

Electronic Supplementary Information

Ferroelectric-enabled significant carbon dioxide molecular adsorption on BaTiO₃(001)

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1. Survey spectra

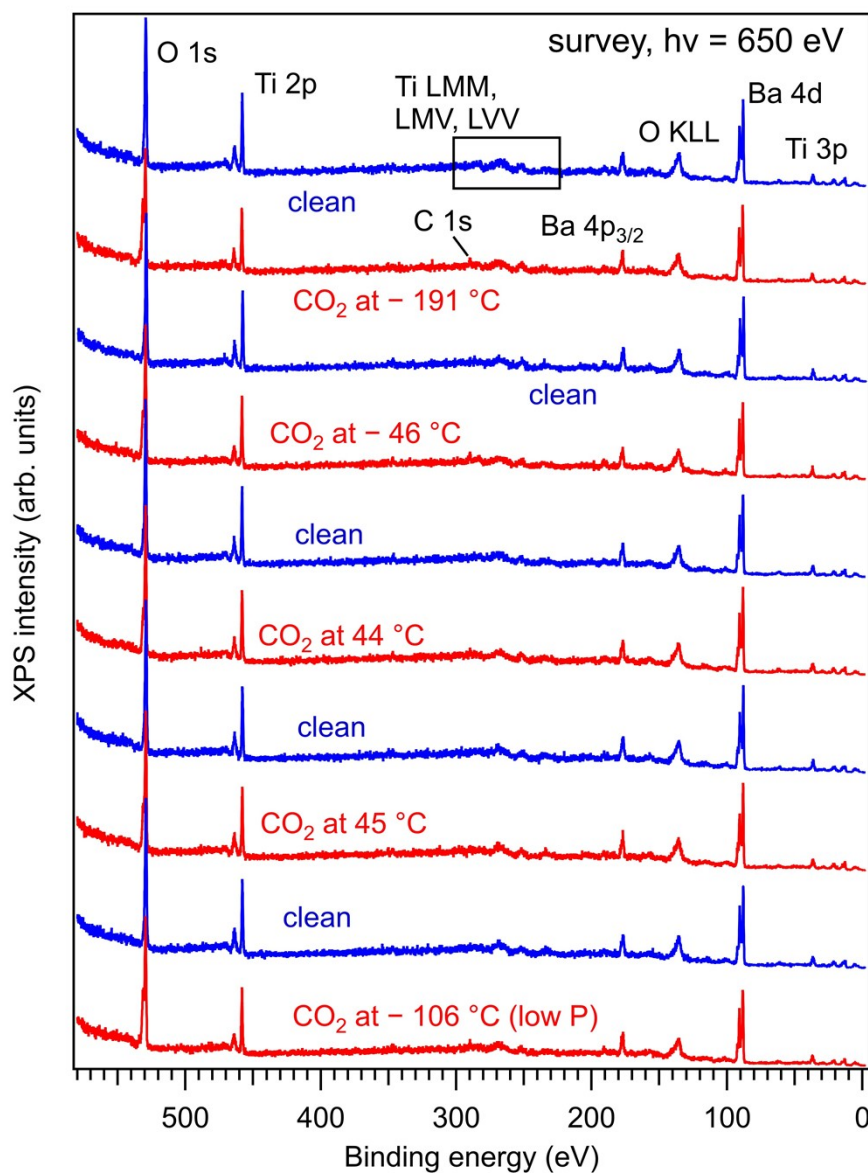


Figure S1. Survey XPS spectra for clean BTO(001) surfaces and after CO dosing (3.4 kL) at different temperatures.

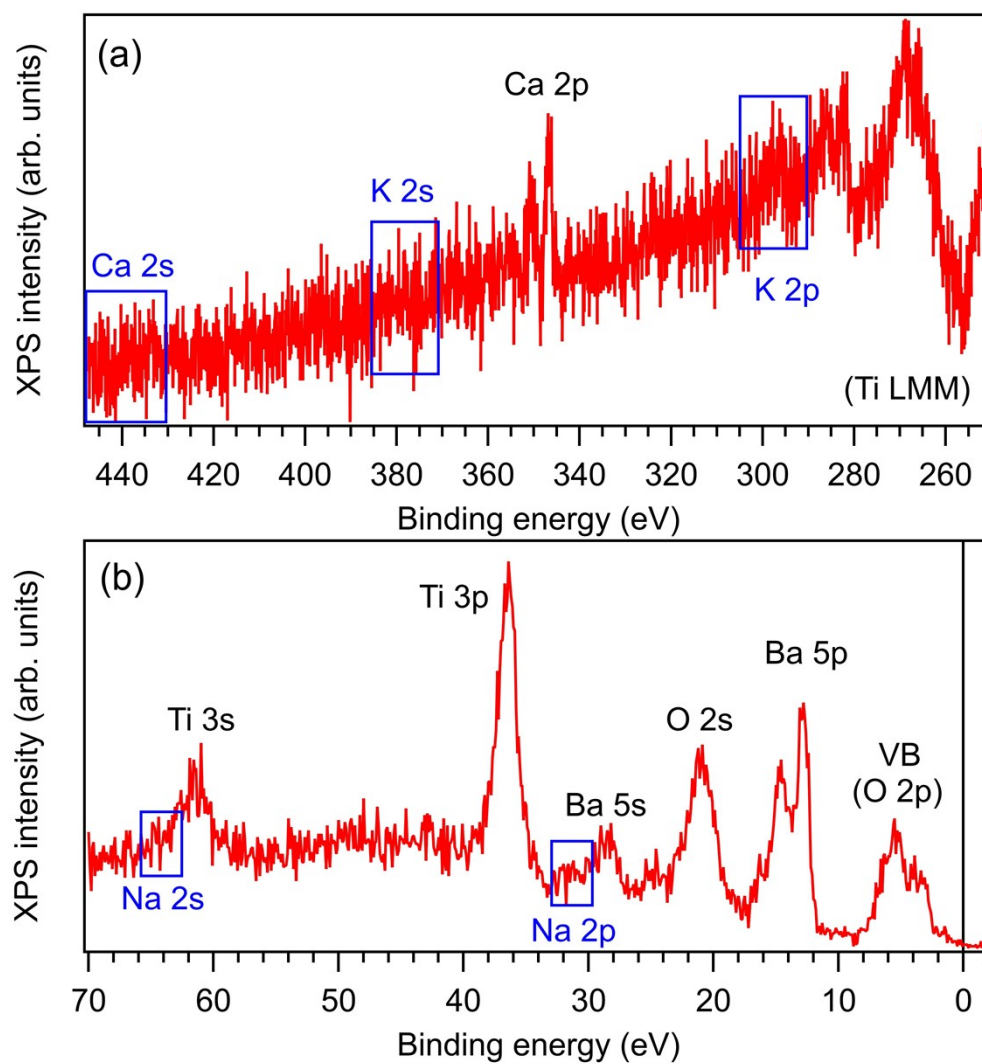


Figure S2. Contamination assessment: (a) The region of K and Ca 2p and 2s core levels. (b) The low binding energy region, with zones where Na 2s and 2p core levels are supposed to show up.

