Gamma'$  are the irreducible representations to which the lower and higher energy coupled states belong to the high symmetry configuration respectively. Then, the following condition must be verified in order to have an actual PJT-symmetry breaking:

$$\Delta < \frac{F^2}{K_0} \quad [3]$$

Since  $\Delta$  can be envisaged as the half of the separation between the two coupled states in their high symmetry configuration, this means that the closer these states are in energy, the stronger the vibronic coupling is and an actual SB is observed. Moreover, when the symmetry breaking takes place, the barrier separating the high symmetry configuration and the lower-energy distorted one can be expressed as follows:

$$E_{barr} = \frac{1}{2} \left( \frac{F^2}{K_0} + K_0 \frac{\Delta^2}{F^2} \right) - \Delta \quad [4]$$

with the curvature of the two coupled states being:

$$K^{\Gamma} = K_0^{\Gamma} - \frac{|F|^2}{\Delta} \quad [5]$$

$$K^{F'} = K_0^{F'} + \frac{|F|^2}{\Delta} \quad [6]$$

Eqs. 5 and 6 show how actually, upon symmetry breaking, the resulting APES of the lower state results to be “softened”, whereas the higher state’s is “hardened”.

**Table S1.** VDEs (in eV) for AuH<sub>2</sub><sup>-</sup> calculated using Koopman's theorem (KT) by the means of approximate 2-component Scalar (SR) and SpinOrbit (SO) ZORA Hamiltonians. Basis set for all calculations is TZ2P. Experimental VDEs are reported for reference.

<b>State / PES Band</b>	<b>Experimental VDE (eV)</b>	<b>SR-ZORA-KT VDE (eV)</b>	<b>SO-ZORA-KT VDE (eV)</b>
$^2\Sigma^+_{1/2u} / X$	3.678	3.892	3.952
$^2\Sigma^+_{1/2g} / A$	3.904	3.705	3.620
$^2\Delta_{5/2g} / B$	4.635	6.512	5.786
$^2\Pi_{3/2g} / C$	4.785	6.810	6.009
$^2\Pi_{1/2g} / D$	5.745	6.810	7.068
$^2\Delta_{3/2g} / E$	6.22	6.510	7.661

**Table S2.** X2C-EOM-CCSD calculated equilibrium energies and bond lengths at linear geometry (centrosymmetric configuration) for AuH<sub>2</sub> ground and first five excited states. Dyall.vtz basis set was used. The energy has been scaled according to the minimum.

<b>State</b>	<b>Energy (eV)</b>	<b>Bond length (Å)</b>
$^2\Sigma^+_{1/2u}$	0	1.64
$^2\Sigma^+_{1/2g}$	0.054	1.63
$^2\Delta_{5/2g}$	0.816	1.64
$^2\Pi_{3/2g}$	0.952	1.66
$^2\Pi_{1/2g}$	1.932	1.66
$^2\Delta_{3/2g}$	2.422	1.64

**Table S3.** X2C-EOM-CCSD calculated energies (in eV) at different geometries (bond length fixed at 1.64 Å) for AuH<sub>2</sub> ground and first five excited states. Dyall.vtz basis set was used. The energy has been shifted according to the minimum. The states are labeled with the symmetry of the minimum energy nuclear configuration.

Angle (degrees)	<sup>2</sup> B <sub>2</sub> (eV)	<sup>2</sup> Σ <sup>+</sup> <sub>1/2g</sub> (eV)	<sup>2</sup> Δ <sub>5/2g</sub> (eV)	<sup>2</sup> Π <sub>3/2g</sub> (eV)	<sup>2</sup> Π <sub>1/2g</sub> (eV)	<sup>2</sup> Δ <sub>3/2g</sub> (eV)
180	0.664	0.713	1.481	1.591	2.595	3.087
170	0.527	0.803	1.536	1.725	2.702	3.155
160	0.317	0.996	1.701	2.007	2.984	3.375
150	0.142	1.295	1.963	2.346	3.327	3.782
140	0.035	1.682	2.309	2.734	3.682	4.329
130	0	2.133	2.718	3.172	4.056	4.918
120	0.029	2.617	3.168	3.656	4.438	5.483

**Table S4.** X2C-EOM-CCSD calculated energies at different geometries (bond length fixed at 1.64 Å) for AuH<sub>2</sub> ground and first five excited states. Dyall.vdz basis set was used. The energy has been shifted according to the minimum.

