Supporting information for
***Ab-initio* investigation of hot electron transfer in CO_2 plasmonic photocatalysis in presence of hydroxyl adsorbate**

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Methods

The investigated structures were built with the open-source atomic simulation environment (ASE)[1] v3.22.0. All geometries were relaxed using the BFGS optimizer in ASE till the residual forces per atoms reached <0.08 eV/atoms. In these calculations we used the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional with the Tkatchenko and Scheffler van der Waals correction[2], double-ζ polarized (dzp) basis sets, a uniform real-space grid spacing of h = 0.2 Å, and a vacuum that extended 12 Å from the Au cluster. The freely available GPAW package[3, 4] v22.1.1b1, with linear combination of atomic orbitals (LCAO)[5] was used to perform DFT calculations on optimized structures and the optical properties and carrier distributions were computed using the LCAO-TDDFT implementation[6]. The orbital-dependent GLLB-SC exchange correlation functional[7] was used for an improved d-band description, a Fermi-Dirac smearing of 0.05 to improve convergence, a grid spacing of h = 0.3 Å and vacuum thickness of 12 Å around the systems. The systems were excited with using the δ-kick technique in the linear-response regime, with the kick applied in the z-direction (kick = [0, 0, k], k=1×10^{-5} eV Å^{-1}) and its response recorded for 30 fs with steps of 20 as. The photoabsorption spectra are the obtained by the Fourier transform of the recorded dipole moment. The photoabsorption spectra, DOS and pDOS were broadened using a Gaussian smearing of 0.1 eV. Subsequently, the systems are excited with a Gaussian pulse –$E(t) = E_0 \cos(\omega_p(t - t_0))\exp(-\sigma^2(t - t_0)^2/2)$– centered at 10 fs and with varying ω_p and FWHM. Plasmon and hot electrons dynamics were are obtained in terms of the Kohn-Sham (KS) electron-hole transition contributions[8].