2. Valence band spectra

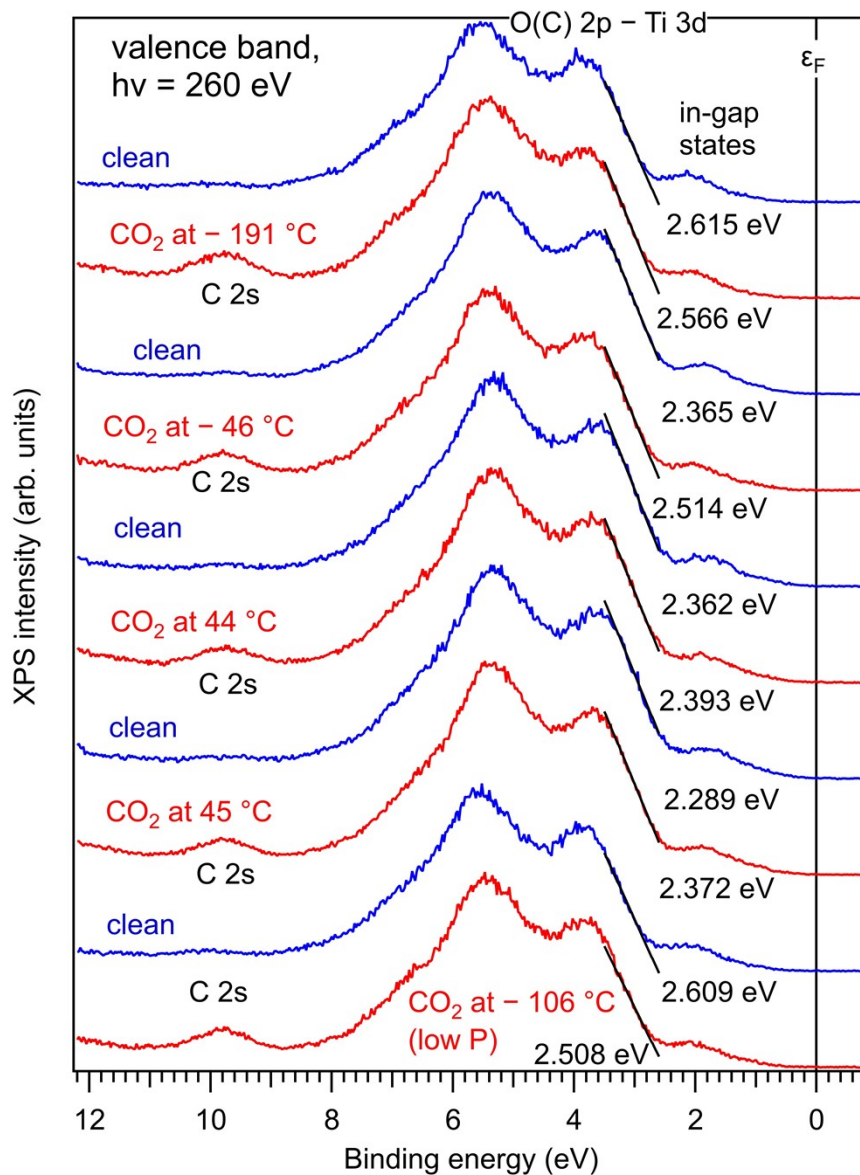


Figure S3. Valence band spectra for clean BTO(001) surfaces and after CO₂ dosing (3.4 kL) at different temperatures. The descending part of the main valence band feature was fitted with a line and the intercepts with the x axis are represented (onsets of the main valence band structures).

3. Survey spectrum for a BTO(001) sample during the cleaning procedure

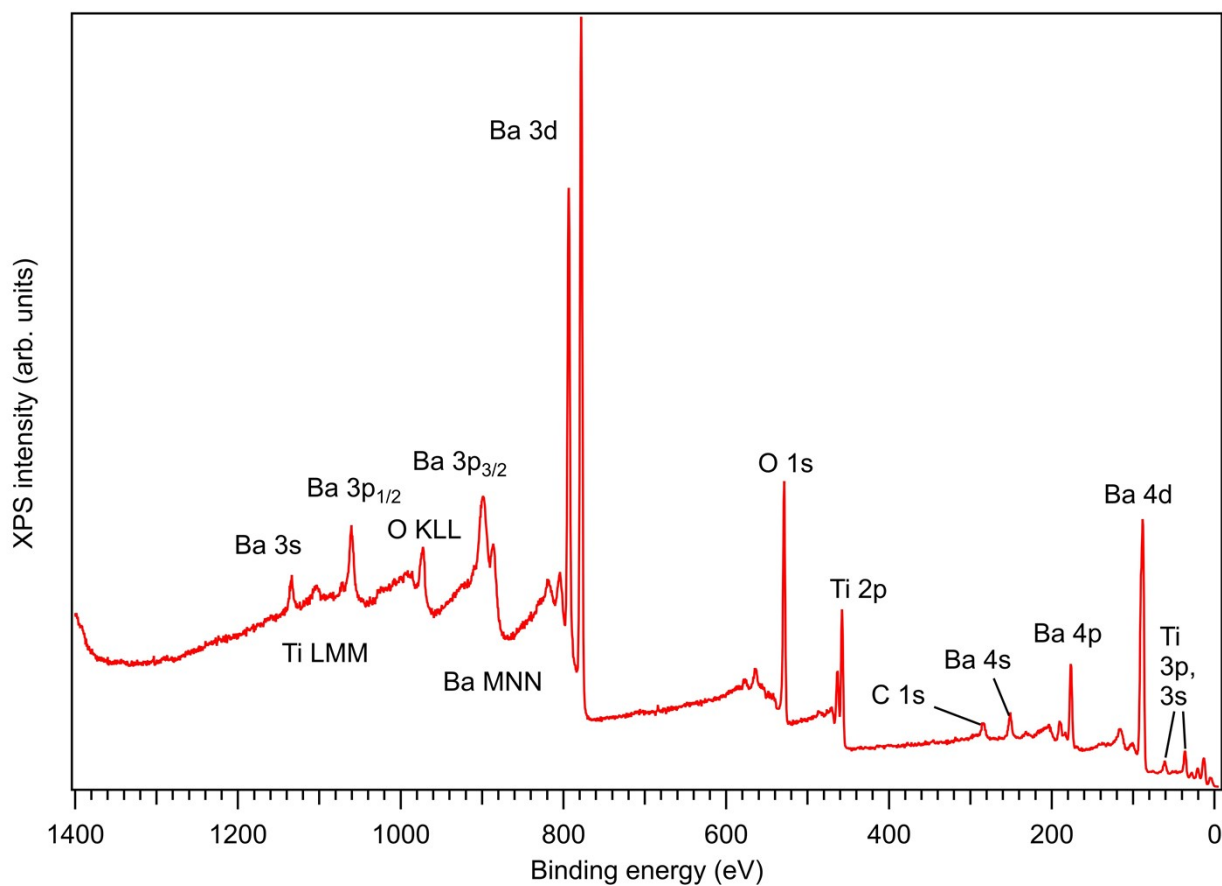


Figure S4. Survey spectrum of a BTO(001) sample not completely clean, after several annealing steps in UHV.

Composition analysis, using the XPS Atomic Sensitivity Factors (ASF) from Ref. [1]

Core level	Integral intensity (eV × cps)	Atomic sensitivity factor (Wagner)	Corrected intensity (eV × cps)
Ba 4d	443373	2.35	188669
Ti 2p	226700	1.8	125944
O 1s	287420	0.66	435485
C 1s	28550	0.25	114200

The approximate composition is $\text{Ba}_{1.50}\text{TiO}_{3.56}$, or $\text{Ba}_{1.20}\text{Ti}_{0.80}\text{O}_{2.77}$, if one normalizes to two cations per formula unit. By taking into account the correction factor for the loss of $2p_{3/2}$ electrons translated in a low branching ratio (1.42 instead of 2 [2]), a correction factor or $3/2.42 \approx 1.24$ is to be introduced in the Ti 2p signal. The composition derived will be $\text{Ba}_{1.21}\text{TiO}_{2.79}$, or $\text{Ba}_{1.10}\text{Ti}_{0.90}\text{O}_{2.52}$, if one normalizes to two cations per formula unit. The carbon contamination is about 0.6 carbon atoms per formula unit. The binding energy of C 1s is about 284.5 eV, hence this carbon is not bound to oxygen, and thus the oxygen stoichiometry is not affected by the contamination.

