Electronic Supplementary Information for:

"CO_2 Interaction with Violarite ($FeNi_2S_4$) Surfaces: A Dispersion-Corrected DFT Study"

Sergio Posada-Pérez,[a] David Santos-Carballal,[b] Umberto Terranova,[b] Alberto Roldan,[b] Francesc Illas,[a] and Nora H. de Leeuw*[b,c]

[a] *Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, c/ Martí i Franquès 1, 08028 Barcelona, Spain*

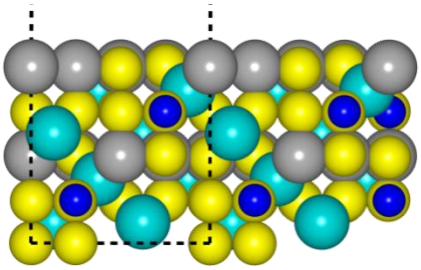
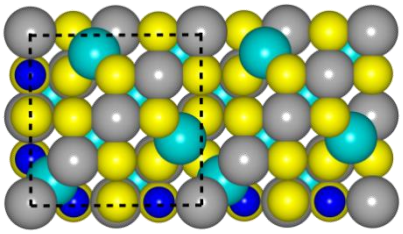
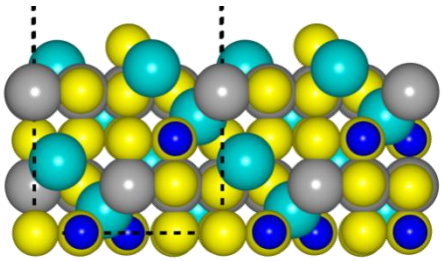
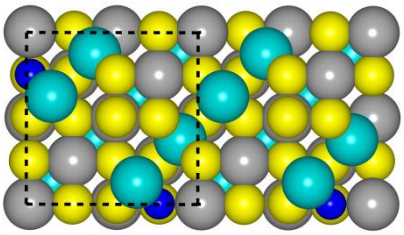
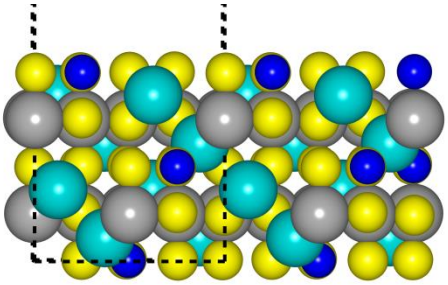
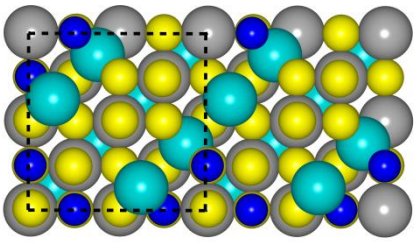
[b] *School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom. E-mail: deLeeuwN@cardiff.ac.uk; Tel: +44 (0)29 2087 0219*