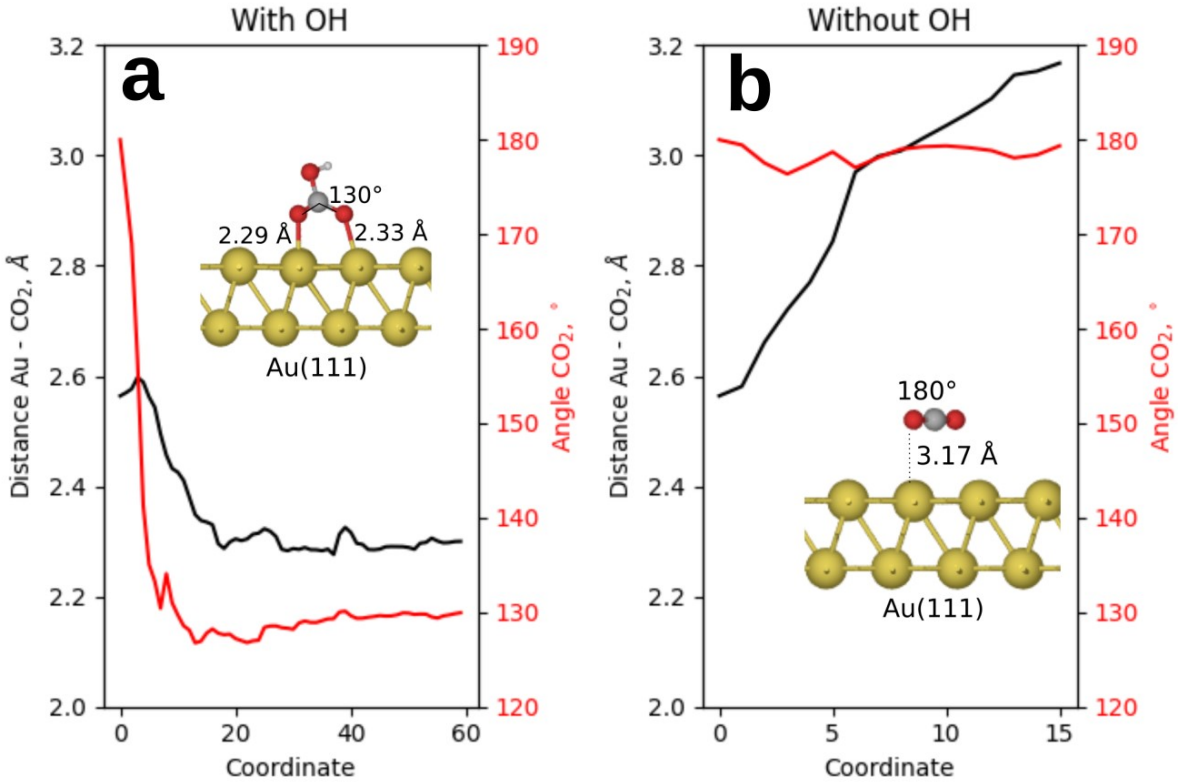

Figure S1. Relaxation of CO_2 on a small periodic Au slab in the presence (a) and absence (b) of a OH group. In both cases, the CO_2 is placed at an initial distance of 2.55 Å and let relax till the residual forces reached < 0.05 eV/atoms. When OH is present the CO2 molecule approaches the surface and reaches equilibrium at a distance of ~2.33 Å, presenting an OCO angle of 130°. In the absence of OH, the most stable configuration is reached when CO_2 flies away from the Au slab and its angle always fluctuates around 180°.

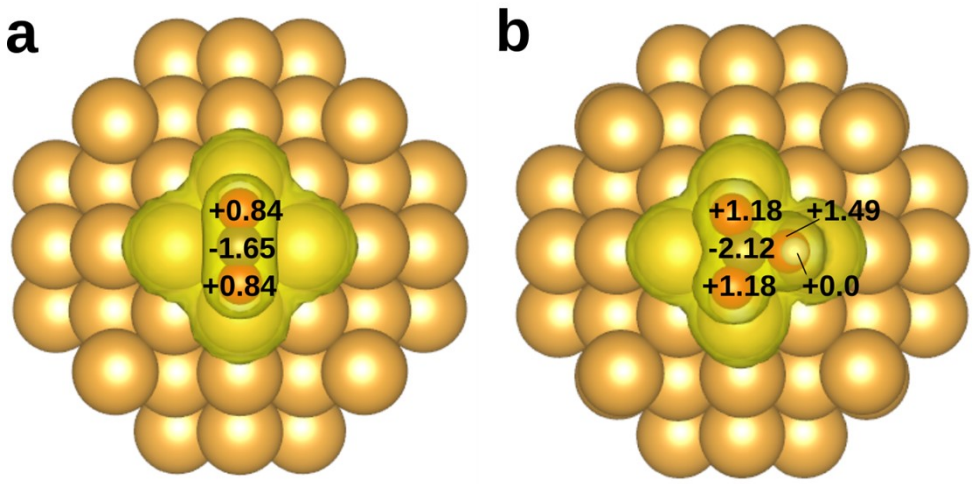

Figure S2. Bader charge analysis for (a) Au+CO_2 and (b) Au+CO_2+OH computed at an initial Au-CO_2 distance of 2 Å. Within this analysis, a positive value of Bader charge stands for the gain of electrons (resulting in a negative charge δ^-) compared to the neutral atoms, while a negative value represents a charge loss (resulting in a positive charge δ^+). This analysis reveals that in the presence of the OH specie, 1.18 electrons are transferred to the O atoms of CO_2, compared to 0.84 electrons transferred to the same atoms without the OH group. This leads to a stronger dipole in the CO_2 molecule, which favours the bending and activation of the molecule on the Au cluster, as seen from Figure 1a in the main text, which shows the change in O=C=O angle as a function of the distance.