[1] C. D. Wagner, L. E. Zeller, J. A. Taylor, R. H. Raymond, and L. H. Gale, *Empirical atomic sensitivity factors for quantitative analysis by electron spectroscopy for chemical analysis*, Surf. Interf. Anal. **3**, 211–225 (1981).

[2] A.-C. Iancu, N. G. Apostol, A. Nicolaev, L. E. Abramiuc, C. F. Chirilă, D. G. Popescu, and C. M. Teodorescu, *Molecular adsorption–desorption of carbon monoxide on ferroelectric BaTiO₃(001)*, *Mater. Adv.* **5**, 5709–5723 (2024).

4. Comparison between XPS spectra of CO and CO₂ adsorbed on BaTiO₃(001) at –46 °C

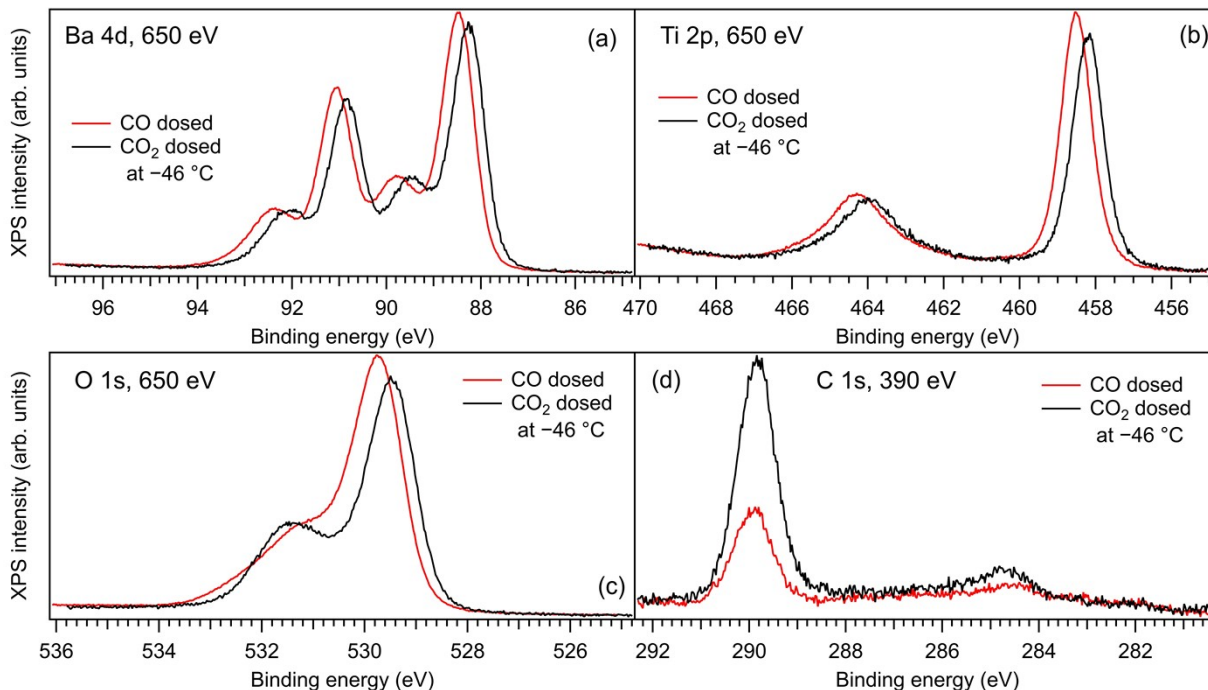


Figure S5. (a) Ba 4d, (b) Ti 2p, (c) O 1s and (d) C 1s spectra for similar amounts of CO and CO₂ (3.4 kL) adsorbed on BTO(001) at –46 °C.

The binding energies for CO/BTO(001) are higher than that of CO₂/BTO(001) by about 0.23 eV for Ba 4d, 0.38 eV for Ti 2p and 0.30 eV for O 1s (only the bulk components considered for Ba 4d and O 1s, while Ti 2p anyway features only the bulk component). The C 1s binding energy is quite similar, within the error bar of 0.01 eV.

5. Time-resolved spectra during CO₂ desorption

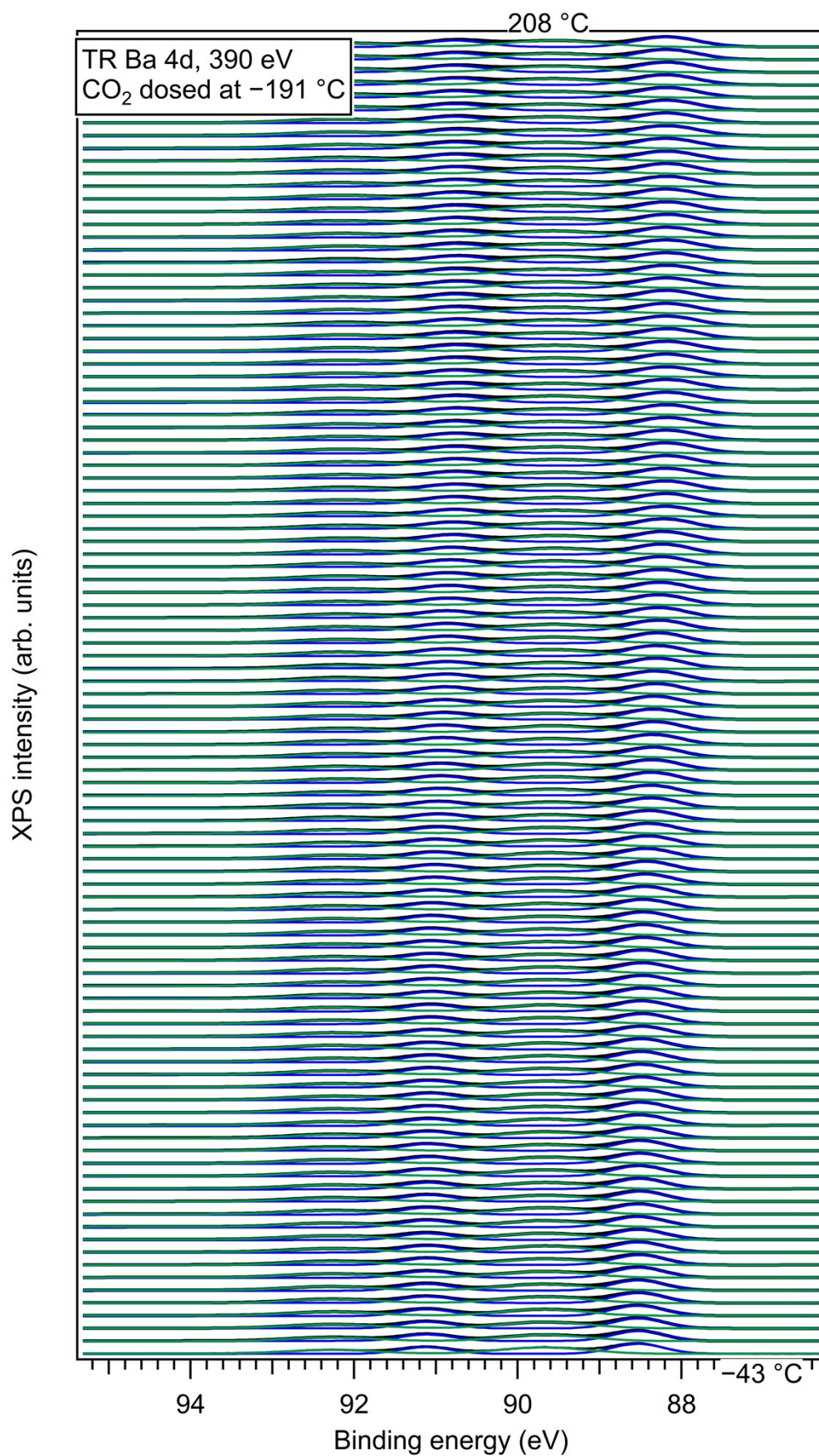


Figure S6. Time-resolved Ba 4d spectra recorded with 390 eV photon energy during sample heating, for CO₂ dosed at low temperature (-191 °C). The spectra are simulated with two Gauss doublets.

