

Supplementary information for

Identification of Adsorbed Species and Surface Chemical State on Ag(111) in the Presence of Ethylene and Oxygen Studied with Infrared and X-ray Spectroscopies

Adva Ben Yaacov,[†], Roey Ben David,[†], David C. Grinter,[‡], Georg Held,[‡], Baran Eren,^{*,†}

[†]Department of Chemical and Biological Physics, Weizmann Institute of Science, 234 Herzl Street, 76100 Rehovot, Israel,

[‡]Diamond Light Source, Didcot, Oxfordshire, OX11 0DE, UK

* E-mail: baran.eren@weizmann.ac.il

Phone: +972 8-934-3708

Here, we show the full set of AP-XPS spectra (Figures S1-S3) and PM-IRRAS spectra (Figure S4). We also performed additional PM-IRRAS spectra at a lower pressure range shown in Figure S5. We also investigated the effect of air exposure; the relevant PM-IRRAS spectra are shown in Figure S8. In Figure S7, we show the comparison of the $m/z=18$ and $m/z=44$ mass spectra peaks attributed to H_2O and CO_2 formation. Finally, some analysis of the main peak in the O 1s region is shown in Figure S6.

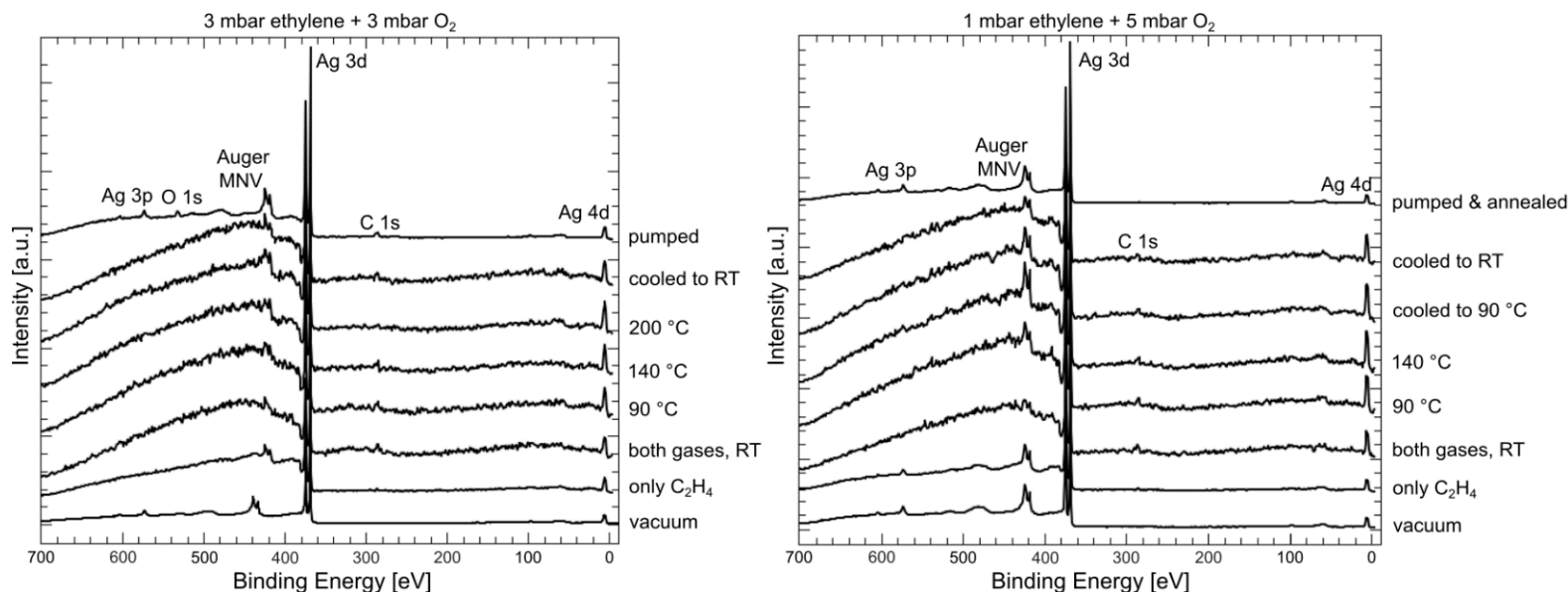


Figure S1 Survey scans of the XPS spectra obtained in different ethylene and oxygen gas mixtures. No peaks other than those related to Ag, O, and C have discernible intensities. $E_{hv} = 770$ eV, except for the first measurement in vacuum where $E_{hv} = 785$ eV. Pass energy was 20 eV.

