Supporting Information
CO_2 ultrathin film growth on a monolayer of CO_2 adsorbed on the NaCl(100) surface: Sticking coefficient and IR-optical signatures in the ν_3 region

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S1 Electric fields

The electric field vectors of polarized IR light at the frontside and at the backside of a transparent, non-absorbing substrate of refractive index n are determined using Fresnel's equations [1]. Consider the geometry shown in Fig. S1 with the two interfaces 01 and 12. The incoming beam strikes the surface at an angle β against the surface normal. The angle of refraction β_1 is determined using Snell's law. The electric field vector of a s-polarized beam oscillates parallel to the surface plane, while in p-polarization, the electric field vector oscillates in the sagittal plane. Then, introducing the Fresnel amplitude coefficients for s-polarization and p-polarization,

$$t_{01,s} = \frac{2\cos\beta}{(\cos\beta + n\cos\beta_1)} \qquad t_{01,p} = \frac{2n\cos\beta}{(n\cos\beta + \cos\beta_1)} \tag{1}$$

$$t_{12,s} = \frac{2n\cos\beta_1}{(\cos\beta + n\cos\beta_1)} \qquad t_{12,p} = \frac{2\cos\beta_1}{(n\cos\beta + \cos\beta_1)} \tag{2}$$

$$r_{01,s} = \frac{\cos\beta - n\cos\beta_1}{(\cos\beta + n\cos\beta_1)} \qquad r_{01,p} = \frac{n\cos\beta - \cos\beta_1}{(n\cos\beta + \cos\beta_1)}, \tag{3}$$

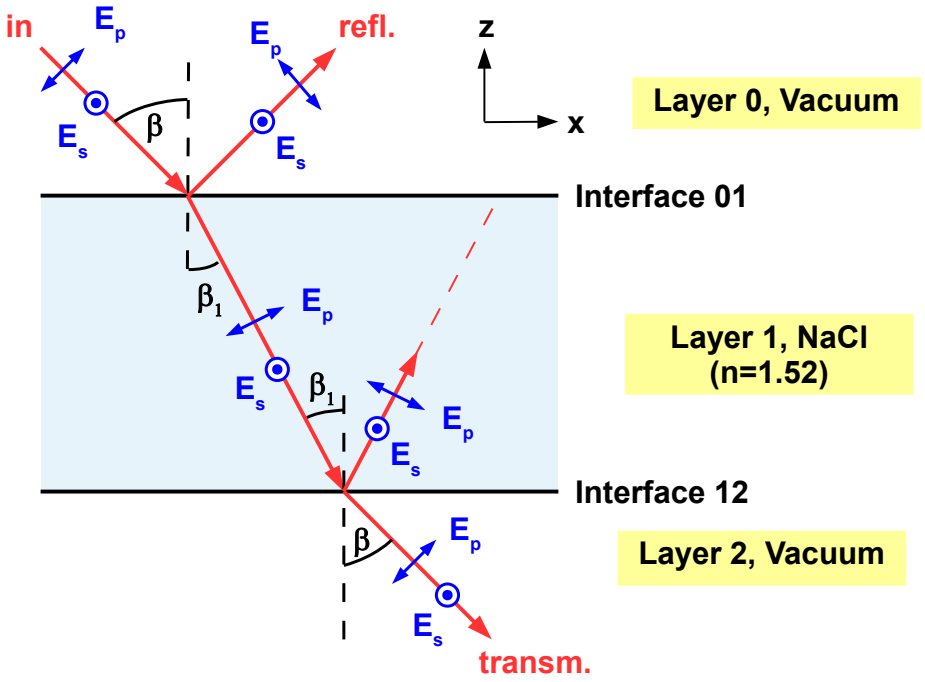

Fig. 1: Partial reflection and transmission of an IR beam at a non-absorbing slab (NaCl). In s-polarization, the electric field vector $\vec{E}_s$ oscillates parallel to the surface plane (symbol $\odot$), while in p-polarized light $\vec{E}_p$ oscillates in the sagittal plane spanned by the surface normal and the direction of the incoming beam ("in").

