Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Ultrafast time-resolved quantum cascade laser diagnostic for enlightening the role of surface formate species in the photocatalytic oxidation of methanol

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Supplementary Information

- **Full *operando* FT-IR spectra at steady state of TiO_2 P25, CA and HA upon photooxidation of methanol at 25 °C and atmospheric pressure (under a reaction flow of 30 mL/min containing 0.1 vol.% of methanol and 20 vol.% of oxygen in argon).**

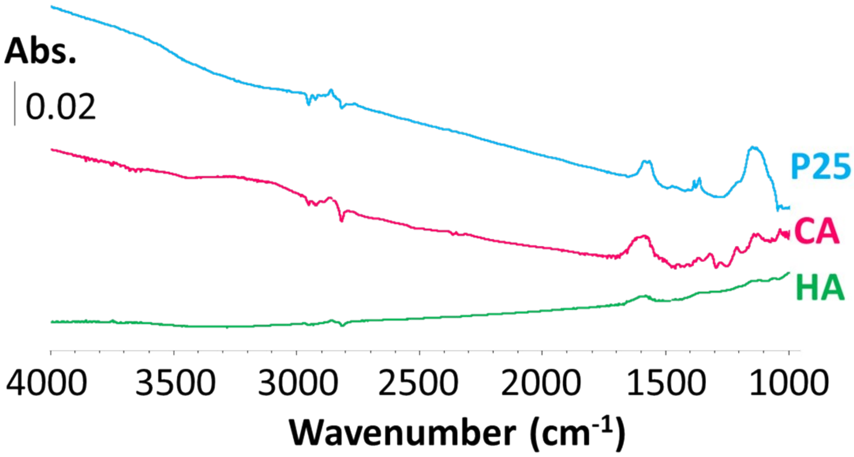

Figure S1. Full *operando* FT-IR spectra at steady state of TiO_2 P25, TiO_2 CA and TiO_2 HA upon photooxidation of methanol at 25 °C and atmospheric pressure, shown after subtraction of the initial spectrum recorded after dehydration pre-treatment under flowing methanol before UV irradiation. Conditions: flow = 30 mL/min; 0.1 and 20 vol.% of methanol and oxygen in argon, respectively; Hg-Xe lamp (200 W) filtered at λ = 365 nm; $I_{0\ (365nm)} \approx 15$ mW/cm^2. “Abs.” means absorbance, and is expressed in arbitrary units.

- **FT-IR spectra of TiO_2 P25 before and during UV irradiation at 25 °C under a flow of 20 vol.% oxygen in argon (no methanol).**

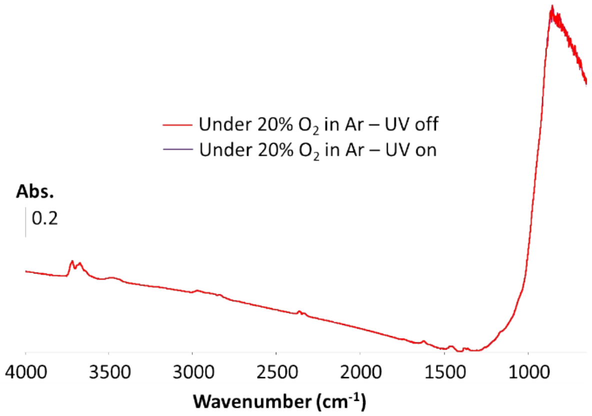

Figure S2. FT-IR spectra of TiO_2 P25 before and during UV irradiation at 25 °C and atmospheric pressure under a flow of 20 vol.% oxygen in argon without methanol. Conditions: flow = 30 mL/min; Hg-Xe lamp (200 W); $I_0 \approx 200$ mW/cm^2. “Abs.” means absorbance, and is expressed in arbitrary units.

- **QCL beam amplitude at 1360 cm^{-1} over TiO_2 P25 at 25 °C under reaction flow (methanol + oxygen/argon) without UV irradiation.**

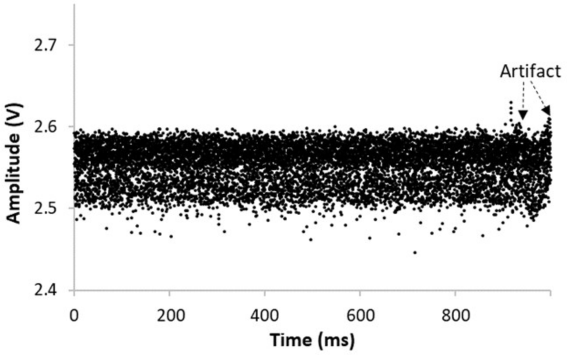

Figure S3. QCL beam amplitude at 1360 cm^{-1} *vs* time over TiO_2 P25 under reaction flow at 25 °C and atmospheric pressure without UV irradiation. Conditions: flow = 30 mL/min; 0.1 and 20 vol.% of methanol and oxygen in argon, respectively.