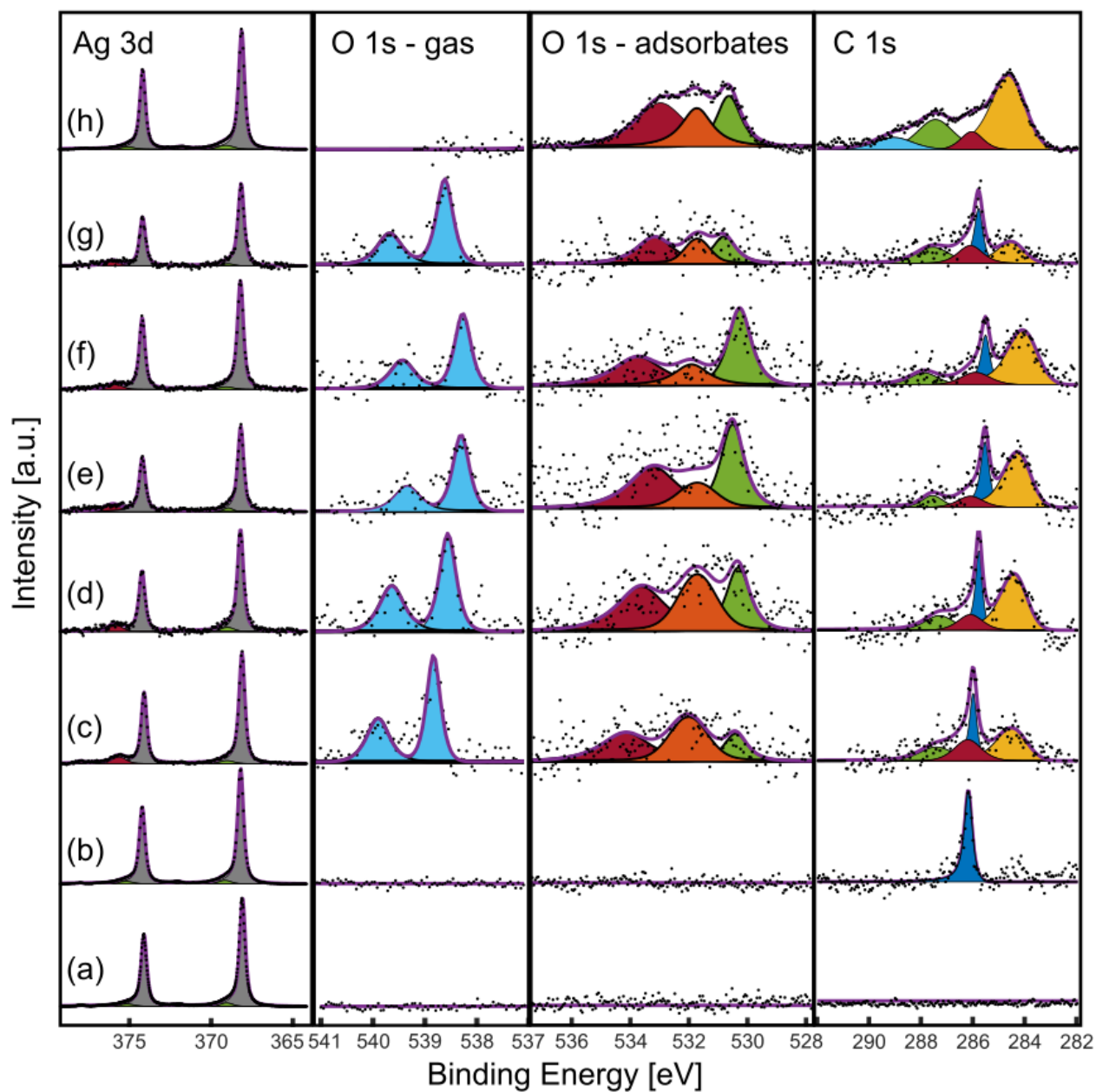


Figure S2 – From left to right: Ag 3d, O 1s, and C 1s regions of the APXPS spectra of Ag(111) under the equal partial pressure conditions studied in this work. Conditions are: (a) in UHV at RT, (b) in the presence of 3 mbar ethylene at RT, (c)-(g) in the presence of 3 mbar ethylene and 3 mbar oxygen at (c) RT, (d) 90 °C, (e) 140 °C, (f) 200 °C, and (g) after cooling back to RT. (h) was acquired after pumping away both gases.