the electric field components in the depicted frame of reference are

$$\vec{\varepsilon}_{\text{front}} = \frac{\vec{E}_{\text{front}}}{E_{\text{in}}} = \begin{pmatrix} (1 - r_{01,p}) \cos\beta \sin\delta \\ t_{01,s} t_{12,s} \cos\delta \\ (1 + r_{01,p}) \sin\beta \sin\delta \end{pmatrix} \tag{4}$$

and

$$\vec{\varepsilon}_{\text{back}} = \frac{\vec{E}_{\text{back}}}{E_{\text{in}}} = \begin{pmatrix} t_{01,p} t_{12,p} \cos\beta \sin\delta \\ (1 + r_{01,s}) \cos\delta \\ t_{01,p} t_{12,p} \sin\beta \sin\delta \end{pmatrix} \tag{5}$$

where the s-polarized field is obtained for $\delta = 0°$, and the p-polarized field is obtained for $\delta = 90°$. For the purpose of domain averaging, the vectors of eq. 4 and eq. 5 is rotated by 90°, 180°, and 270° around the surface normal in the substrate fixed frame of reference:

$$\vec{\varepsilon}^{j}_{\text{front}} = \vec{\varepsilon}_{\text{front}} \begin{pmatrix} \cos\left(\frac{j\pi}{2}\right) \\ \sin\left(\frac{j\pi}{2}\right) \\ 0 \end{pmatrix} \quad j = 0, 1, 2, 3 \tag{6}$$

$$\vec{\varepsilon}^{j}_{\text{back}} = \vec{\varepsilon}_{\text{front}} \begin{pmatrix} \cos\left(\frac{j\pi}{2}\right) \\ \sin\left(\frac{j\pi}{2}\right) \\ 0 \end{pmatrix} \quad j = 0, 1, 2, 3 \tag{7}$$

S2 Potential calculations for vibrational exciton model

The SAPT-s pair potential model by Bukowski et al. [2] for CO_2 uses 5 centers O-M-C-M-O to account for the intermolecular interaction between two molecules A and B at distance r_{AB}. It is defined by

$$V_{MM,AB} = \sum_{a \in A} \sum_{b \in B} \left[e^{\alpha_{ab} - \beta_{ab} r_{ab}} + f_1(\delta_1^{ab} r_{ab}) \frac{q_a q_b}{r_{ab}} - f_6(\delta_6^{ab}) \frac{C_6^{ab}}{r_{r_{ab}}^6} - f_8(\delta_8^{ab}) \frac{C_8^{ab}}{r_{r_{ab}}^8} \right] \tag{8}$$

$$f_n(x) = 1 - e^{-x} \sum_{k=0}^{n} \frac{x^k}{k!}. \tag{9}$$

	α	β [Å^{-1}]	δ_1 [Å^{-1}]	δ_6 [Å^{-1}]
O-O	1.1210441e+1	4.0202795	1.4968485	2.5924278
O-C	1.1333682e+1	4.5074401	1.8797629	1.8139783
C-C	1.1399839e+1	5.0932632	2.1958809	1.7584847
O-M			1.9648279	
C-M			2.6032461	
M-M			5.2350982	

	δ_8 [Å^{-1}]	C_6 [kcal mol^{-1}Å^6]	C_8 [kcal mol^{-1}Å^8]
O-O	1.0769328	1.0426642e+3	-1.3516797e+4
O-C	0.6747229	-1.3834479e+3	2.0217414e+4
C-C	3.0176726	3.4808543e+3	-2.6899552e+4

q_O	0.2379
q_C	1.6317
q_M	-1.0537

Tab. S1: SAPT-s parameter set for CO_2 from [2]. Energies are given in kcal mol^{-1}, partial charges q in multiples of the elementary charge. The 5 interaction sites O-M-C-M-O are situated on the molecular axis with r_{C-M}=0.8456 Å and r_{M-O}=0.3164 Å.