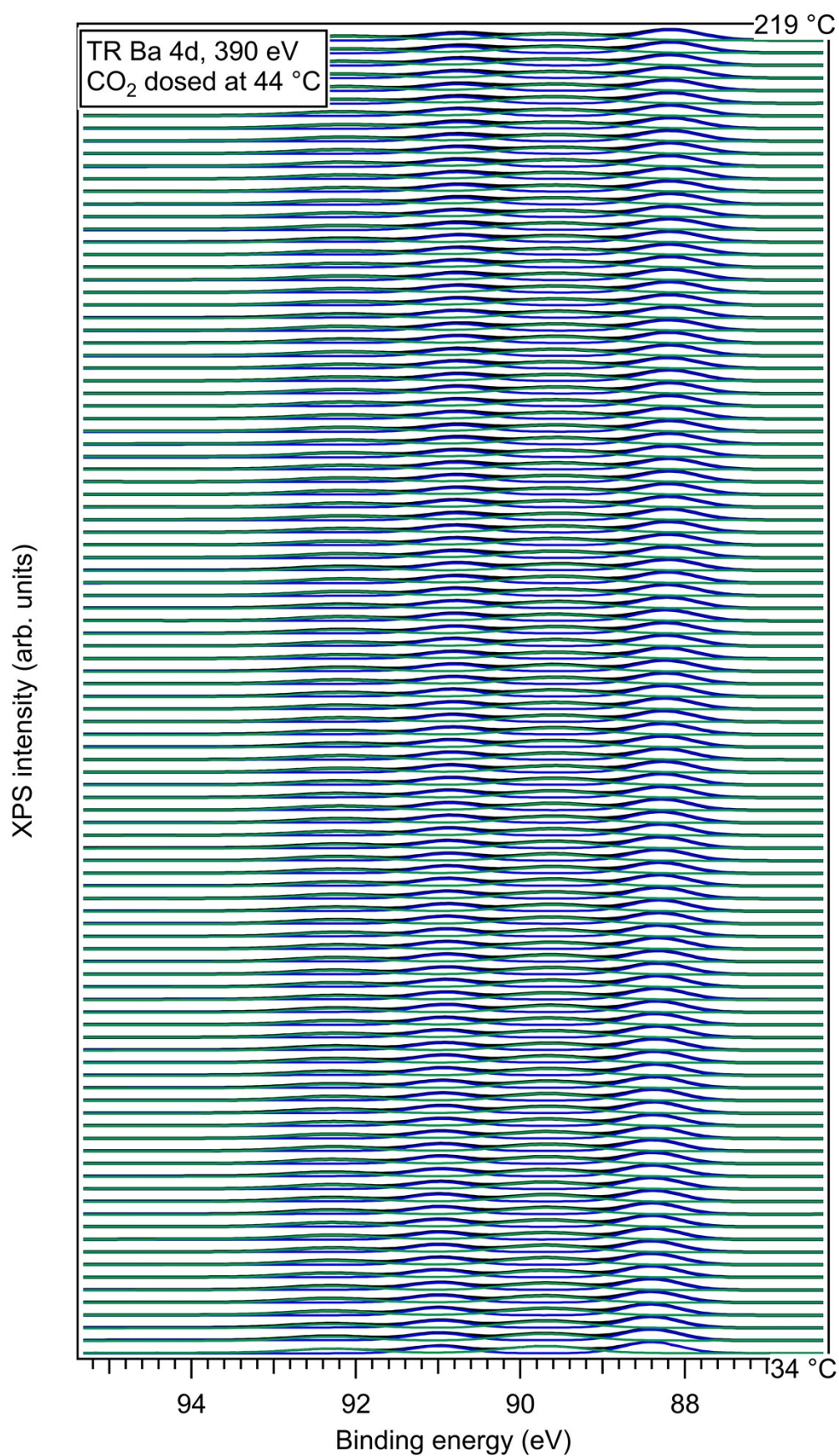


Figure S7. Time-resolved Ba 4d spectra recorded with 390 eV photon energy during sample heating for CO₂ dosed at high temperature (44 °C). The spectra are simulated with two Gauss doublets.