Angle (degrees)	<sup>2</sup> B <sub>2</sub> (eV)	<sup>2</sup> Σ <sup>+</sup> <sub>1/2g</sub> (eV)	<sup>2</sup> Δ <sub>5/2g</sub> (eV)	<sup>2</sup> Π <sub>3/2g</sub> (eV)	<sup>2</sup> Π <sub>1/2g</sub> (eV)	<sup>2</sup> Δ <sub>3/2g</sub> (eV)
180	0.711	0.713	1.378	1.494	2.517	2.984
170	0.551	0.808	1.433	1.639	2.627	3.053
160	0.326	0.993	1.598	1.927	2.911	3.281
150	0.144	1.285	1.862	2.267	3.248	3.708
140	0.035	1.665	2.211	2.657	3.598	4.268
130	0	2.105	2.622	3.096	3.971	4.864
120	0.030	2.577	3.072	3.580	4.354	5.430

**Table S5.** X2C-EOM-CCSD calculated energies at different geometries (bond length fixed at 1.64 Å) for AuH<sub>2</sub> first excited state. Dyll.vdz basis set were used. Experimental values are reported for reference. The energy has been shifted according to the minimum.

<b>Bond angle (°)</b>	<b>Energy (eV)</b>
180	0.000
178	0.016
176	0.033
174	0.052
172	0.068
170	0.095



**Table S6.** X2C-EOM-CCSD calculated energies at different geometries (bond length fixed at 1.64 Å) for AuH<sub>2</sub> first excited state. Dyall.vtz basis sets were used. Experimental values are reported for reference. The energy has been shifted according to the minimum.

<b>Bond angle (°)</b>	<b>Energy (eV)</b>
180	0.000
178	0.008
176	0.024
174	0.043
172	0.065
170	0.092

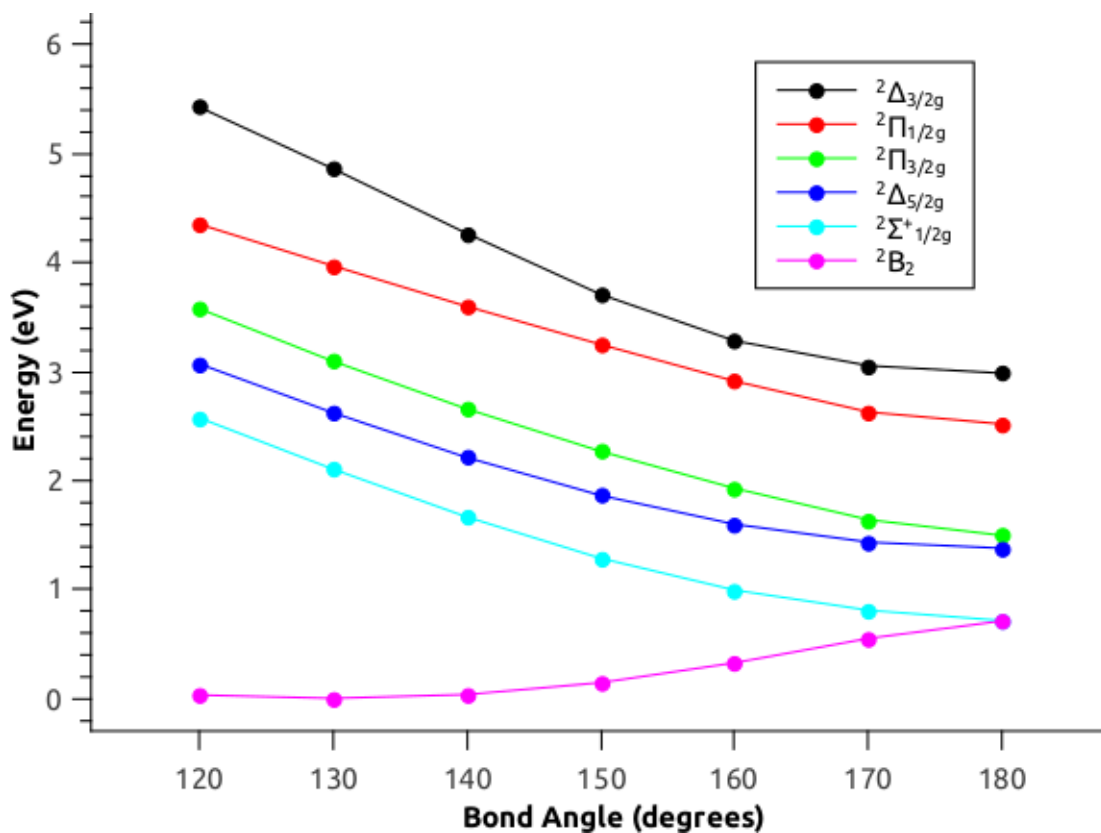
**Table S7.** Difference in the Zero Point Energy between the AuH<sub>2</sub><sup>-</sup> anion and the neutral AuH<sub>2</sub> ( $\Delta ZPE_{0-0}$ ) calculated at the DFT level (PBE functional) with different double-, triple- and quadruple-type basis sets.