interaction site	ϵ [kJ mol^{-1}]	σ [Å]
CO_2 (Ref. [3]):		
C	0.2398	2.7918
O	0.6874	3.0000
NaCl [4]		
Na	0.5443	2.350
Cl	0.4187	4.450
lattice constant: 5.60 Å		

Tab. S2: Lennard-Jones parameters for short-range molecule-surface interaction between CO_2 and NaCl.

with the values given in Tab. S1. The short-range part of the molecule-surface potential V_{MS} between a CO_2 molecule and the NaCl(100) surface is represented by a Lennard-Jones pair-potential with potential parameters given in Tab. S2.

In a 3D-periodic optimization of bulk α-CO_2 with the SAPT-s parameters a lattice parameter of 5.48 Å was obtained (Experiment, 80 K: 5.58 Å [5]). The bulk cohesive energy was 29.5 kJ mol^{-1}.

Cohesive energy minimizations of CO_2 films assumed a rigid NaCl(100) surface without surface rumpling and a lattice parameter of 5.60 Å. The cohesive energy for NaCl(100)/c(2×2)-CO_2 for a film with 8 layers was 28.5 kJ mol^{-1}. The calculated cohesive energy of the monolayer NaCl(100)/p(2×1)-CO_2 was 26.8 kJ mol^{-1}.

For a film of 8 layer thickness, the center of mass coordinates as well as the tilt and azimuth angles defining the molecular orientation are given in Tab. S3 (cf. Fig. 5 of the main manuscript). The wave numbers and absorptions A_s and A_p in s-polarization and p-polarization obtained from vibrational exciton calculations using the parameter presented in Tab. 3 of the main manuscript are shown in Tab. S4.

Molecule	x	y	z	θ	ϕ
1A	-1.1110	-0.1391	3.2368	-35.3964	25.1129
1B	1.6882	2.9290	3.2373	-35.4475	-25.0311
2A	-1.1985	2.8160	6.0146	34.7851	44.1722
2B	1.6017	-0.0286	6.0144	34.7569	-44.1878
3A	-1.1984	-0.0040	8.7046	-35.3868	46.8459
3B	1.6016	2.7924	8.7047	-35.3618	-46.8675
4A	-1.1979	2.7955	11.3810	35.6706	46.9479
4B	1.6019	-0.0049	11.3810	35.6972	-46.9093
5A	-1.2007	-0.0038	14.0549	-35.8183	46.9735
5B	1.5991	2.7959	14.0548	-35.8057	-46.9835
6A	-1.2032	2.7960	16.7303	35.8369	46.9838
6B	1.5966	-0.0038	16.7303	35.8392	-46.9819
7A	-1.2067	-0.0038	19.4068	-35.8670	46.9301
7B	1.5933	2.7960	19.4072	-35.8740	-46.9307
8A	-1.2094	2.7970	22.0819	35.8416	47.0013
8B	1.5909	-0.0030	22.0813	35.8436	-46.9380

Tab. S3: Center of mass coordinates x, y, z, tilt angle θ, and azimuth angle ϕ of the 16 inequivalent molecules in an 8 layer film NaCl(100)/-c(2×2)CO_2, as obtained from potential calculations. Coordinates are given in Å, angles in degrees. θ is measured relative to the surface plane. The origin of the coordinate system is at the site of a surface Na^+. The angle ϕ is measured relative to the y-axis pointing towards a neighboring Cl^-.