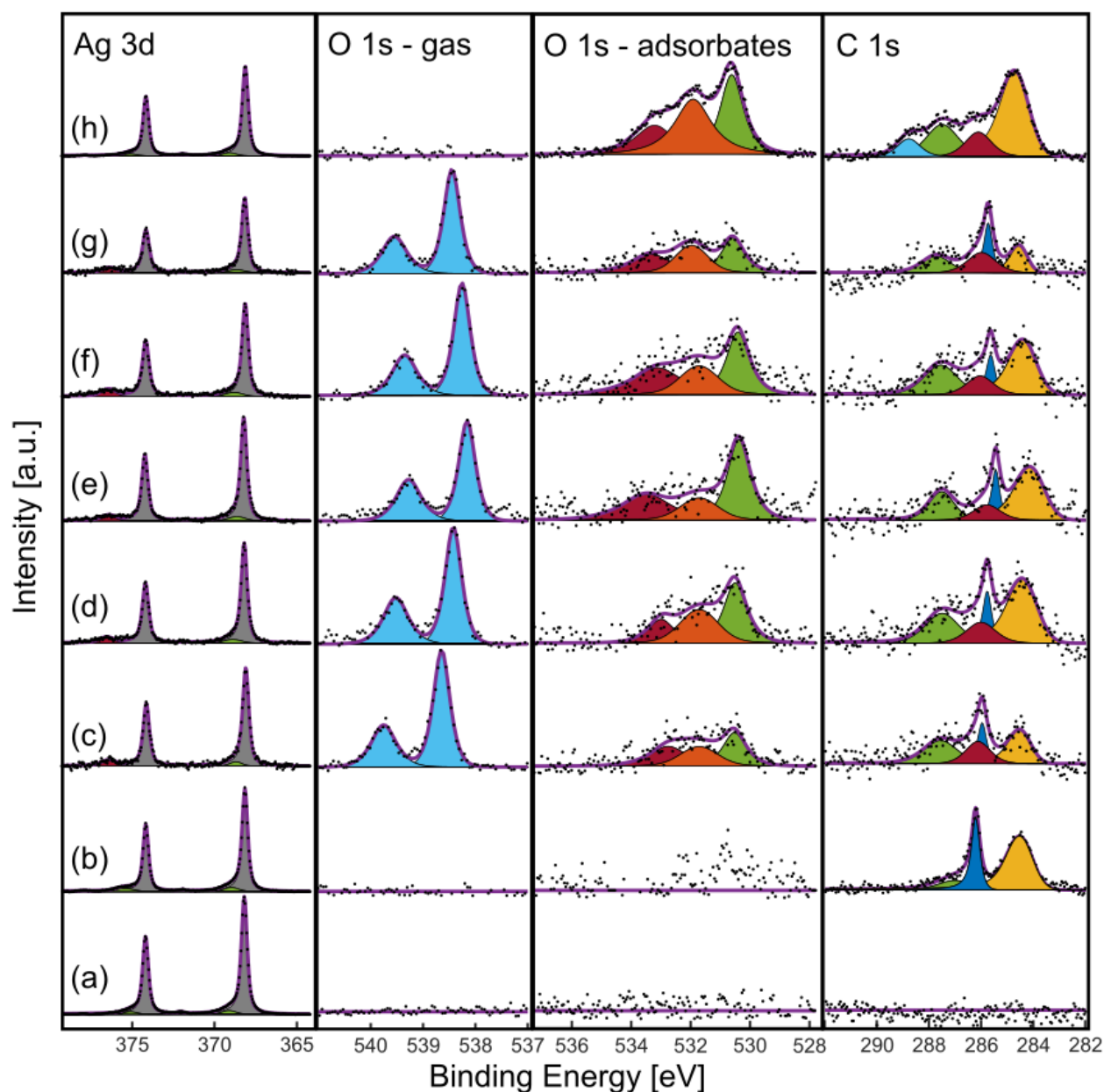


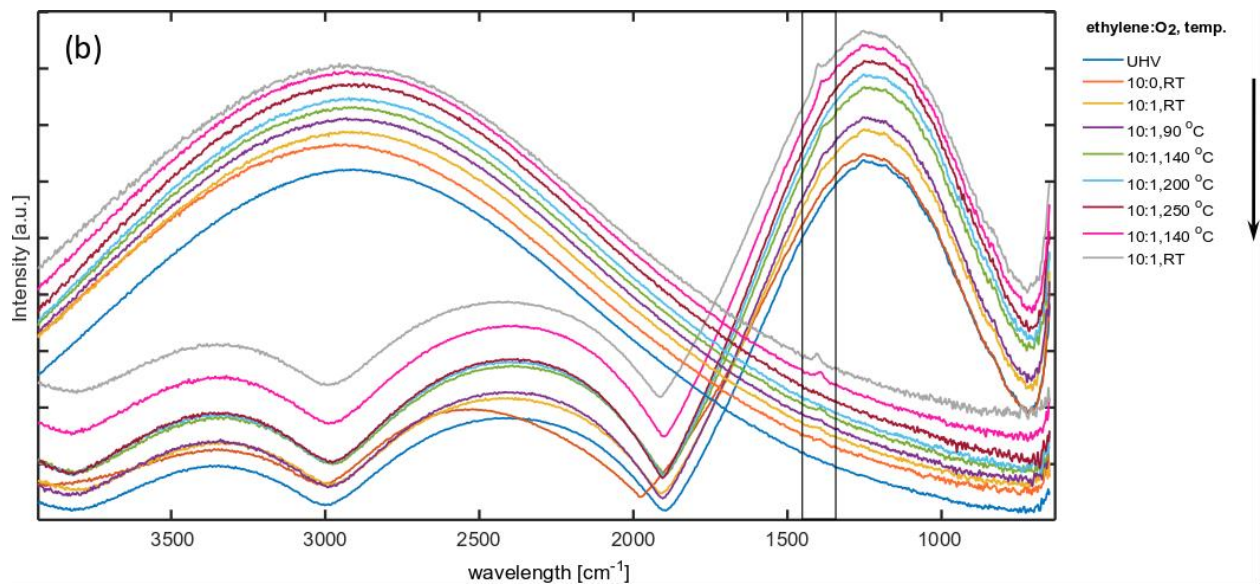
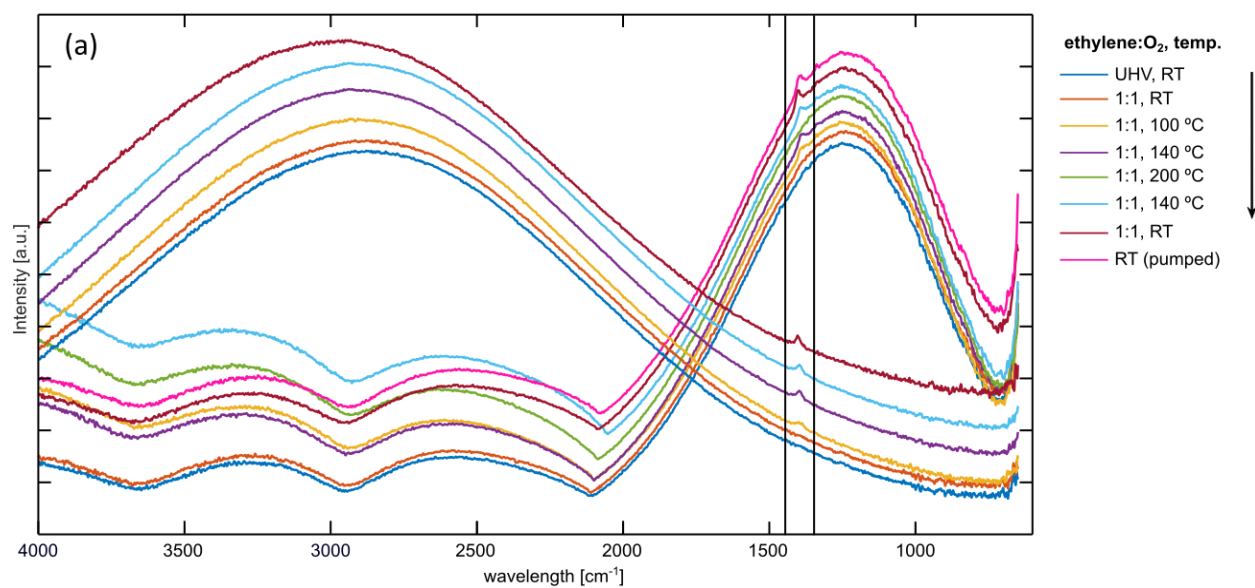
Figure S3 – From left to right: Ag 3d, O 1s, and C 1s regions of the APXPS spectra of Ag(111) under the oxygen-rich conditions studied in this work. Conditions are: (a) in UHV at RT, (b) in the presence of 1 mbar ethylene at RT, (c)-(g) in the presence of 1 mbar ethylene and 5 mbar oxygen at (c) RT, (d) 90 °C, (e) 140 °C, after cooling back to (f) 90 °C and (g) RT. (h) was acquired after pumping away both gases.