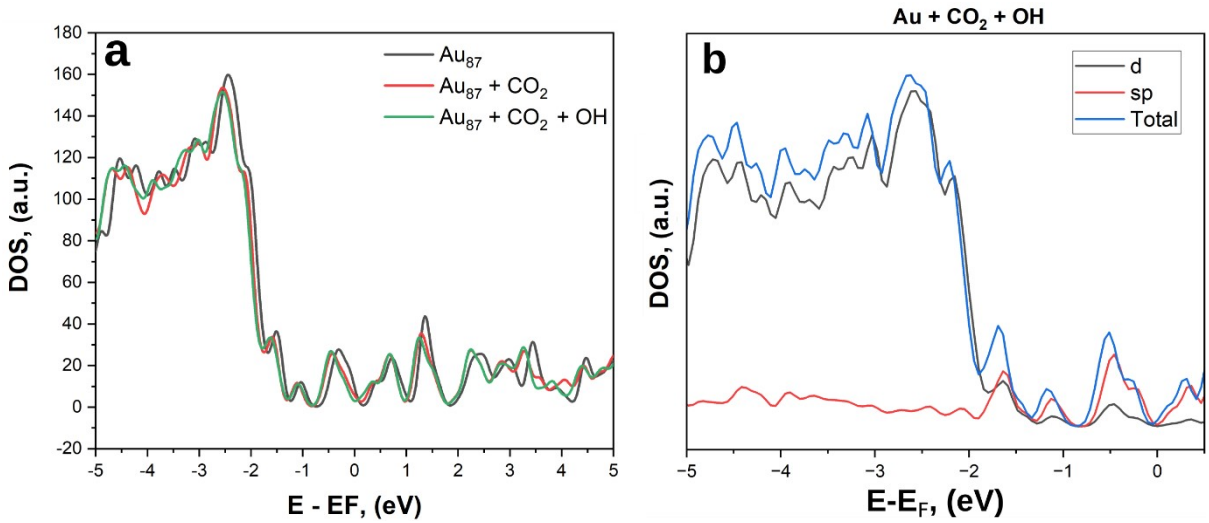

Figure S3. a) Total density of states for the different investigated systems. For Au+CO_2 and Au+CO_2+OH the DOS has been computed at a Au-CO_2 distance of 2 Å. b) DOS of Au+CO2+OH showing the relative contribution of the d-band and sp-band of Au.