Exciton	$\tilde{\nu}$ (cm^{-1})	A_s	A_p
1	2331.91	0.726E-05	0.469E-05
2	2333.38	0.203E-04	0.131E-04
3	2335.69	0.430E-03	0.277E-03
4	2338.29	0.156E-03	0.101E-03
5	2340.62	0.172E-02	0.111E-02
6	2342.42	0.843E-01	0.544E-01
7	2343.15	0.356E+00	0.231E+00
8	2344.75	0.160E+00	0.103E+00
9	2345.34	0.425E-03	0.938E-02
10	2348.85	0.952E-01	0.614E-01
11	2349.93	0.428E-01	0.299E-01
12	2355.82	0.341E-03	0.286E-01
13	2362.45	0.141E-01	0.103E-01
14	2368.99	0.893E-03	0.869E-01
15	2375.32	0.235E-02	0.209E-02
16	2379.83	0.818E-04	0.439E+00

Tab. S4: Wavenumbers $\tilde{\nu}$ and IR absorption in s-polarization (A_s) and p-polarization (A_p) of a film with 8 layers as obtained from vibrational exciton calculations.

Element	x	y	z
O	4.08580	2.24480	15.20223
C	3.33045	2.88676	14.57668
O	2.57318	3.53876	13.95821
O	1.23603	0.71008	15.20257
C	0.48061	0.06818	14.57705
O	-0.27668	-0.58377	13.95859
O	-0.20570	2.22963	12.35894
C	0.48743	2.90820	11.69969
O	1.18109	3.58806	11.04122
O	2.64427	0.72567	12.35918
C	3.33744	0.04717	11.69986
O	4.03114	-0.63261	11.04133
O	4.03615	2.21664	9.53384
C	3.35336	2.89986	8.86809
O	2.67226	3.58289	8.20050
O	1.18681	0.73888	9.53404
C	0.50346	0.05605	8.86847
O	-0.17811	-0.62660	8.20101
O	-0.11395	2.24258	6.66779
C	0.59465	2.90210	6.00421
O	1.30465	3.55763	5.33940
O	2.73450	0.71390	6.66210
C	3.44413	0.05119	6.00279
O	4.15491	-0.60765	5.34220
O	4.41439	2.32706	3.71619
C	3.55389	2.79800	3.07494
O	2.67777	3.26726	2.45005
O	1.56035	0.60959	3.70283
C	0.70019	0.12616	3.07066
O	-0.17520	-0.35665	2.45502
Na	-0.51346	-0.05505	-0.05519
Cl	2.34651	0.04492	0.04885
Na	2.33800	2.89147	-0.05504
Cl	-0.50182	2.79192	0.05918
Cl	-0.46861	-0.04767	-2.85571
Na	2.38017	-0.01765	-2.80239
Cl	2.38113	2.83101	-2.85632
Na	-0.46940	2.80169	-2.79743
Na	-0.42603	-0.05039	-5.70321
Cl	2.42292	-0.04375	-5.64933
Na	2.42382	2.80593	-5.70371
Cl	-0.42677	2.79938	-5.64682
Cl	-0.39216	-0.05121	-8.56313
Na	2.45872	-0.04903	-8.44785
Cl	2.45753	2.80035	-8.56214
Na	-0.39142	2.79807	-8.44542

Tab. S5: Structure of a film with 8 layers as obtained from DFT-D total energy minimization. All values are given in Å.

S3 Plane-wave DFT-D calculations

Cartesian coordinates of an optimized NaCl(100)/-c(2×2)CO_2 surface slab with four substrate layers and eight adsorbate layers are given in Tab. S5.
In tables S6 to S11, DFT-D results of wavenumbers, IR intensities for s- and p-polarization, as well as the components of the polarization vectors are given for a monolayer with p(2×1) symmetry, and films with 4 to 8 layers thickness.