- **QCL signal at 1360 cm^{-1} *vs* time over TiO_2 P25 in 3 repetitions of the UV on-off cycle under reaction flow at 25 °C.**

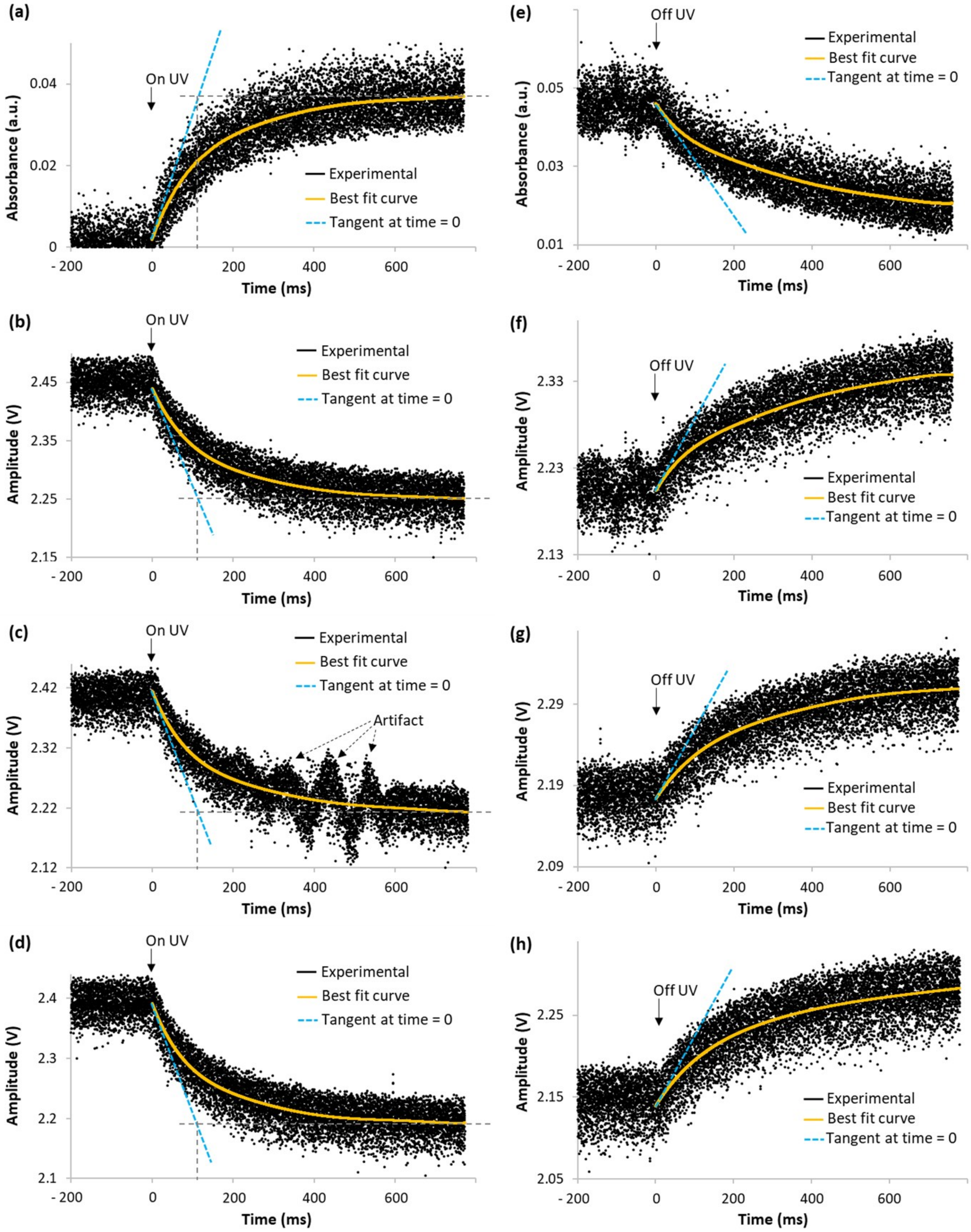

Figure S4. QCL signal at 1360 cm^{-1} *vs* time over TiO_2 P25 during repeated UV on-off cycles (UV on: a-b-c-d, UV off: e-f-g-h; two panels on the same horizontal line forming one UV on-off cycle) under reaction flow at 25 °C and atmospheric pressure. (a) and (e) show the same UV on-off cycle as (b) and (f), but with a y axis expressed in absorbance instead of amplitude. Conditions: flow = 30 mL/min; 0.1 and 20 vol.% of methanol and oxygen in argon, respectively; Hg-Xe lamp (200 W); $I_0 \approx$ 200 mW/cm^2. In (a-b-c-d), time = 0 corresponds to the moment when the shutter in-between the lamp and the UV-light guide directed to the IR cell was opened to irradiate the sample. During the preceding 200 ms, the sample was already under reaction flow but still in the dark. In (e-f-g-h), time = 0 corresponds to the moment when the shutter was closed again, still under reaction flow. The times to open and close the shutter were around 6.5 ms and 3.2 ms, respectively.

- **QCL signal at 1360 cm^{-1} *vs* time over TiO_2 CA in 3 repetitions of the UV on-off cycle under reaction flow at 25 °C.**