<b>Basis set</b>	<b><math>\Delta ZPE_{0-0}</math> (eV)</b>
DZ	0.030
TZ2P	0.029
QZ4P	0.038

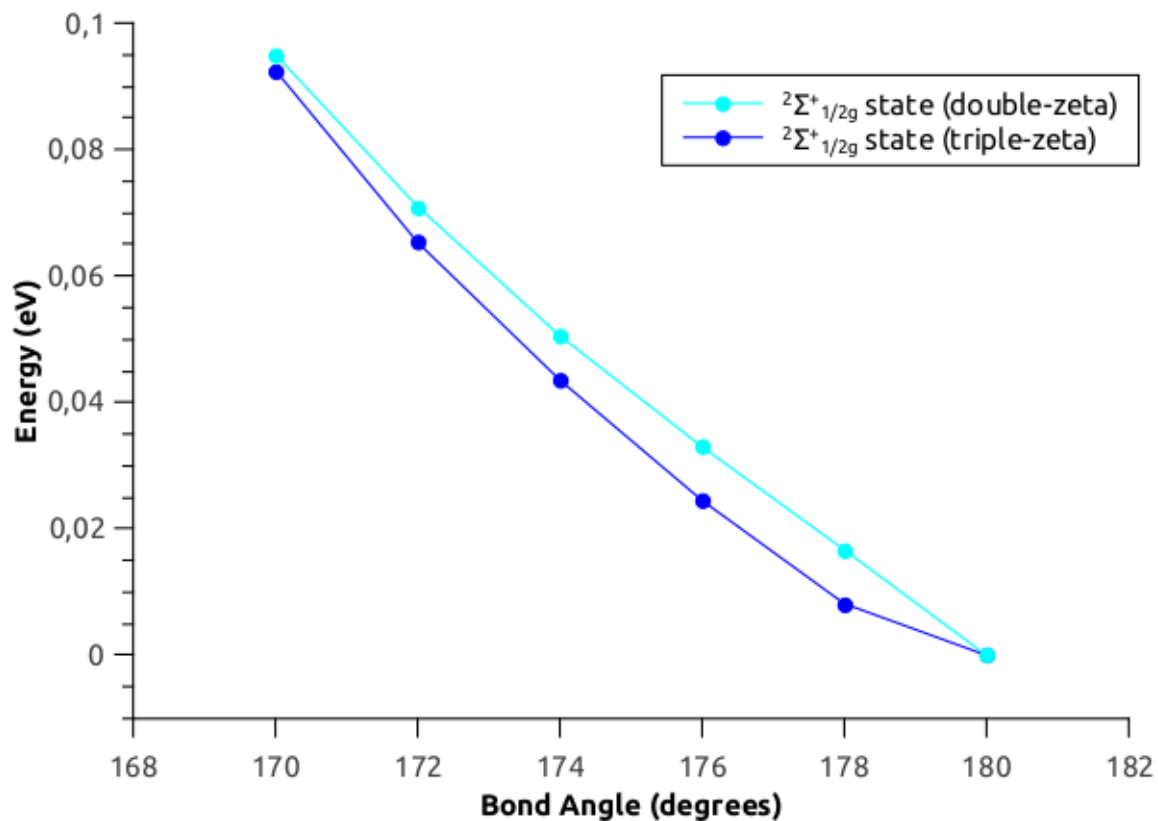
**Table S8.** X2C-EOM-CCSD calculated dipole expectation values ( $\langle\mu\rangle$ ) at different asymmetric displacements ( $\Delta R$ ) with a fixed H-H' distance (3.3 Å) for gold dihydride's ground state. Calculations have been performed with dyall.vdz basis set.