$\tilde{\nu}$ (cm^{-1})	I_s	I_p	p_x	p_y	p_z	$A_{s,\text{exptl.}}$	$A_{p,\text{exptl.}}$
2349.36	9.646746	12.222557	0.0168	0.0196	0.0160	0.1058	0.1026
2356.46	7.883683	5.182599	0.0176	-0.0153	0.0008	0.0667	0.0427

Tab. S6: Wavenumbers $\tilde{\nu}$ and IR intensities of a film with monolayer coverage from pw-DFT-D calculations in s-polarization (I_s) and p-polarization (I_p). IR intensities are given in (Debye/Å)^2 amu^{-1}. Also given are the components p_x, p_y, and p_z of the mode polarization vector in Rydberg atomic units. $A_{s,\text{exptl.}}$ and $A_{p,\text{exptl.}}$ are experimental integrated absorbances in units of cm^{-1} which have been added for the purpose of comparison. The ratio I_s/I_p for the mode ML+ is 0.79, the respective ratio for ML- is 1.52. Experimental data have A_s/A_p values of 1.03 (ML+) and 1.56 (ML-).

$\tilde{\nu}$ (cm^{-1})	I_s	I_p	p_x	p_y	p_z
2344.11	0.453962	0.297807	-0.0000	0.0056	0.0001
2350.07	0.022246	0.014814	-0.0003	-0.0012	0.0001
2356.80	39.484476	25.965858	0.0521	-0.0025	-0.0019
2357.52	16.227074	10.637006	0.0035	0.0333	-0.0000
2362.45	0.422408	5.192131	0.0054	0.0000	0.0146
2367.28	10.695292	7.011789	0.0001	-0.0272	0.0002
2372.21	0.361499	0.745426	-0.0050	-0.0000	-0.0047
2383.02	0.046948	24.997531	-0.0018	0.0000	-0.0329

Tab. S7: Wavenumbers $\tilde{\nu}$ and IR intensities of a film with 4 layers from pw-DFT-D calculations in s-polarization (I_s) and p-polarization (I_p). IR intensities are given in (Debye/Å)^2 amu^{-1}. Also given are the components p_x, p_y, and p_z of the mode polarization vector in Rydberg atomic units.

$\tilde{\nu}$ (cm^{-1})	I_s	I_p	p_x	p_y	p_z
2343.23	0.046436	0.030661	0.0003	-0.0018	0.0001
2347.95	0.495713	0.325178	0.0005	0.0058	0.0001
2353.37	1.252559	0.821295	0.0001	-0.0093	0.0001
2356.52	47.831621	32.940552	-0.0575	-0.0001	-0.0083
2357.68	23.577049	15.454986	-0.0007	0.0403	-0.0000
2360.32	0.722773	0.492707	0.0070	0.0005	-0.0009
2366.61	10.239418	6.735074	0.0001	-0.0266	-0.0010
2367.9	0.279957	7.391316	-0.0041	0.0016	-0.0177
2375.93	0.114262	0.654148	-0.0028	-0.0001	-0.0050
2385.17	0.041956	33.107721	-0.0017	0.0001	-0.0379

Tab. S8: Wavenumbers $\tilde{\nu}$ and IR intensities of a film with 5 layers from pw-DFT-D calculations in s-polarization (I_s) and p-polarization (I_p). IR intensities are given in (Debye/Å)^2 amu^{-1}. Also given are the components p_x, p_y, and p_z of the mode polarization vector in Rydberg atomic units.

$\tilde{\nu}$ (cm^{-1})	I_s	I_p	p_x	p_y	p_z
2343.37	0.355583	0.233088	-0.0000	0.0050	-0.0000
2347.16	0.175541	0.115306	0.0005	0.0034	-0.0001
2349.95	2.061491	1.351559	0.0007	0.0119	-0.0001
2354.29	4.865167	3.189164	-0.0003	0.0183	0.0000
2356.44	56.582043	37.092157	-0.0625	0.0005	0.0003
2358.04	26.965507	17.687476	0.0001	-0.0431	-0.0007
2358.80	0.092224	3.379107	0.0021	0.0014	-0.0120
2365.82	6.802517	4.518221	0.0026	0.0215	0.0016
2365.93	3.419619	2.353018	0.0038	-0.0149	0.0022
2372.61	0.126061	10.496919	-0.0029	0.0005	-0.0212
2379.36	0.047913	0.389445	-0.0018	-0.0000	-0.0039
2387.55	0.005373	42.744641	-0.0006	0.0001	-0.0430

Tab. S9: Wavenumbers $\tilde{\nu}$ and IR intensities of a film with 6 layers from pw-DFT-D calculations in s-polarization (I_s) and p-polarization (I_p). IR intensities are given in (Debye/Å)^2 amu^{-1}. Also given are the components p_x, p_y, and p_z of the mode polarization vector in Rydberg atomic units.