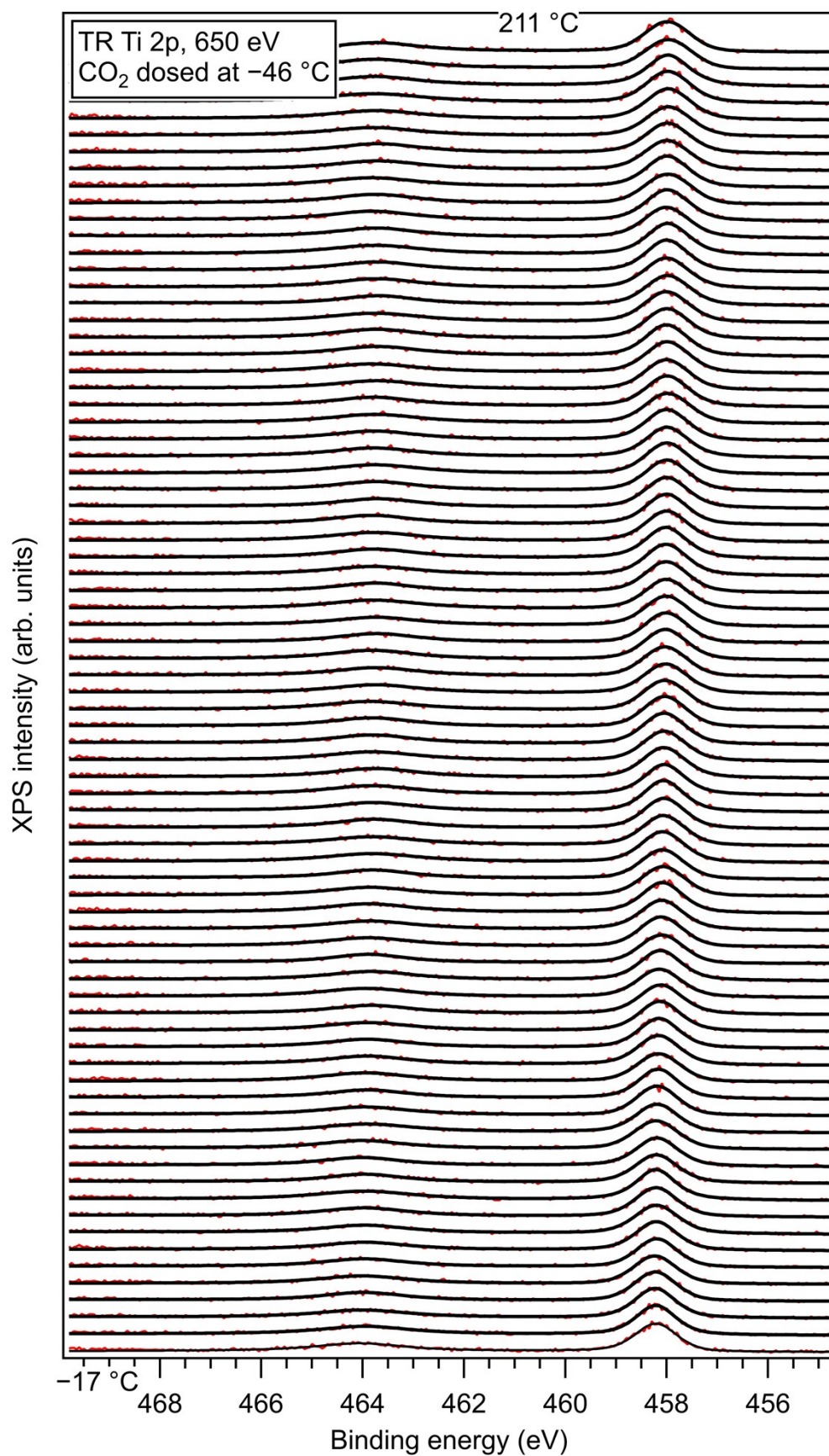


Figure S8. Time-resolved Ti 2p spectra recorded recorded with 650 eV photon energy during sample heating for CO₂ dosed at low temperature (-46 °C). The spectra are simulated with one Voigt doublet.

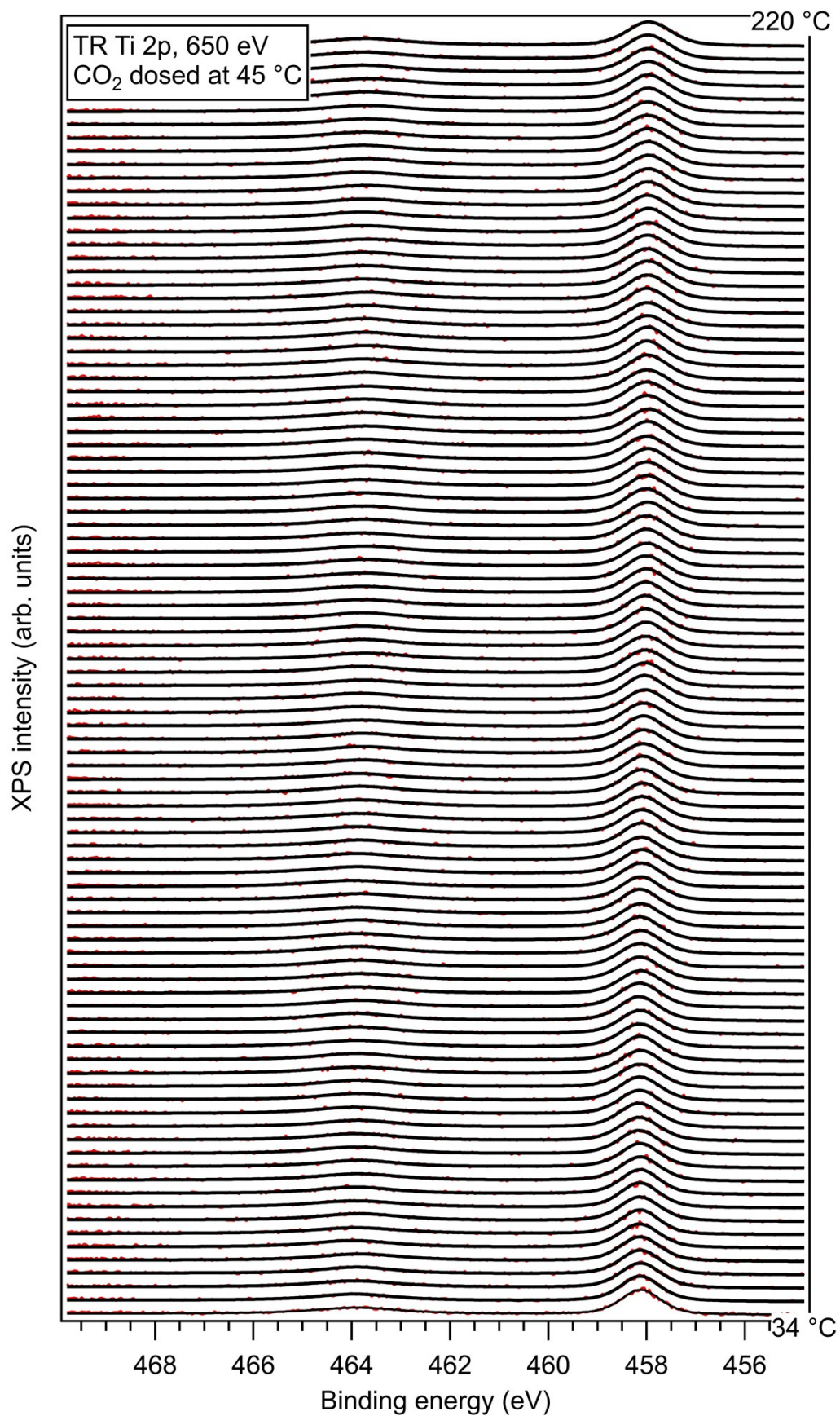


Figure S9. Time-resolved Ti 2p spectra recorded recorded with 650 eV photon energy during sample heating for CO₂ dosed at high temperature (45 °C). The spectra are simulated with one Voigt doublet.