$\Delta R$ (Å)	$\langle\mu\rangle$ (D)
-0.12	0.77
-0.10	0.72
-0.08	0.57
-0.06	0.38
-0.04	0.30
-0.02	0.11
0.00	0.00
0.02	-0.11
0.04	-0.30
0.06	-0.38
0.08	-0.57
0.10	-0.72
0.12	-0.77

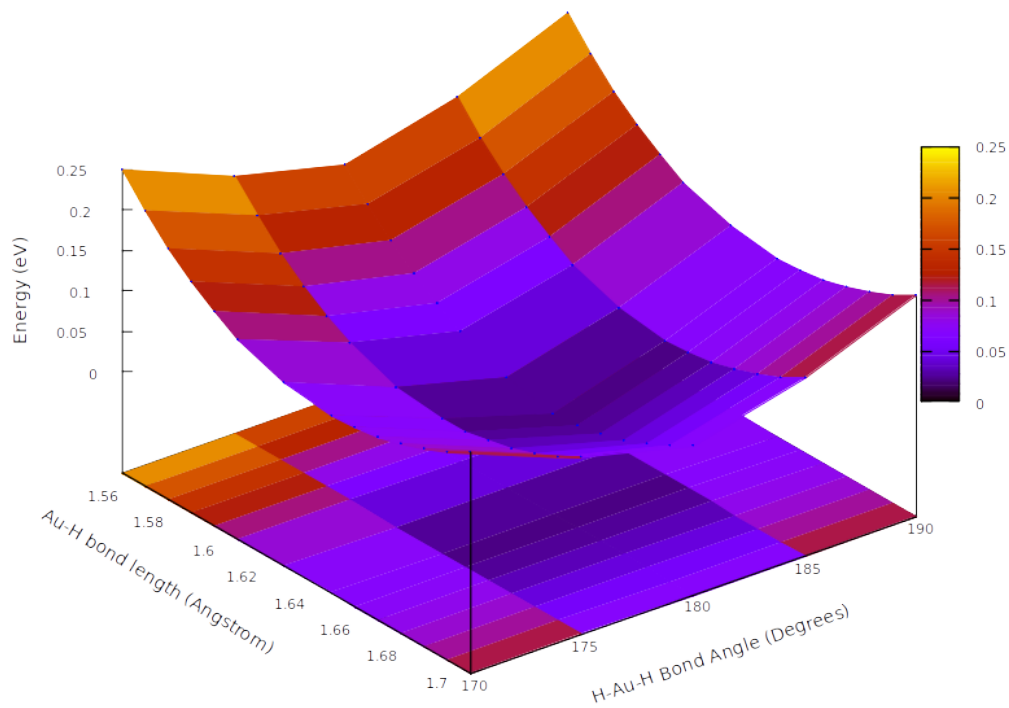
**Figure S1.** X2C-EOM-CCSD calculated APESs (bond length frozen at 1.64 Å) for AuH<sub>2</sub> ground and first five excited states. Basis set: dyall.vdz. The energy has been shifted relative to the minimum.



**Figure S2.** X2C-EOM-CCSD calculated close-up of the APES (bond length frozen at 1.64 Å) of AuH<sub>2</sub> first excited state. Dyall.vdz and dyall.vtz basis sets were used. The energy has been shifted according to the minimum.



**Figure S3.** 3D plot of the first excited state's APES of AuH<sub>2</sub>. Calculations have been performed at the X2C-EOM-CCSD level. Dydall.vdz basis sets was used. The energy has been shifted according to the minimum.



## References

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