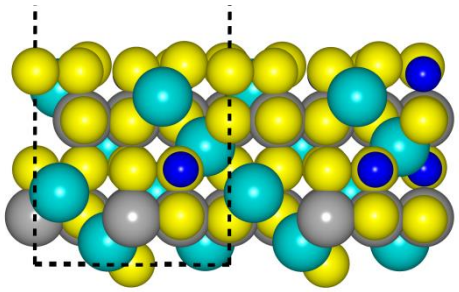
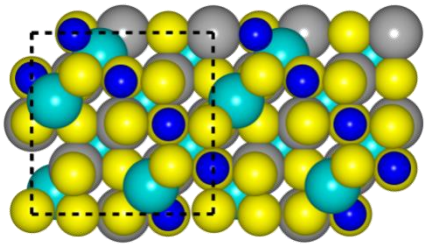
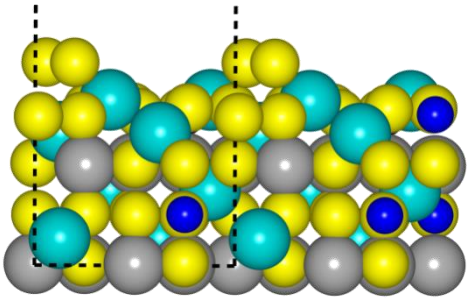
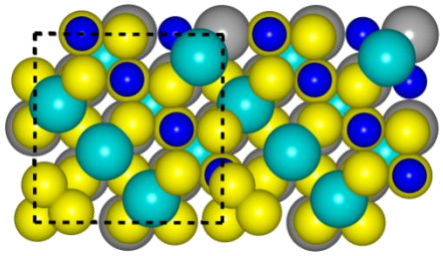
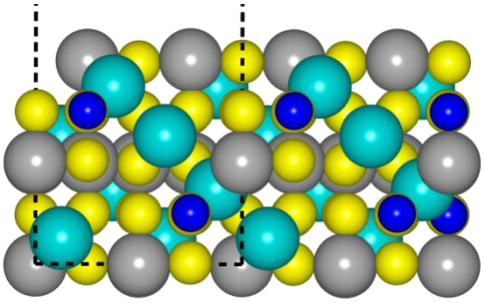
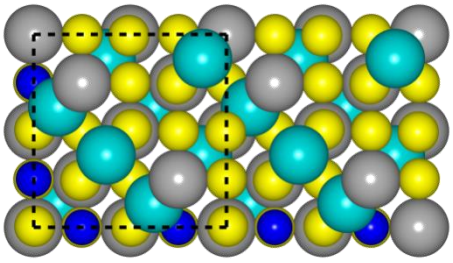
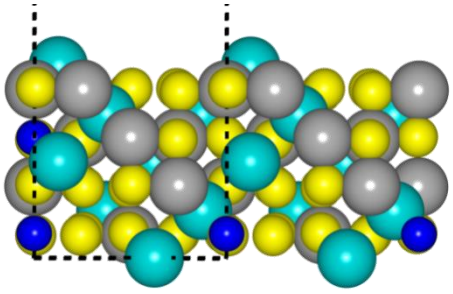
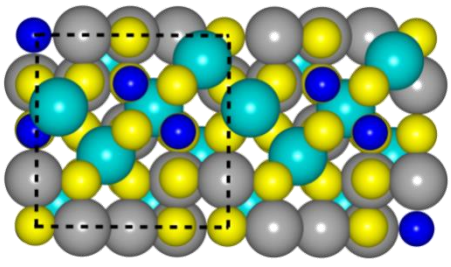
[c] *Department of Earth Sciences, Utrecht University, Princetonplein 9, 3584 CC Utrecht, The Netherlands*

Electronic Supplementary Information contains:

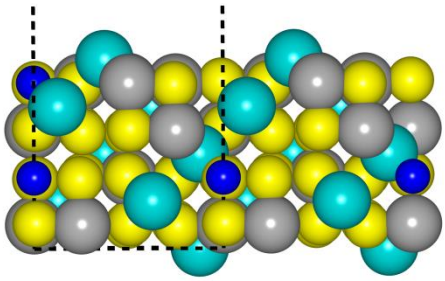
- Figures showing the side and top views as well as the stacking of the atomic layer of the unrelaxed and relaxed $FeNi_2S_4${001} and {111} surface terminations.
- Figures showing the initial and final geometries used for the simulation of the CO_2 interaction with the $FeNi_2S_4${001} and {111} surfaces.
- Tables showing the adsorption energies and structural parameters of the CO_2 adsorption with the $FeNi_2S_4$ {001} and {111} surfaces.
- Tables showing the simulated wavenumbers of the fundamental vibrational modes for the isolated and adsorbed CO_2 molecule on the $FeNi_2S_4${001} and {111} surfaces.

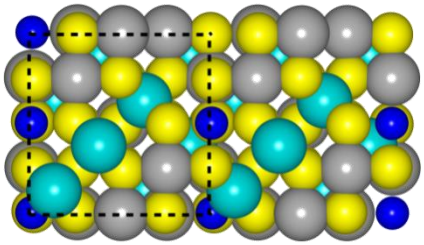
Fig. ESI-1 Side, top views and stacking of unrelaxed $FeNi_2S_4${001} surface terminations (*N*). Balls in yellow, grey, soft blue, and dark blue represent the S, Fe, Ni_A, and Ni_B atoms, respectively. Ni_A atoms are represented using bigger balls than Ni_B ions.