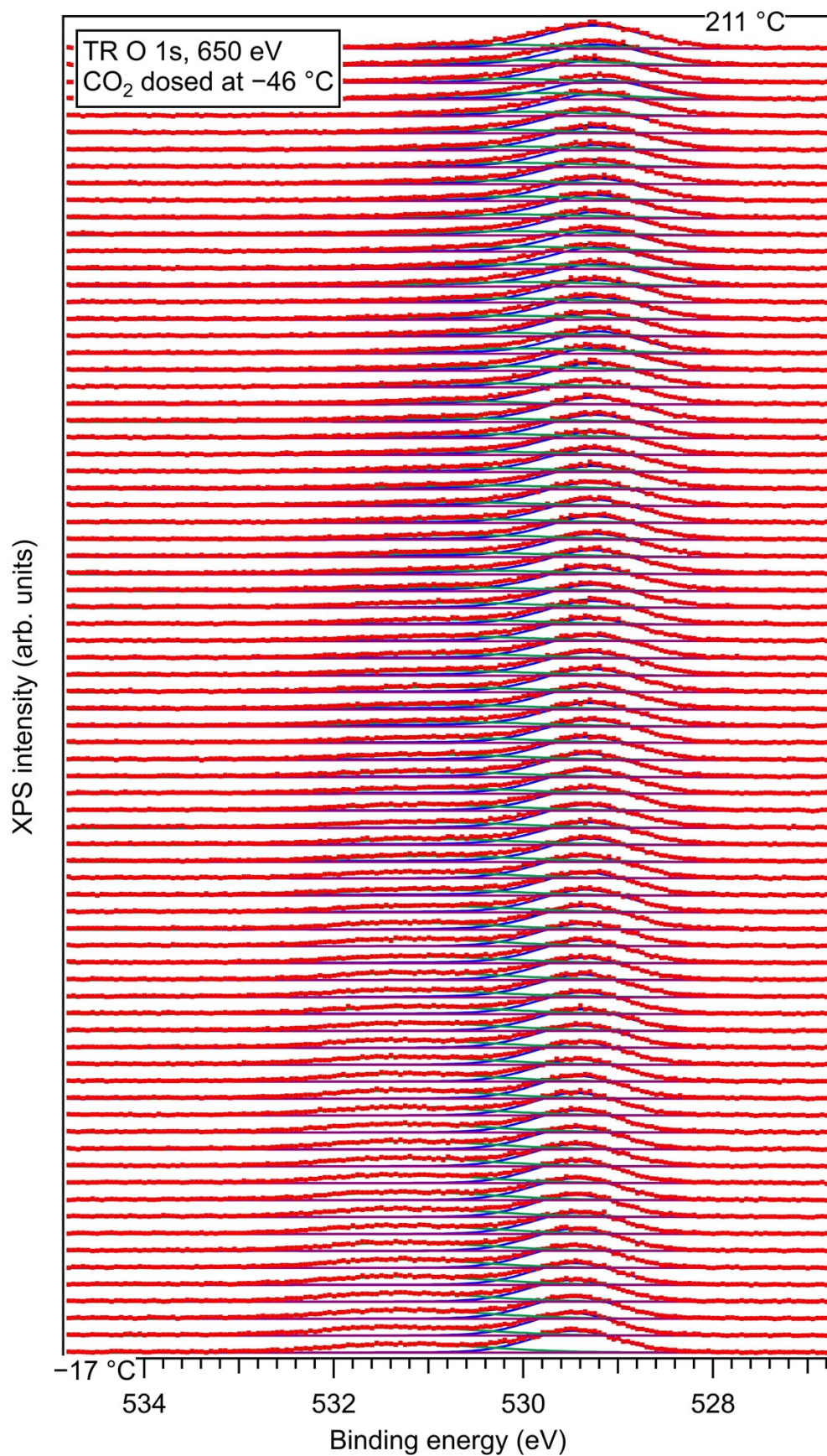


Figure S10. Time-resolved O 1s spectra recorded with 650 eV photon energy during sample heating for CO₂ dosed at low temperature (-46 °C). The spectra are simulated with three Voigt lines.

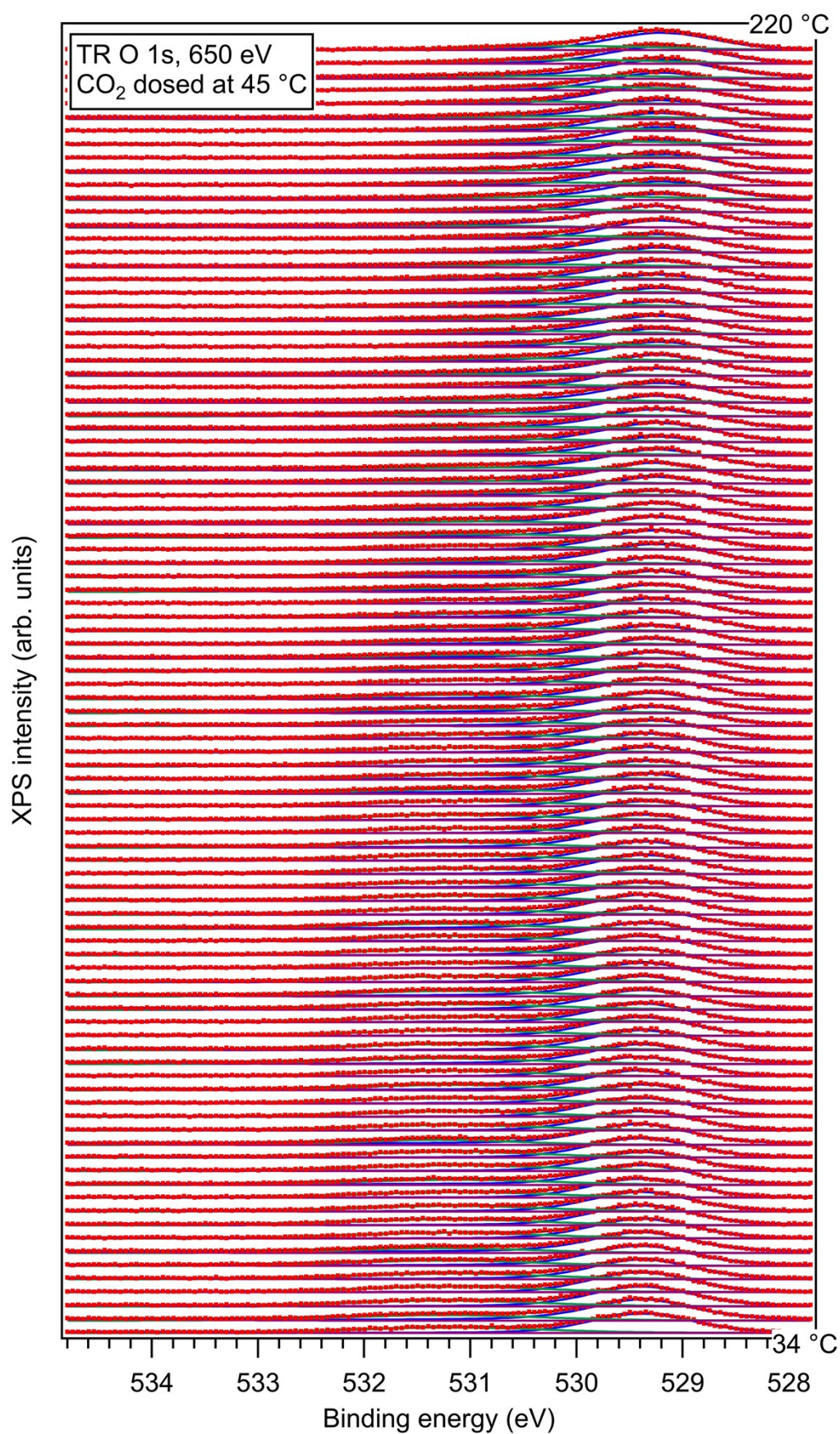


Figure S11. Time-resolved O 1s spectra recorded with 650 eV photon energy during sample heating for CO₂ dosed at high temperature (45 °C). The spectra are simulated with three Voigt lines.