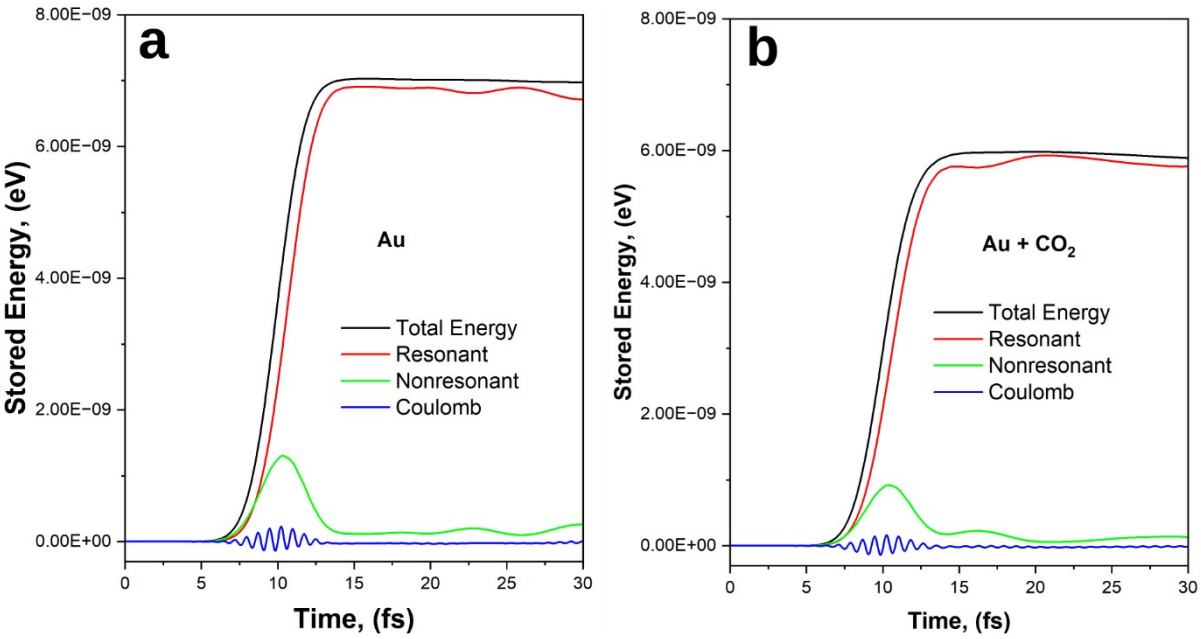

Figure S4. Contributions to the stored energy for (a) Au and (b) Au + CO_2 as a function of the time evolution of the system.

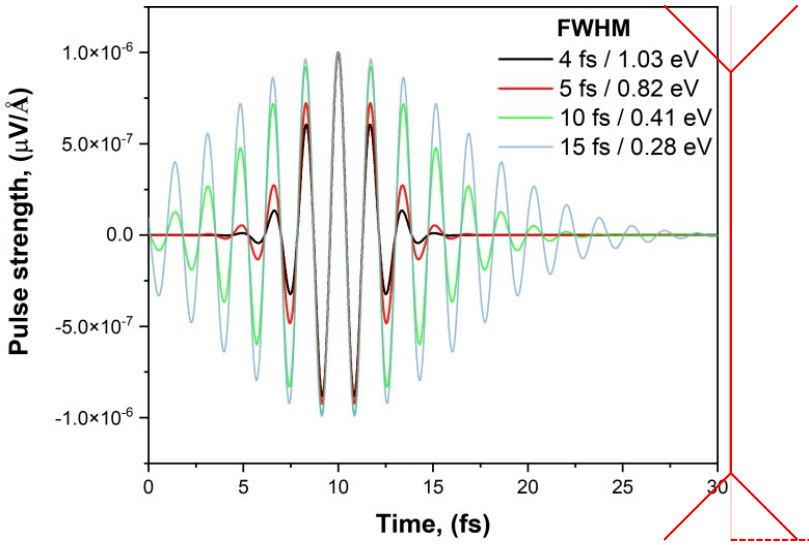

Figure S5. Profile of the different pulses in the time domain.

Comment [D]: Graphs **e** and **f**:
Correct energy uncertainty in the legends as per comment above, i.e.
DE = 0.52 eV for 4 fs,
DE = 0.41 eV for 5 fs,
DE = 0.21 eV for 10 fs,
DE = 0.14 eV for 15 fs.