We cannot use the C 1s and O 1s regions of our AP-XPS spectra to confirm our PM-IRRAS results because of contamination issues and/or beam-induced effects that become significantly more pronounced in the few mbar pressure range. The former is due to increased interaction of gases with the chamber walls that results in more hydrocarbons depleting from the chamber walls. The latter is due to two reasons: the

secondary electron creation in the solid activating adsorbed species, and the number of scattering events occurring within a given volume increasing with increasing pressure, thereby increasing the amount of energy absorbed and the associated radical generation. In fact, beam-induced effects at or around 1 mbar O₂ are well-documented for higher flux undulator beamlines [S1]. Despite lower flux of the bending-magnet radiation used in the present study, increase in total pressure to 6 mbar can generate radicals. On top of these, as we previously mentioned, the signal is attenuated ~20 times more in 6 mbar compared to 1 mbar due to scattering of electrons with gas-phase molecules. Nevertheless, we present the C 1s and O 1s regions of the AP-XPS spectra in Figures S2 and S3 obtained in both equal partial pressure and O₂-rich conditions. Although the surface is free of any adsorbed species including Et and contaminants both in UHV and in the presence of pure Et in the first experiment (only discernible feature is the sharp peak situated at roughly 286.3 eV produced by the gas-phase Et, aliphatic hydrocarbon contamination maybe merely visible), multiple species are present when both gases are present: The peak at around 284.5 eV is due to aliphatic hydrocarbon contamination, peaks at 286.2 eV, 287.5 eV, 531.8 eV, and above 533 eV due to oxygenated hydrocarbons. There are multiple different oxygenated hydrocarbon species, which typically fall in this region both in O 1s and C 1s region, including various carbonyl, carboxyl, ether, and alcohol groups [45]. It is not possible to determine the exact species from XPS alone, because of too many peaks overlap in a rather small binding energy range [45]. We should note that oxygenated hydrocarbon contaminants are very common in AP-XPS experiments, and they are often mistaken for reaction products. Thanks to our PM-IRRAS results, we can certainly claim that they are not reaction products, with the exception of the peak at 287.5 eV, which is partially due to carbonate formation [17,19-24]. Since none of these species should have existed in the first place, exact identification of other species is not critical to the present work.

An important result of the O 1s spectra is that no discernible peak is produced below 530 eV. Another important feature is the peak between 530 eV and 531 eV, which we discuss in the main text.

[S1] Jiang, P.; Porsgaard, S.; Borondics, F.; Köber, M.; Caballero, A.; Bluhm, H.; Besenbacher, F.; Salmeron, M. Room-Temperature Reaction of Oxygen with Gold: An In situ Ambient-Pressure X-ray Photoelectron Spectroscopy Investigation. *J. Am. Chem. Soc.* **2010**, *132*, 2858–2859.