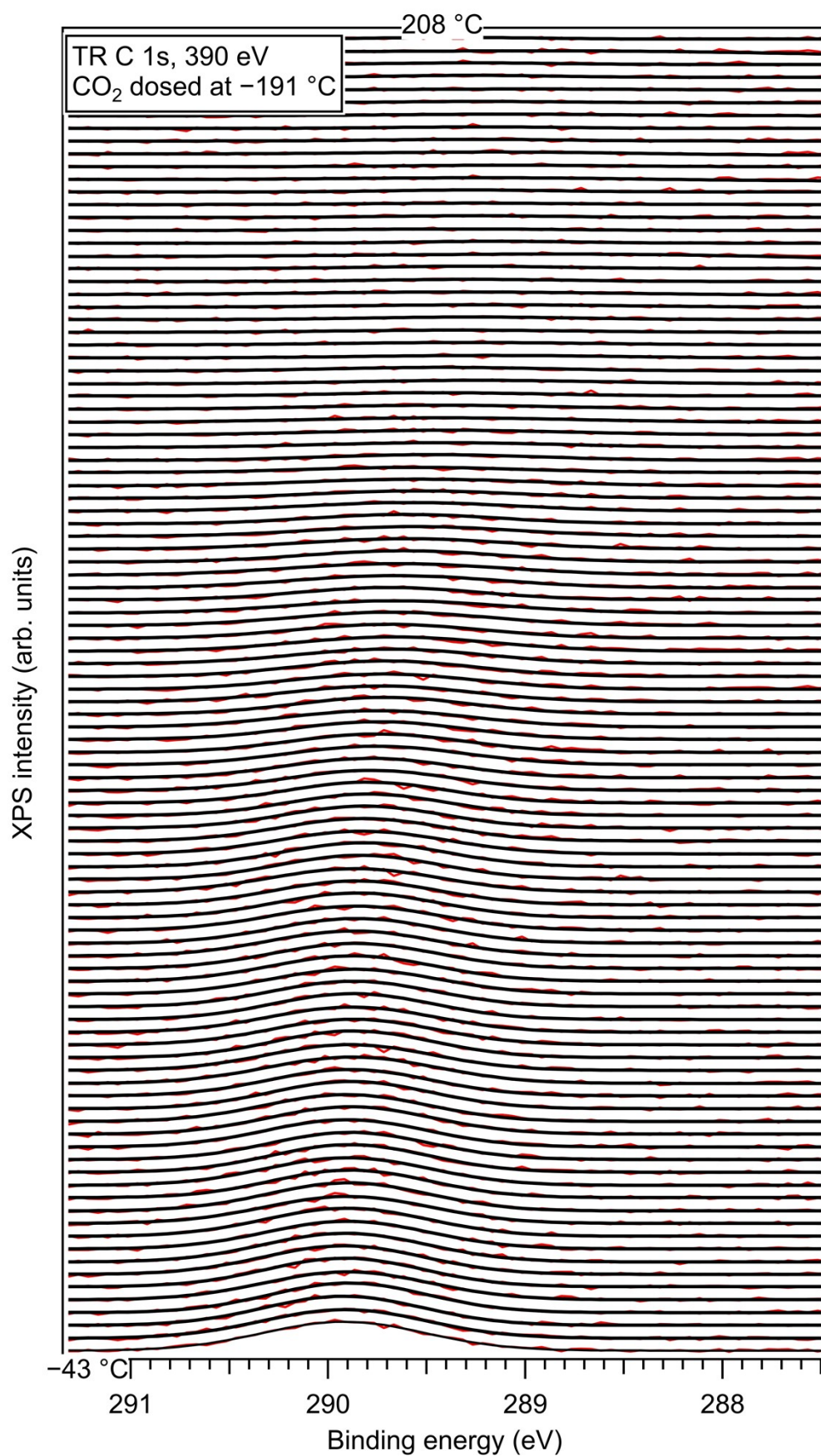


Figure S12. Time-resolved C 1s spectra recorded with 390 eV photon energy during sample heating for CO₂ dosed at low temperature (-191 °C). The spectra are simulated one Gauss (+ background) line.

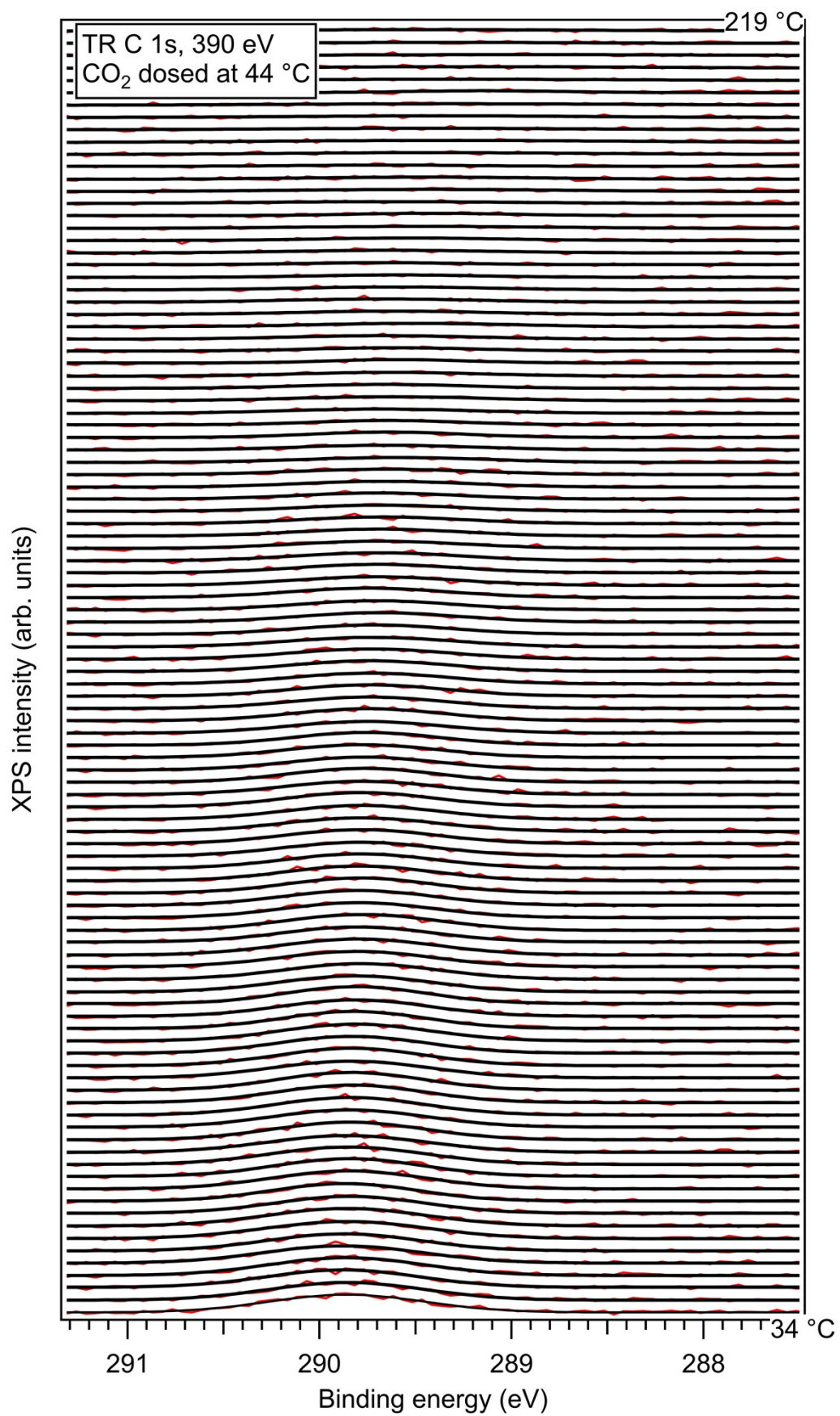


Figure S13. Time-resolved C 1s spectra recorded with 390 eV photon energy during sample heating for CO₂ dosed at high temperature (44 °C). The spectra are simulated one Gauss (+ background) line.

6. Considerations about adsorption geometries

From the main text it was concluded that CO₂ is mostly adsorbed on top of surface oxygen atoms, since the O2 component in photoemission is the strongest affected by adsorption. Also, the surface C(1):O(2) ratio (Table 2) ranges between 2 and 3, and this can be explained starting with the proposed adsorption geometries sketched in Fig. 7: the signal from the surface oxygen which initially belonged to BaO will be attenuated by the adsorbed molecule and its contribution will correspond to some fraction of an atom. The aim of this section is to discriminate between different azimuthal orientations of CO₂ adsorbed on top on oxygen. The most probable geometries which can be proposed from symmetry considerations are sketched in Fig. 7 and detailed in Fig. S14.