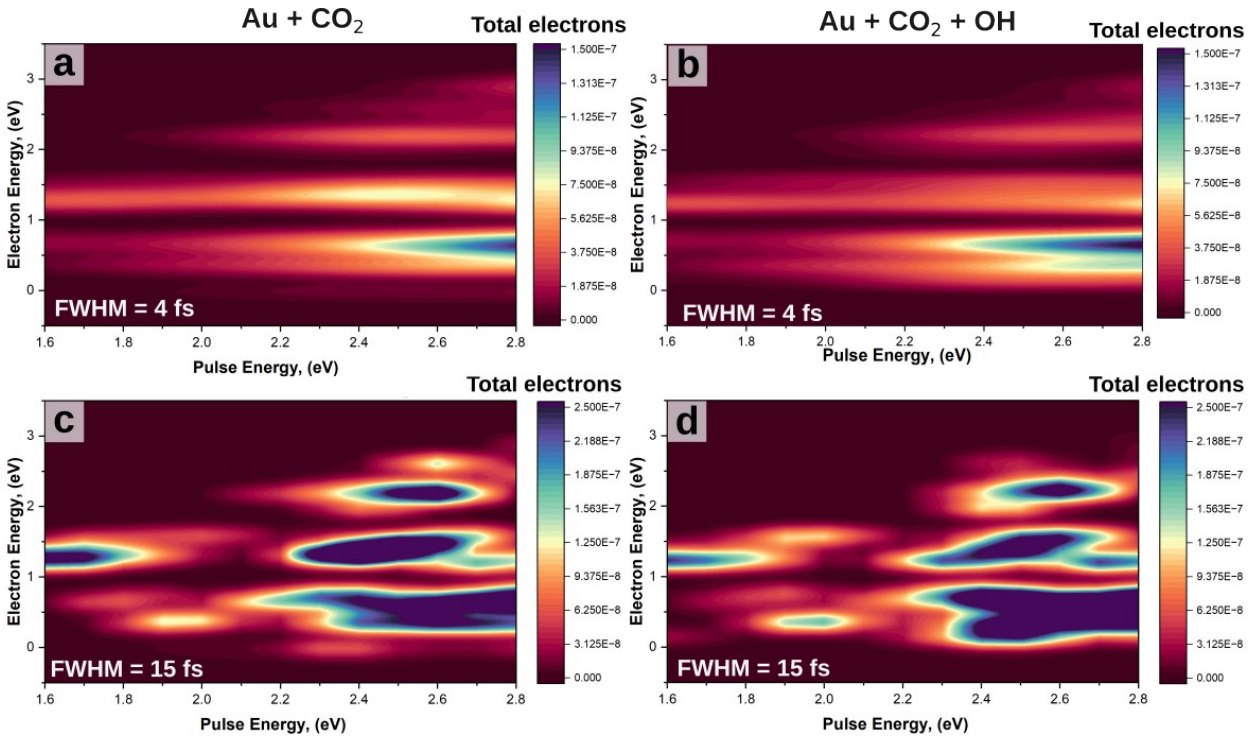

Figure S6. a-d) Total hot electrons generated in the Au + CO_2 and Au + CO_2 + OH as a function of their energy and pulse excitation, for FWHM of 4 fs and 15 fs.

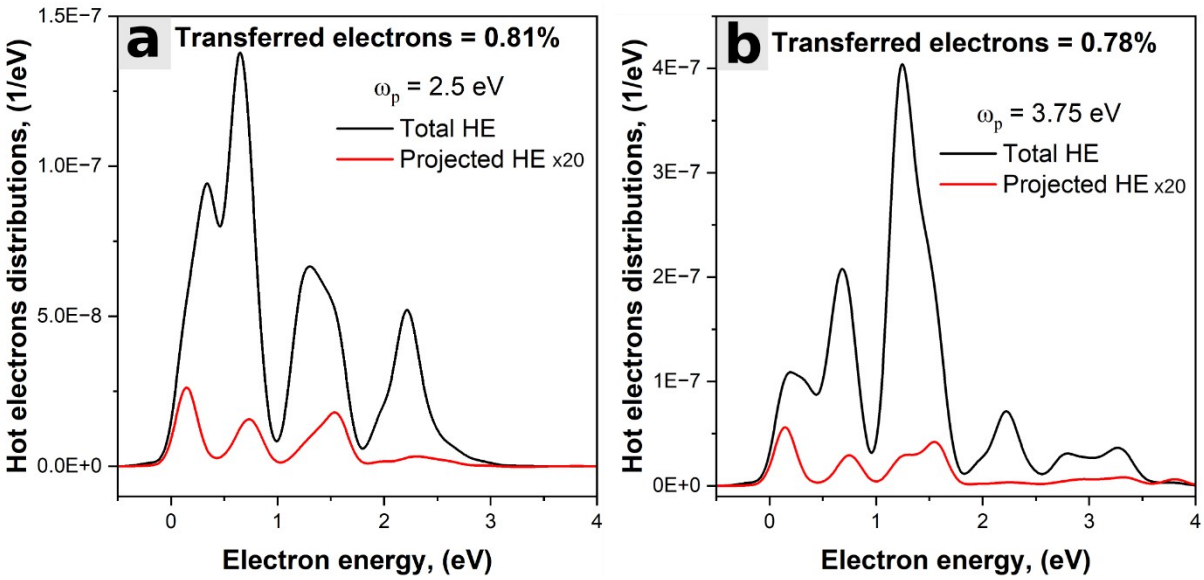

Figure S7. (a-b) Total and projected hot electron energy distributions for pulses with ωp = 2.5 eV (plasmon resonance), and 3.75 eV (interband transitions), respectively.