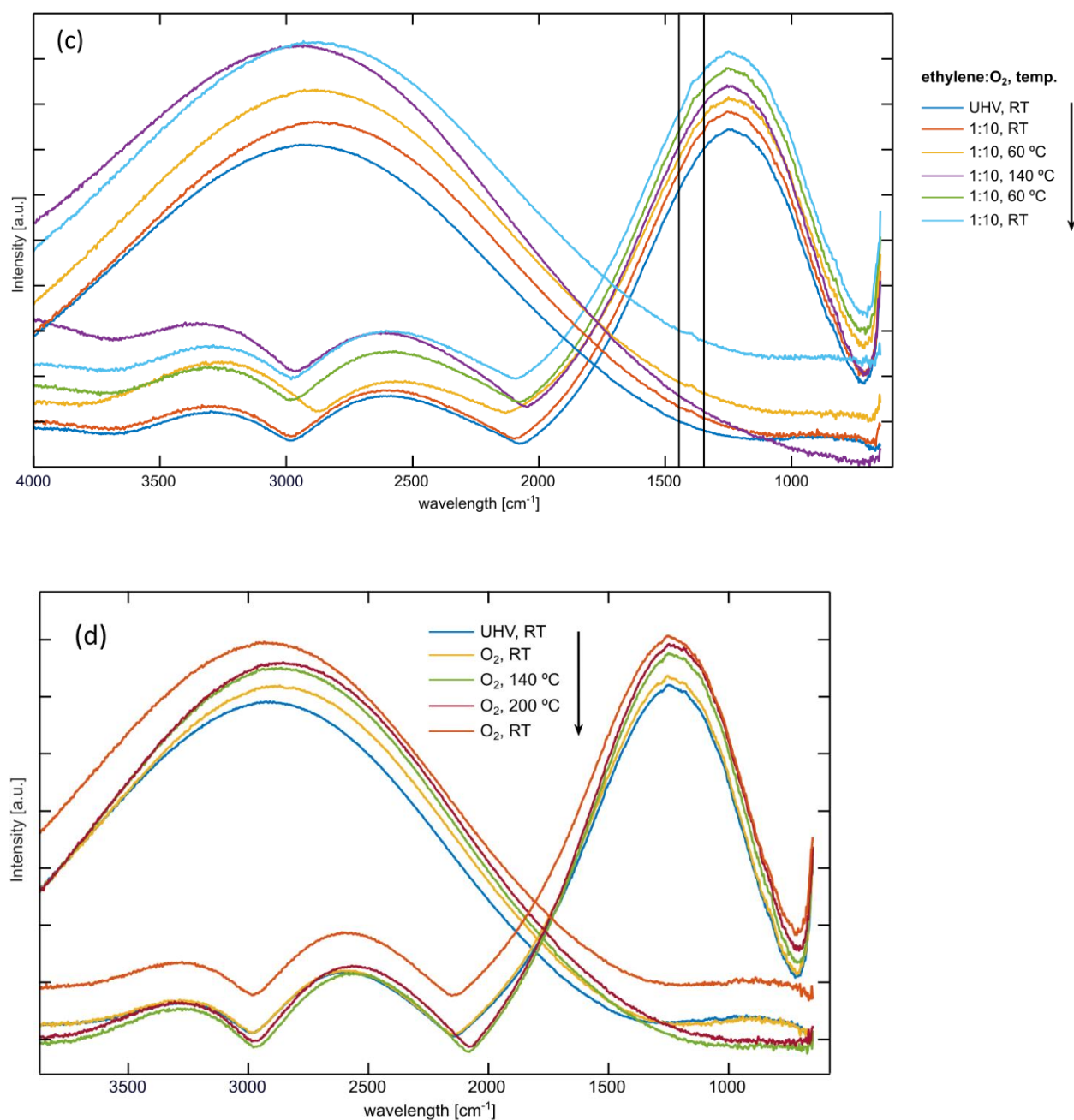


Figure S4 – PM-IRRAS spectra acquired with a maximum dephasing (ϕ_0) of 1000 cm^{-1} and 2600 cm^{-1} under different conditions. Spectra are shown without subtracting the Bessel function. The arrows indicate the order of changing conditions during the experiment. (a) to (d) indicate different experiments with different ethylene and oxygen partial pressures. (a) ethylene:O₂ is 1:1, total pressure is 10 mbar. (b) ethylene:O₂ is 10:1, total pressure is 11 mbar, hence ethylene-rich conditions. (c) ethylene:O₂ is 1:10, total pressure is 11 mbar, hence oxygen-rich conditions. (d) In the presence of 10 mbar O₂.

