Table S1.

IRRAS spectra of CO adsorbed on a series of oxide single crystals. The vCO values are provided for surface saturation at the lowest investigated temperatures. Slight shifts to higher wavenumber due to coverage effect were sometimes reported (see relevant references below).

Single crystal	vCO (cm ⁻¹)	Adsorption	Reference	Adsorption	Reference
		Temperature		energy (meV)	
		(K)			
TiO ₂ (110)-rutile	2178	30	i	407ª	ii
				38 ^b	iii
TiO ₂ (101)-	2180	70	iv	461°	v
anatase				37 ^d	60
ZnO(101bar0)	2170	60	vi	210 ^e	vii
				32 ^f	61
α-Fe ₂ O ₃ (0001)	2169	65	viii	250 ^g	63
CeO ₂ (111)	2154	68	ix	290 ^h	64
UO ₂ (111)	2160	70	This work	302 ⁱ	This work
				270–0.290 ^j	This work

a.Computed: vdW DF2; 0.5 ML.

b. Experimental, temperature programmed desorption (TPD).

- c.DFT-PBE-D2.
- d. Experimental TPD.
- e. Computed: DFT-PBE, 0.5 ML.
- f. Experimental: IRRAS.
- g. Experimental: IRRAS.
- h. Computation: HSE06 D3, atop configuration, 1 ML.
- i. HSE06-SOC (SOC: spin-orbit coupling)-this work, 1 ML (see Table 1).
- j. Experimental: IRRAS, simulated TPD (surface near saturation).





Figure S1.

The UO₂(111) single crystal during Ar ion sputtering (3 x 10^{-5} torr, 2 kV, 9 mA) at about 1000 K (left) and at 370 K (right). Note the luminescence from the crystal which indicates that the complete surface is being ion sputtered. The luminescence originates from the U6d-O2p and U6d-U5f decay and is more intense at low temperatures.





Figure S2:

Schematic representation of (a) the computed UO₂ slab with an adsorbed CO molecule: side view (left) and top view (right); and (b) the oxidized UO₂ slab. The oxygen atom from the CO molecule is highlighted in light blue to distinguish it from the oxygen atoms within the UO₂ slab. Partial density of states obtained with c) DFT+U in the collinear formalism for the non-tilted configuration and d) HSE06 in the non-collinear formalism with spin-orbit coupling. In blue, the projection on the 5f U states, in red on the sp states of the surface UO₂ oxygen atoms, and in green on the CO molecular orbitals. The green arrow indicates the 5σ - 2π * molecular gap.

In **Figure S2**, we show the partial density of states of the CO-UO₂(111) system computed with DFT+U in the collinear formalism for the non-tilted CO configuration and with HSE06 in the non-collinear formalism with spin-orbit coupling. It can be seen that in both cases the unoccupied $2\pi^*$ molecular orbitals of the CO molecule (green) are pinned at the top of the uranium 5f-5f gap. The main difference between the two formalisms is that the 5σ - $2\pi^*$ molecular gap is significantly smaller in DFT+U than in HSE06. Similar to what happens in the CO-CeO₂ system⁶, the distance between the carbon atom and the U⁴⁺ site is shorter for DFT+U. This results in spurious charge donation between the molecule and the surface, thereby affecting the C-O bond and consequently, the vibrational frequency, as described in the main text.



Figure S3.

IRRAS was obtained after exposure of the clean $UO_2(111)$ single crystal at 73 K at the indicated Langmuir exposure (one Langmuir = 10^{-6} torr s).



В







Figure S4.

(A) to (F) Integrated vCO and O-U-O IR peaks as a function of heating to the indicated temperature. Data are collected at 73 K.







Figure S6.

Changes in the vCO frequency with the d_{CO} distance were computed using different (a) DFT+U and (b) HSE06 methods.



Figure S7.

IRRAS of the clean UO₂(111) single crystal surface at 74 K (reference), the ¹³CO dosed surface (0.02 and 0.2 L) and Log(dosed surfaces/reference surface).

O-U-O terminated UO₂ (111) surfaces



Figure S8.

Top and side views of surfaces with different coverages of O atoms and CO molecules. $\sqrt{3} \times \sqrt{3}$ supercells with 9 atomic layers were employed using the DFT + U approach. The main asymmetric vibrational frequencies v_{UO} of the surface U and the adsorbed O atoms and their O adsorption energies per atom are indicated. The adsorbed oxygen atoms are shown in light blue. E_a : adsorption energy per O atom is equal to

 $E_a = \frac{E_{(slab + 0_{ads})} - E_{(slab)} - \frac{n}{2}E(0_2)}{n}$ where *n* is the number adsorbed atoms.

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