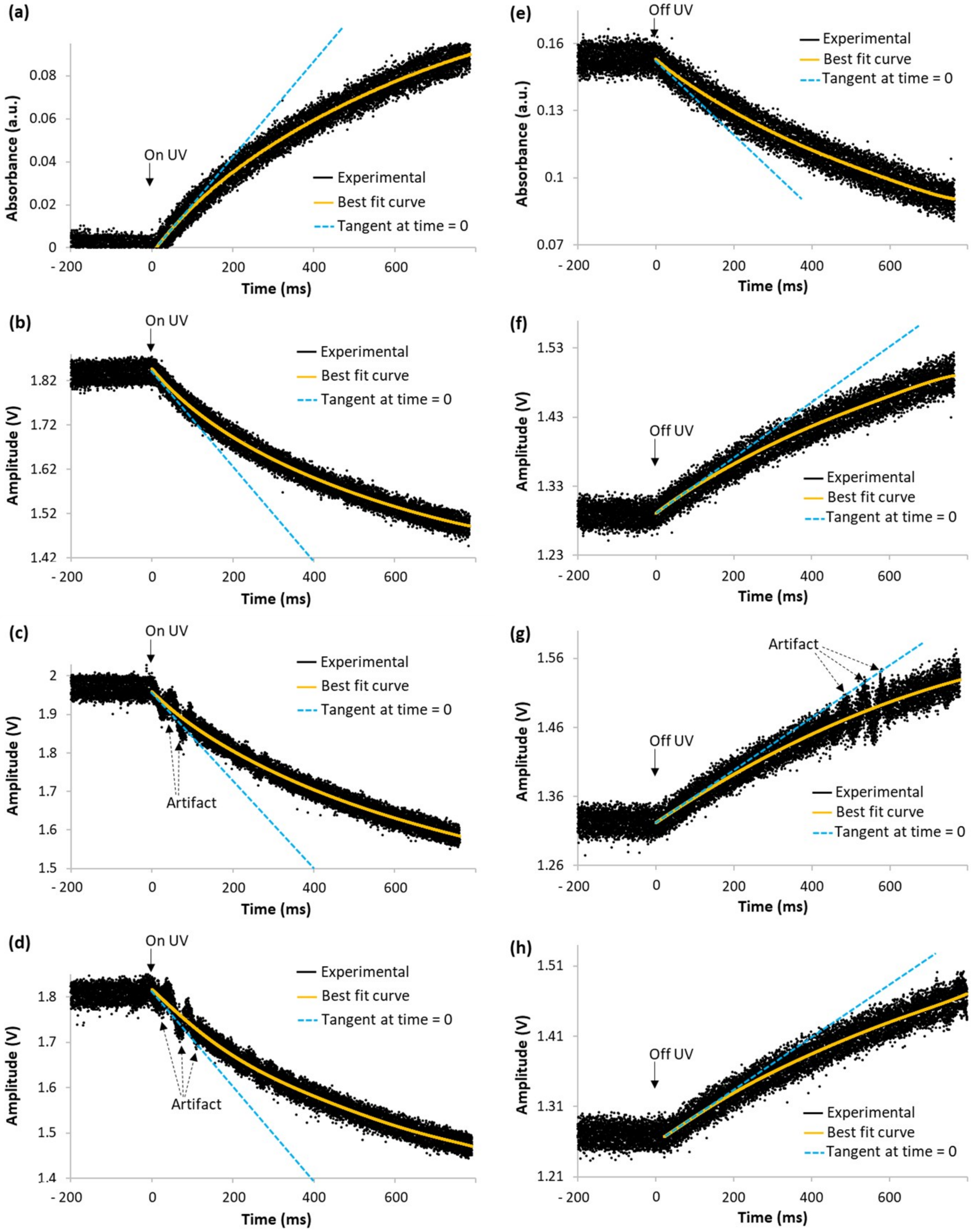

Figure S5. QCL signal at 1360 cm^{-1} *vs* time over TiO_2 CA during repeated UV on-off cycles (UV on: a-b-c-d, UV off: e-f-g-h; two panels on the same horizontal line forming one UV on-off cycle) under reaction flow at 25 °C and atmospheric pressure. (a) and (e) show the same UV on-off cycle as (b) and (f), but with a y axis expressed in absorbance instead of amplitude. Conditions: flow = 30 mL/min; 0.1 and 20 vol.% of methanol and oxygen in argon, respectively; Hg-Xe lamp (200 W); $I_0 \approx 200$ mW/cm^2. In (a-b-c-d), time = 0 corresponds to the moment when the shutter in-between the lamp and the