N	Side View	Top View	Stacking
1			$(S)_6(Fe_B)_4$ $(Ni_A)_2$ $(S)_8(Ni_B)_4$ $(Ni_A)_2$ $(S)_8(Fe_B)_4$ $(Ni_A)_2$ $(S)_8(Ni_B)_4$ $(Ni_A)_2$ $(S)_2$
2			S $(Ni_A)_2$ $(S)_8(Fe_B)_4$ $(Ni_A)_2$ $(S)_8(Ni_B)_4$ $(Ni_A)_2$ $(S)_8(Fe_B)_4$ $(Ni_A)_2$ $(S)_7(Ni_B)_4$
3			$(S)_4(Ni_B)_2$ $(Ni_A)_2$ $(S)_8(Fe_B)_4$ $(Ni_A)_2$ $(S)_8(Ni_B)_4$ $(Ni_A)_2$ $(S)_8(Fe_B)_4$ $(Ni_A)_2$ $(S)_4(Ni_B)_2$

4			$(S)_7(Ni_B)_4$ $(Ni_A)_2$ $(S)_8(Fe_B)_4$ $(Ni_A)_2$ $(S)_8(Ni_B)_4$ $(Ni_A)_2$ $(S)_8(Fe_B)_4$ $(Ni_A)_2$ S
5			$(S)_2$ $(Ni_A)_2$ $(S)_8(Ni_B)_4$ $(Ni_A)_2$ $(S)_8(Fe_B)_4$ $(Ni_A)_2$ $(S)_8(Ni_B)_4$ $(Ni_A)_2$ $(S)_6(Fe_B)_4$
6			$(S)_4(Fe_B)_2$ $(Ni_A)_2$ $(S)_8(Ni_B)_4$ $(Ni_A)_2$ $(S)_8(Fe_B)_4$ $(Ni_A)_2$ $(S)_8(Ni_B)_4$ $(Ni_A)_2$ $(S)_4(Fe_B)_2$
7			(Ni_A) $(S)_8(Ni_B)_3Fe_B$ $(Ni_A)_2$ $(S)_8(Ni_B)_2(Fe_B)_2$ $(Ni_A)_2$ $(S)_8Ni_B(Fe_B)_3$ $(Ni_A)_2$ $(S)_8(Ni_B)_2(Fe_B)_2$ (Ni_A)

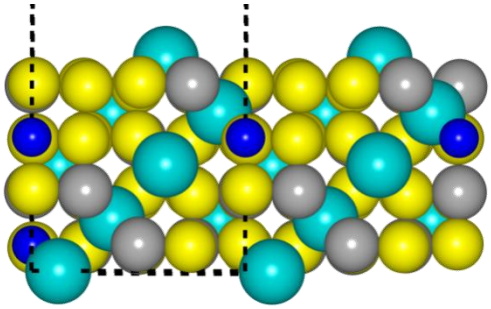
8

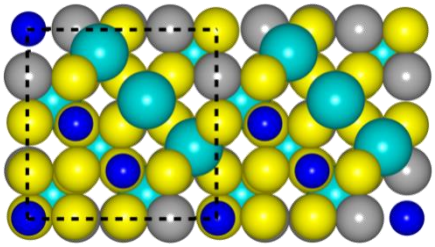




(Ni_A)
$(S)_8(Ni_B)_2(Fe_B)_2$
$(Ni_A)_2$
$(S)_8(Ni_B)_2(Fe_B)_2$
$(Ni_A)_2$
$(S)_8(Ni_B)_2(Fe_B)_2$
$(Ni_A)_2$
$(S)_8(Ni_B)_2(Fe_B)_2$
(Ni_A)