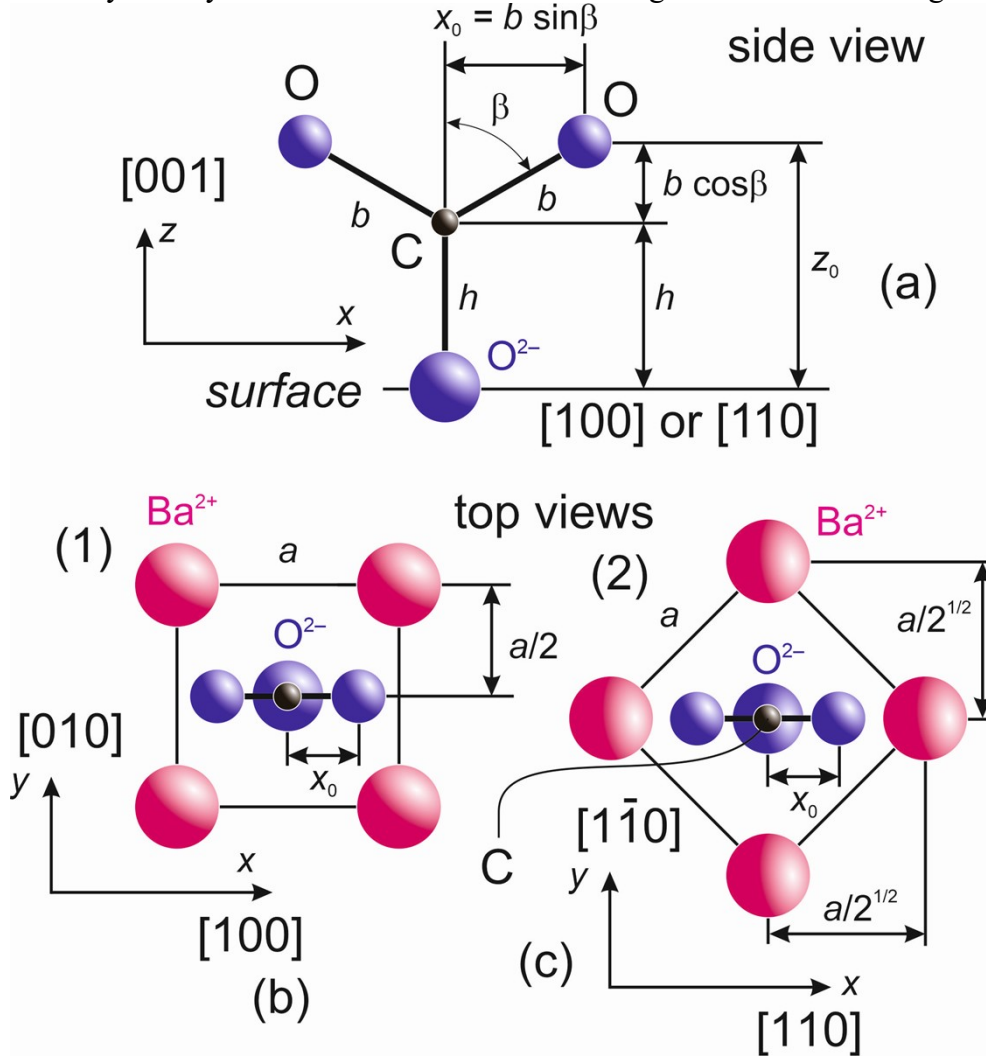


Figure S14. Typical distances for the molecule adsorbed on the surface, side view (a) and for the two proposed azimuthal orientation of the molecule, top view (b, c).

The distances from the terminal oxygens to all four Ba ions can be easily derived with the help of Fig. S14. The electrostatic interaction potential of the terminal oxygens (supposed to have an anionic character) with the four nearest Ba ions is proportional to:

$$V_{Ba}^{(1)} \propto -4 \left\{ \left[\left(\frac{a}{2} - x_0 \right)^2 + \frac{a^2}{4} + z_0^2 \right]^{-1/2} + \left[\left(\frac{a}{2} + x_0 \right)^2 + \frac{a^2}{4} + z_0^2 \right]^{-1/2} \right\} \quad (\text{S1})$$

$$V_{Ba}^{(2)} \propto -2 \left\{ \left[\left(\frac{a}{\sqrt{2}} - x_0 \right)^2 + z_0^2 \right]^{-1/2} + \left[\left(\frac{a}{\sqrt{2}} + x_0 \right)^2 + z_0^2 \right]^{-1/2} + 2 \left[x_0^2 + \frac{a^2}{2} + z_0^2 \right]^{-1/2} \right\} \quad (\text{S2})$$

where (see Fig. S4):

$$z_0 = h + b \cos \beta \quad \text{and} \quad x_0 = b \sin \beta \quad (\text{S3})$$

for the two azimuthal orientations (1, 2) represented in Figures 7 and S14. Figure S15 represents variations of $V_{Ba}^{(1)} - V_{Ba}^{(2)}$ for various values of b and h , with $a = 3.905 \text{ \AA}$ and two angles between terminal oxygens $2\beta = 120^\circ$ and 150° . Tests performed at various angles 2β revealed that for the whole investigated range $2\beta = 120 - 180^\circ$ $V_{Ba}^{(1)} > V_{Ba}^{(2)}$, hence the second adsorption site (2) from Figures 7 and S14, with the plane of the CO_3 radical intersecting the surface along a $[110]$ axis, seems to be the most stable.

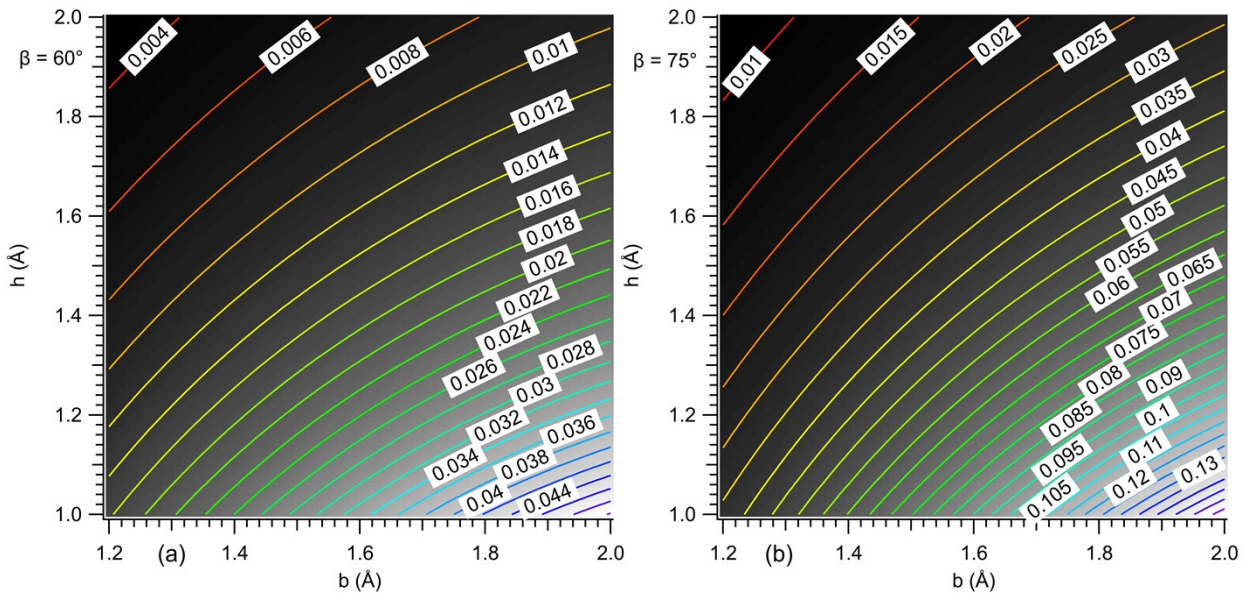


Figure S15. Difference between the electrostatic potentials of interaction between terminal oxygens from adsorbed CO_2 and surface barium ions from the unit cell $V_{Ba}^{(1)} - V_{Ba}^{(2)}$, for a wide range of the distance between the adsorbed carbon and the surface h and for the bond between carbon and the terminal oxygens, and for two angles between $\text{C}=\text{O}$ bonds of the molecule $\beta = 60^\circ$ (left) and $\beta = 75^\circ$ (right).