UV-light guide directed to the IR cell was opened to irradiate the sample. During the preceding 200 ms, the sample was already under reaction flow but still in the dark. In (e-f-g-h), time = 0 corresponds to the moment when the shutter was closed again, still under reaction flow. The times to open and close the shutter were around 6.5 ms and 3.2 ms, respectively.

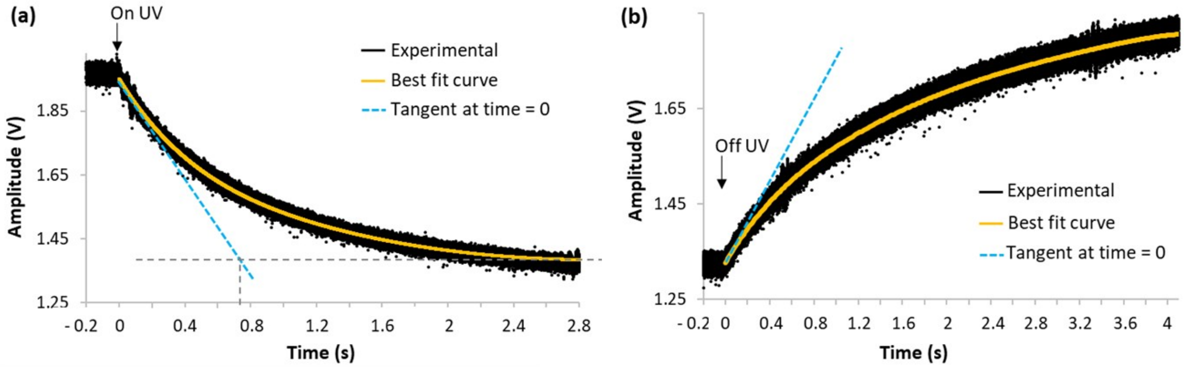

Figure S6. Same UV on(a)-off(b) cycle as shown on Figure S5 (c and g, respectively), but over a longer time scale.

- **QCL signal at 1360 cm^{-1} *vs* time over TiO_2 HA in 3 repetitions of the UV on-off cycle under reaction flow at 25 °C.**