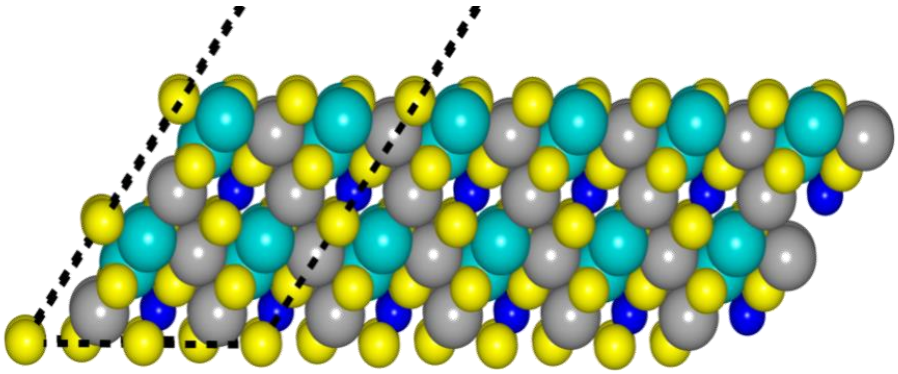
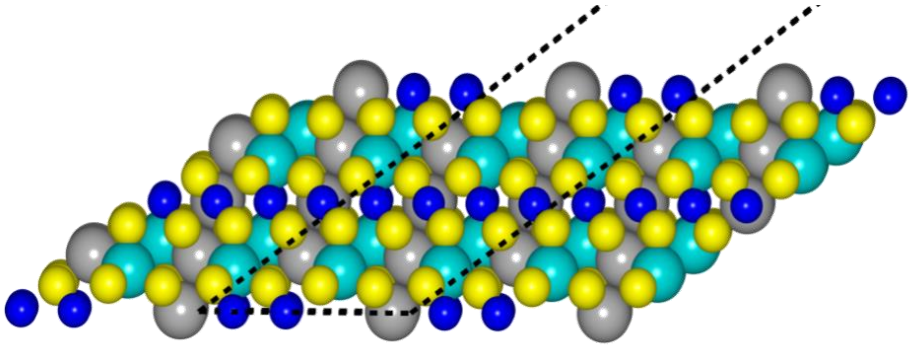
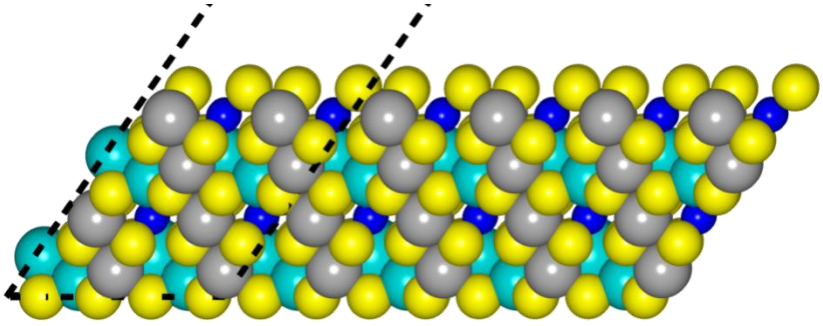
9



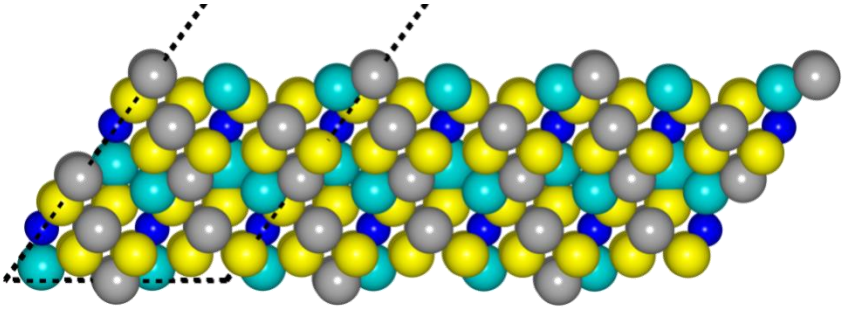


(Ni_A)
$(S)_8(Ni_B)_2(Fe_B)_2$
$(Ni_A)_2$
$(S)_8Ni_B(Fe_B)_3$
$(Ni_A)_2$
$(S)_8(Ni_B)_2(Fe_B)_2$
$(Ni_A)_2$
$(S)_8(Ni_B)_3Fe_B$
(Ni_A)

Fig. ESI-2 Side, top views and stacking of unrelaxed $FeNi_2S_4${111} surface terminations (*N*). Balls in yellow, grey, soft blue, and dark blue represent the S, Fe, Ni_A, and Ni_B atoms, respectively. Ni_A atoms are represented using bigger balls than Ni_B ions.