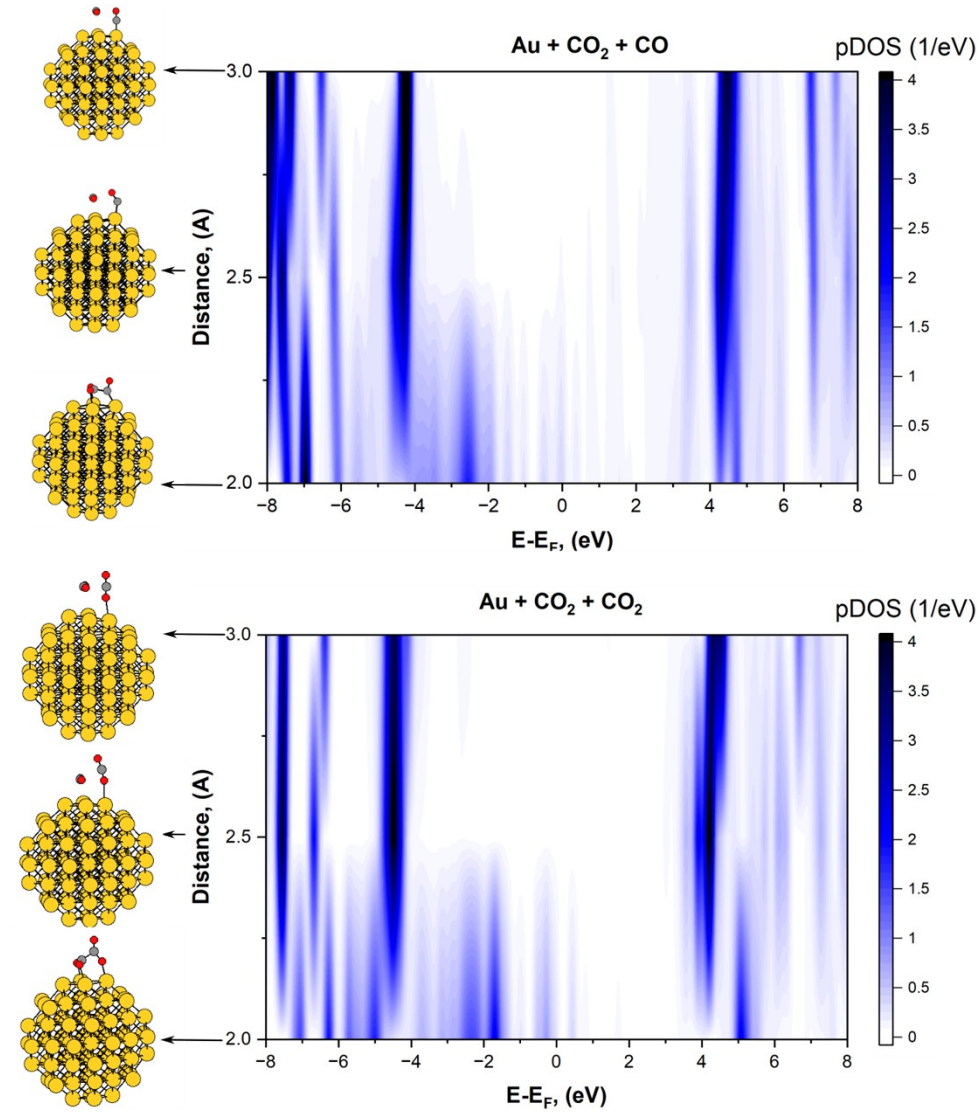

Figure S8. Effect of CO_2/CO (top) and CO_2/CO_2 (bottom) co-adsorbates on the hybridization process visualized through a pDOS analysis.

References

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