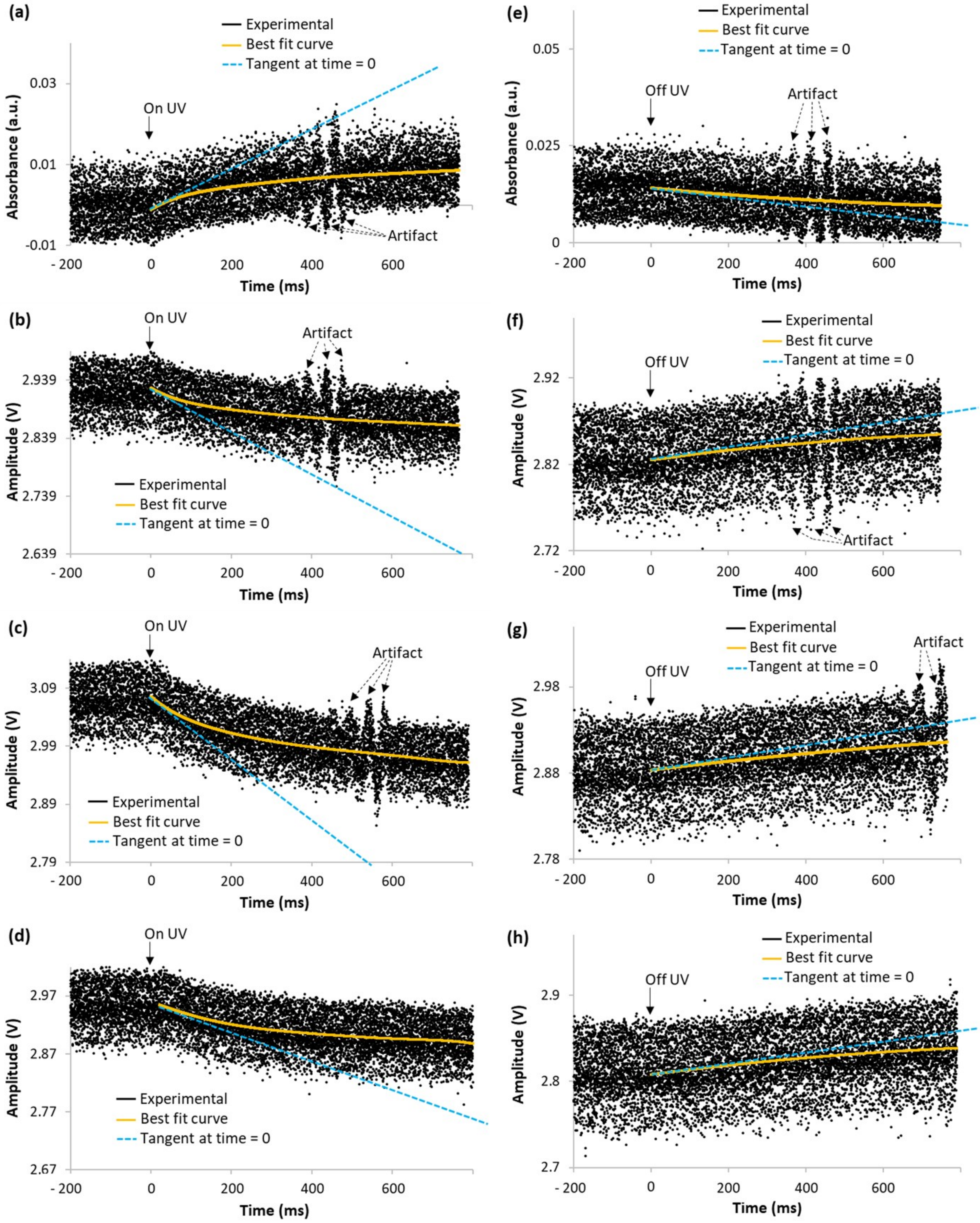

Figure S7. QCL signal at 1360 cm^{-1} *vs* time over TiO_2 HA during repeated UV on-off cycles (UV on: a-b-c-d, UV off: e-f-g-h; two panels on the same horizontal line forming one UV on-off cycle) under reaction flow at 25 °C and atmospheric pressure. (a) and (e) show the same UV on-off cycle as (b) and (f), but with a y axis expressed in absorbance instead of amplitude. Conditions: flow = 30 mL/min; 0.1 and 20 vol.% of methanol and oxygen in argon, respectively; Hg-Xe lamp (200 W); $I_0 \approx$ 200 mW/cm^2. In (a-b-c-d), time = 0 corresponds to the moment when the shutter in-between the lamp and the UV-light guide directed to the IR cell was opened to irradiate the sample. During the preceding 200 ms, the sample was already under reaction flow but still in the dark. In (e-f-g-h), time = 0 corresponds to the moment when the shutter was closed again, still under reaction flow. The times to open and close the shutter were around 6.5 ms and 3.2 ms, respectively.