N	Side View	Stacking
1		$(S)_4$ $(Ni_A)_2$ $(Fe_B)_2$ $(Ni_A)_2$ $(S)_8$ $(Fe_B)_2(Ni_B)_4$ $(S)_8$ $(Ni_A)_2$ $(Fe_B)_2$ $(Ni_A)_2$ $(S)_8$ $(Fe_B)_2(Ni_B)_4$ $(S)_4$
2		$Fe_B(Ni_B)_2$ $(S)_8$ $(Ni_A)_2$ $(Fe_B)_2$ $(Ni_A)_2$ $(S)_8$ $(Fe_B)_2(Ni_B)_4$ $S)_8$ $(Ni_A)_2$ $(Fe_B)_2$ $(Ni_A)_2$ $(S)_8$
3		$Fe_B(Ni_B)_2$ $(S)_4$ $(Fe_B)_2(Ni_B)_4$ $(S)_8$ $(Ni_A)_2$ $(Fe_B)_2$ $(Ni_A)_2$ $(S)_8$ $(Fe_B)_2(Ni_B)_4$ $(S)_8$ $(Ni_A)_2$ $(Fe_B)_2$ $(Ni_A)_2$ $(S)_4$

4



Fe_B
$(Ni_A)_2$
$(S)_8$
$(Fe_B)_2(Ni_B)_4$
$(S)_8$
$(Ni_A)_2$
$(Fe_B)_2$
$(Ni_A)_2$
$(S)_8$
$(Fe_B)_2(Ni_B)_4$
$(S)_8$
$(Ni_A)_2$
Fe_B

Fig. ESI-3 Sketch of the initial geometries of the CO_2 molecule adsorbed on the {001} $FeNi_2S_4$ surfaces as an example. The CO_2 molecule was placed perpendicularly to the surface, interacting through C atom (left), the C and O atom (middle), and two O atoms (right). Balls in yellow, grey, soft blue, dark blue, red and green represent the S, Fe, Ni_A, Ni_B, O and C atoms, respectively. Ni_A atoms are represented using bigger balls than Ni_B ions.