$\tilde{\nu}$ (cm^{-1})	I_s	I_p	p_x	p_y	p_z
2344.66	0.032305	0.021409	0.0010	-0.0011	0.0001
2345.28	0.443902	0.291214	0.0004	-0.0055	0.0001
2350.90	0.753946	0.494447	-0.0015	-0.0071	-0.0001
2352.70	5.142243	3.376544	-0.0053	-0.0181	-0.0005
2355.94	8.259198	5.472808	-0.0144	0.0191	-0.0016
2356.52	60.733024	41.038308	-0.0640	-0.0101	-0.0073
2357.34	31.766981	20.868827	-0.0096	0.0458	-0.0014
2358.07	1.665999	1.097821	-0.0084	0.0067	0.0005
2362.61	0.402107	5.636013	0.0050	0.0017	0.0153
2365.84	9.378510	6.148630	-0.0008	0.0254	-0.0002
2369.75	0.064418	1.015799	0.0021	0.0002	0.0065
2376.85	0.256851	9.698213	-0.0042	0.0002	-0.0203
2382.00	0.018715	0.133497	0.0011	-0.0003	0.0023
2388.87	0.009860	57.247368	-0.0008	0.0002	-0.0498

Tab. S10: Wavenumbers $\tilde{\nu}$ and IR intensities of a film with 7 layers from pw-DFT-D calculations in s-polarization (I_s) and p-polarization (I_p). IR intensities are given in $(\text{Debye}/\text{Å})^2$ amu^{-1}. Also given are the components p_x, p_y, and p_z of the mode polarization vector in Rydberg atomic units.

$\tilde{\nu}$ (cm^{-1})	I_s	I_p	p_x	p_y	p_z
2344.49	0.266973	0.175233	0.0001	-0.0043	-0.0001
2344.94	0.188547	0.124514	0.0024	0.0027	-0.0002
2348.96	1.514418	0.993640	0.0032	-0.0097	-0.0002
2351.84	0.036434	0.024123	0.0015	0.0004	0.0001
2353.89	5.476878	3.593821	0.0077	-0.0179	-0.0004
2356.17	6.416616	4.244973	-0.0122	-0.0172	0.0013
2357.04	66.344598	43.822417	-0.0667	0.0115	0.0038
2357.37	40.703769	26.696454	-0.0146	-0.0510	-0.0008
2358.01	3.000127	6.055514	0.0122	-0.0076	0.0133
2361.90	0.213071	0.140596	-0.0025	0.0029	-0.0002
2365.85	9.461972	6.500951	0.0019	0.0255	0.0036
2366.95	0.255327	7.426880	-0.0023	0.0035	-0.0177
2372.64	0.144228	1.623789	0.0027	-0.0016	0.0081
2379.30	0.130240	8.934658	-0.0030	0.0000	-0.0196
2383.61	0.020803	0.493574	-0.0011	0.0005	-0.0046
2389.09	0.008416	74.262561	-0.0007	-0.0003	-0.0567

Tab. S11: Wavenumbers $\tilde{\nu}$ and IR intensities of a film with 8 layers from pw-DFT-D calculations in s-polarization (I_s) and p-polarization (I_p). IR intensities are given in (Debye/Å)^2 amu^{-1}. Also given are the components p_x, p_y, and p_z of the mode polarization vector in Rydberg atomic units.

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