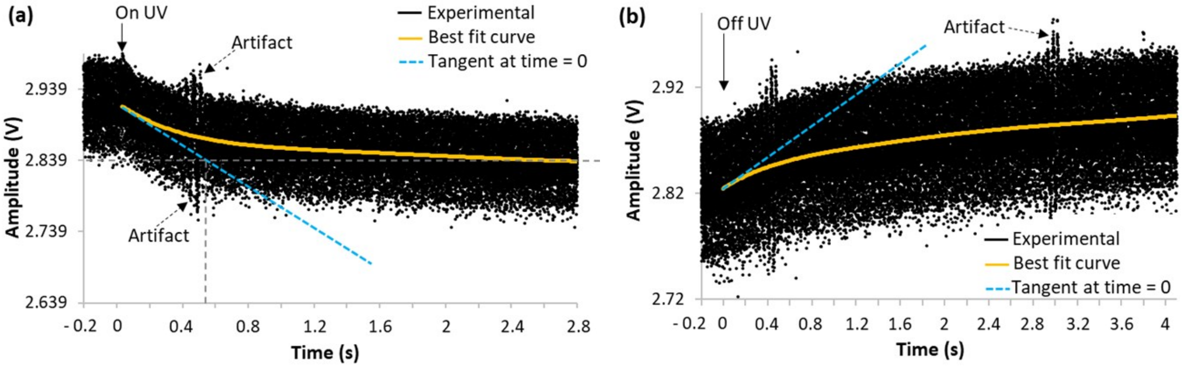

Figure S8. Same UV on(a)-off(b) cycle as shown on Figure S7 (b and f, respectively), but over a longer time scale.

- **QCL beam absorbance at 1360 cm^{-1} *vs* time over TiO$_2$ P25 under reaction flow at 25 °C, in the UV off period following an UV on period of 300 ms *vs* 5 s.**

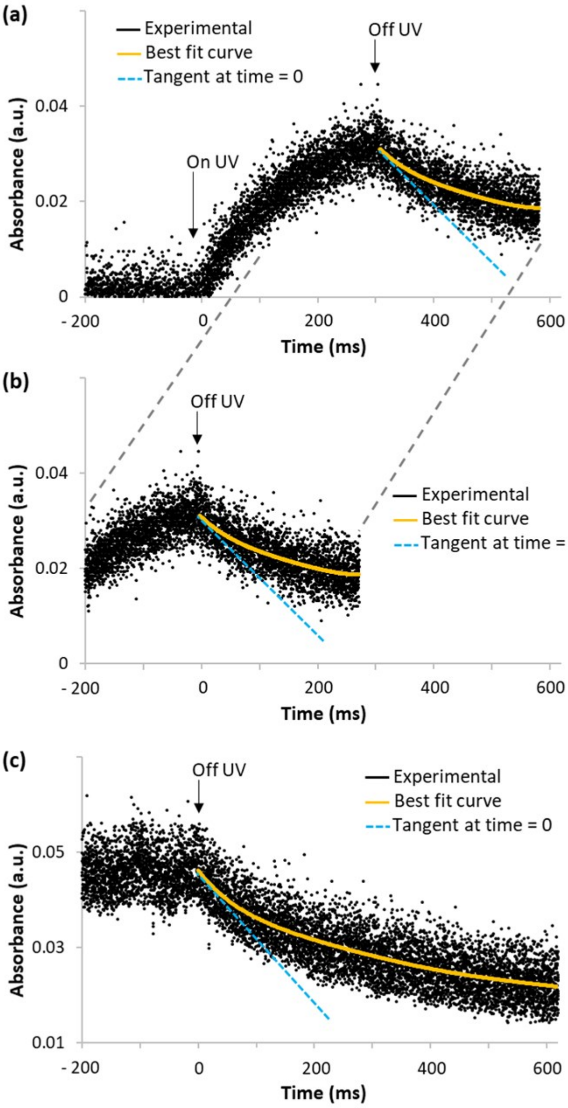

Figure S9. QCL beam absorbance at 1360 cm^{-1} *vs* time over TiO$_2$ P25 under reaction flow at 25 °C and atmospheric pressure during (a-b) a UV on-off cycle with on and off periods of 300 ms and (c) the same UV off cycle as shown on Figure S3e, i.e. after a UV on period of 5 s. Conditions: flow = 30 mL/min; 0.1 and 20 vol.% of methanol and oxygen in argon, respectively; Hg-Xe lamp (200 W); I$_0$ ≈ 200 mW/cm^2. In (a), time = 0 corresponds to the moment when the shutter in-between the lamp and the

UV-light guide directed to the IR cell was opened to irradiate the sample. During the preceding 200 ms, the sample was already under reaction flow but still in the dark. In (b-c), time = 0 corresponds to the moment when the shutter was closed again, still under reaction flow. The times to open and close the shutter were around 6.5 ms and 3.2 ms, respectively. Extracted $R_{app,r}$ values are 0.12 in (b) *vs* 0.15 in (c).