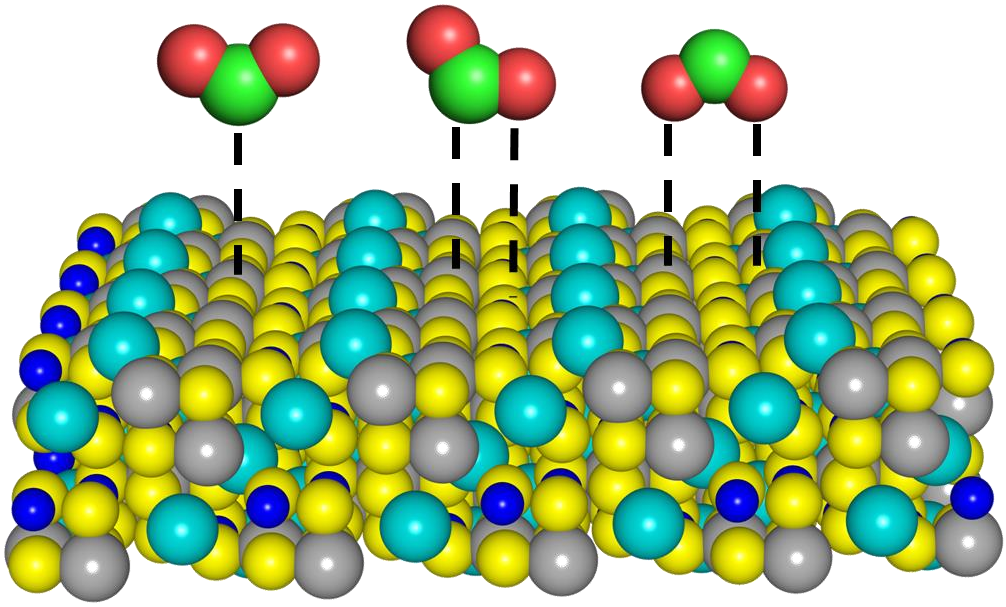


Table ESI-1 Adsorption energy and structural parameters of the CO_2 adsorption on the terminations 8 and 2 of the $FeNi_2S_4$ {001} surface using the PW9-D2+*U* functional. Sketches of the adsorption configurations are shown in Fig. ESI-4.

E_{ads} /(eV)	*d*(C−O) /Å	α(OCO) /º	ΔQ (CO_2) /e^-	ν (C=O strecth) /cm^{-1}	*d*(CO_2-Surf) /Å	Sketches
			Termination 8			
−0.21	1.18	179.2	0.01	2345	3.00	A
−0.21	1.18	179.4	0.00	2341	3.11	B
			Termination 2			
−0.26	1.18	179.8	0.00	2342	2.70	C
−0.21	1.17	179.3	0.01	2336	3.20	D
−0.20	1.17	179.6	0.00	2349	2.91	E
−0.17	1.18	179.4	0.00	2347	3.23	F

Table ESI-2 Adsorption energy and structural parameters for the CO_2 adsorption on the surface termination 2 of $FeNi_2S_4${001} surface using the PBE-D2+*U* and PBE-D3+*U* functionals. Sketches of the adsorption configurations are shown in Fig. ESI-4.

E_{ads} /(eV)	*d*(C−O) /Å	*α*(OCO) /º	ΔQ (CO_2) /e^-	ν (C=O strecth) /cm^{-1}	*d*(CO_2-Surf) /Å	Sketches
			PBE−D2+*U*			
−0.18	1.17	175.0	0.00	2516	2.92	G
0.09	1.17	174.8	0.00	2508	2.93	H
			PBE−D3+*U*			
−0.68	1.18	176.9	0.01	2460	3.13	I
−0.42	1.18	176.8	0.01	2510	3.08	J
−0.41	1.18	174.2	0.01	2496	3.06	K

Fig. ESI-4 Sketches of the final CO_2 adsorption modes on $FeNi_2S_4$ {001} surfaces. Adsorption energies and structural parameters of the adsorption configurations A-K are reported in Tables ESI-1 and ESI-2. Balls in yellow, grey, soft blue, dark blue, red and green represent the S, Fe, Ni_A, Ni_B, O and C atoms, respectively. Ni_A atoms are represented using bigger balls than Ni_B ions.