- **QCL beam absorbance at 1360 and 1310 cm^{-1} *vs* time over TiO$_2$ P25 getting UV-irradiated under flowing methanol at 25 °C in the absence *vs* presence of oxygen.**

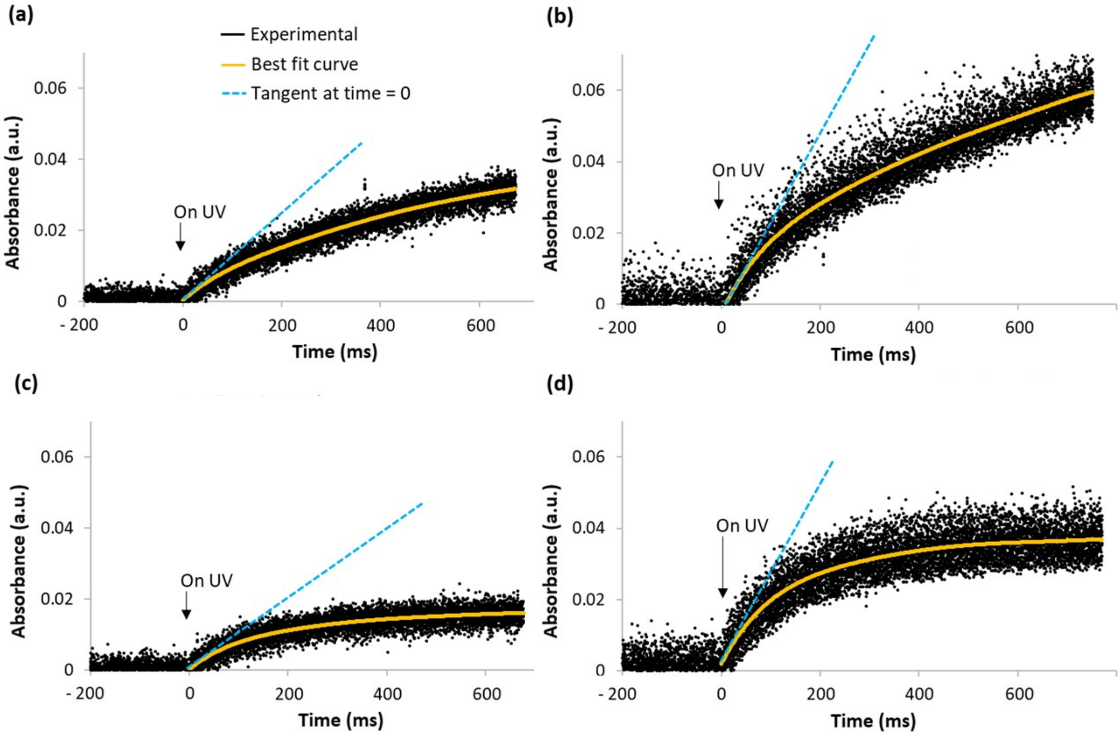

Figure S10. QCL beam absorbance at 1310 cm^{-1} (a and c) and 1360 cm^{-1} (b and d) *vs* time over TiO$_2$ P25 getting UV-irradiated under flowing methanol at 25 °C and atmospheric pressure in the absence (a-b) or presence (c-d) of oxygen. Conditions: flow = 30 mL/min; 0.1 vol.% of methanol in argon, with 20 vol.% of oxygen if present; Hg-Xe lamp (200 W); $I_0 \approx 200$ mW/cm^2. Time = 0 corresponds to the moment when the shutter in-between the lamp and the UV-light guide directed to the IR cell was opened to irradiate the sample. During the preceding 200 ms, the sample was already under flowing methanol (without oxygen in a-b, with oxygen in c-d) but still in the dark. The time to open the shutter was around 6.5 ms.