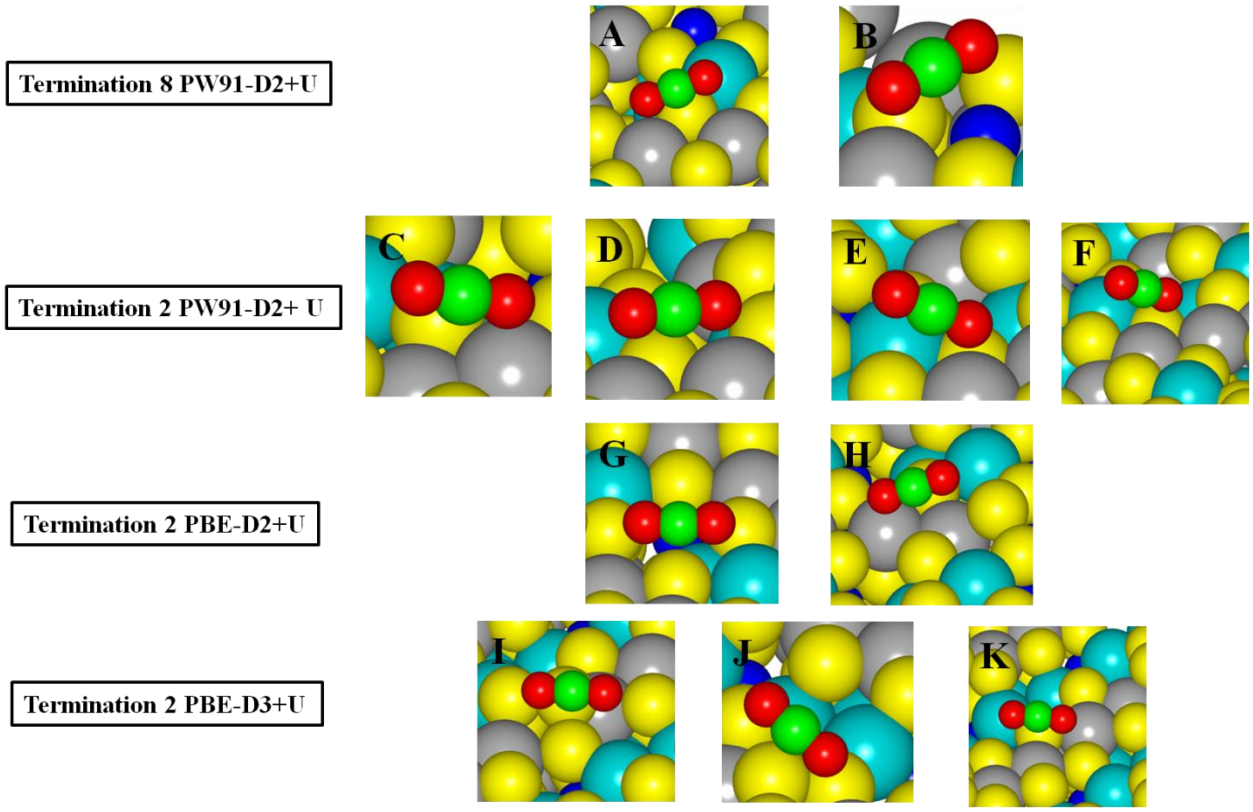


Table ESI-3 Simulated wavenumbers of the fundamental vibrational modes (ν) in cm^{-1} for the isolated CO_2 molecule and the most favourable adsorption geometries on selected terminations of the $FeNi_2S_4${001} surface.

Isolated molecule	Termination 8	Termination 2			Fundamental vibrational mode
PBE	PW91-D2+*U*	PW91-D2+*U*	PBE−D2+*U*	PBE−D3+*U*	
	A	C	G	I	
2365	2345	2342	2516	2460	Asymmetric Stretching
1319	1310	1313	1521	1794	Symmetric Stretching
633	603	611	1147	1493	Bending
631	602	609	1078	1436	Bending

Table ESI-4 Adsorption energy data CO_2 adsorption on $FeNi_2S_4${001} surface using the PBE-D3+*U* obtained in Table ESI-2 and PBE+*U* functional.

Geometry	E_{ads} PBE+*U*	E_{ads} PBE−D3+*U*
I	-0.49	-0.68
J	-0.27	-0.42
K	-0.15	-0.41

Table ESI-5 Adsorption energy and structural parameters of the CO_2 adsorption on $FeNi_2S_4${111} surface using the PW91-D2+*U* functional. Sketches of the adsorption configurations are shown in Fig. ESI-5.

E_{ads} /(eV)	*d*(C−O) /Å	α(OCO) /º	ΔQ (CO_2) /e^-	ν (C=O strecth) /cm^{-1}	*d*(CO_2-Surf) /Å	Sketches
−0.18	1.18	179.2	0.01	2344	3.52	L
−0.17	1.18	179.3	0.00	2341	3.71	M
−0.16	1.18	179.8	0.01	2346	3.33	N

Table ESI-6 Adsorption energy and structural parameters of the CO_2 adsorption on $FeNi_2S_4${111} surface using the PBE-D2+*U* and PBE-D3+*U* functionals. Sketches of the adsorption configurations are shown in Fig. ESI-5.

E_{ads} /(eV)	*d*(C−O) /Å	α(OCO) /º	ΔQ (CO_2) /e^-	ν (C=O strecth) /cm^{-1}	*d*(CO_2-Surf) /Å	Sketches
			PBE−D2+*U*			
−0.56	1.18	176.3	0.00	2423	3.03	O
−0.24	1.19	179.2	0.00	2372	3.05	P
			PBE−D3+*U*			
−0.56	1.19	175.2	0.01	2436	2.39	Q
−0.52	1.18	178.1	0.00	2298	2.81	R
−0.32	1.18	174.4	0.01	2388	3.63	S
−0.25	1.19	175.4	0.00	2357	3.25	T

Fig. ESI-5: Sketches of the final CO_2 adsorption modes on $FeNi_2S_4$ {111} surfaces. Adsorption energies and structural parameters of the adsorption configurations L-T are reported in Tables ESI-3 and ESI-4. Balls in yellow, grey, soft blue, dark blue, red and green represent the S, Fe, Ni_A, Ni_B, O and C atoms, respectively. Ni_A atoms are represented using bigger balls than Ni_B ions.

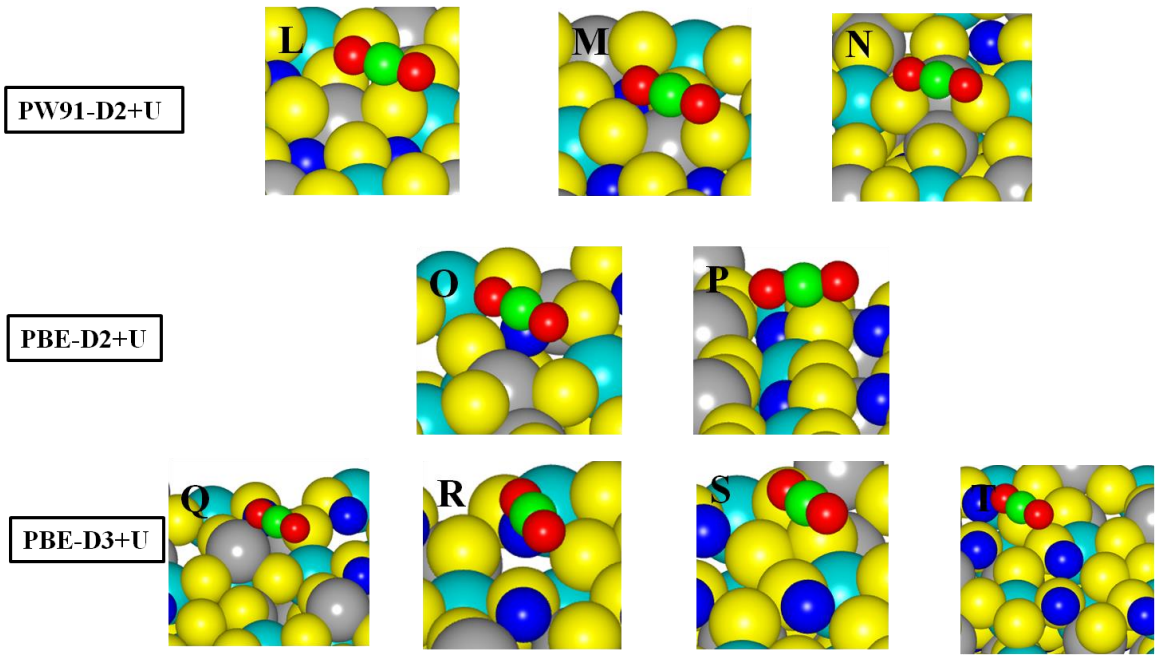


Table ESI-7 Simulated wavenumbers of the fundamental vibrational modes (ν) in cm^{-1} for the isolated CO_2 molecule and the most favourable adsorption geometries on selected terminations of the $FeNi_2S_4${111} surface.

Isolated molecule	Termination 2			Fundamental vibrational mode
PBE	PW91-D2+*U*	PBE−D2+*U*	PBE−D3+*U*	
	L	O	Q	
2365	2344	2423	2436	Asymmetric Stretching
1319	1300	1467	1528	Symmetric Stretching
633	957	991	949	Bending
631	933	925	888	Bending