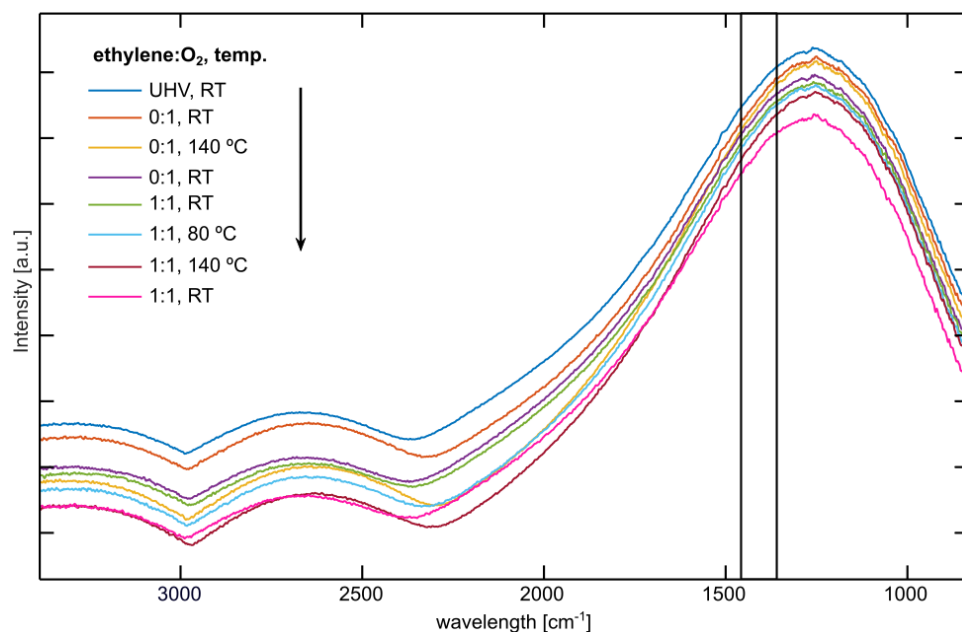


Figure S5 – PM-IRRAS spectra in the presence of 1 mbar ethylene and 1 mbar oxygen. The conditions are very similar to those presented in Figure S3a, with the exception of total pressure set to 10 mbar in one case and 2 mbar in other. No carbonate peak appears when the total pressure range is 2 mbar. Spectra were obtained with $\varphi_0 = 1000 \text{ cm}^{-1}$ and presented without subtracting the Bessel function.

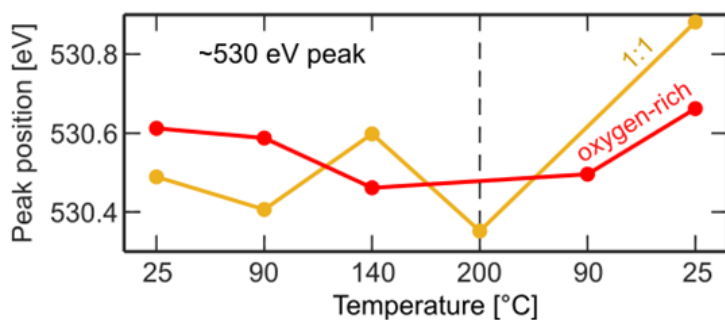


Figure S6 –Peak position of the '530 eV peak', as function of surface temperature. Since this peak is separated from the other peaks in binding energy, it is used for further analysis in the main text.

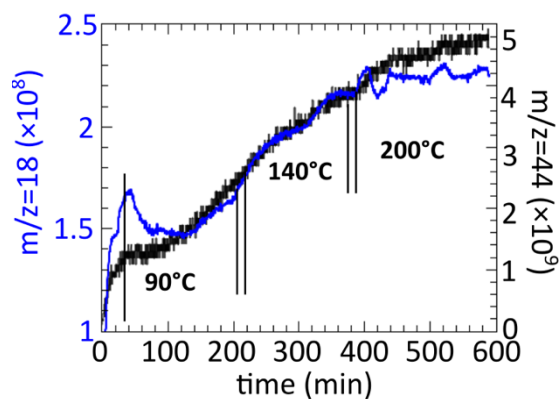


Figure S7 – Comparison of the $m/z=18$ signal due to water vapor formation and $m/z=44$ signal due to CO_2 formation as a function of surface temperature. Data was collected during AP-XPS measurements in equal partial pressure reaction conditions.

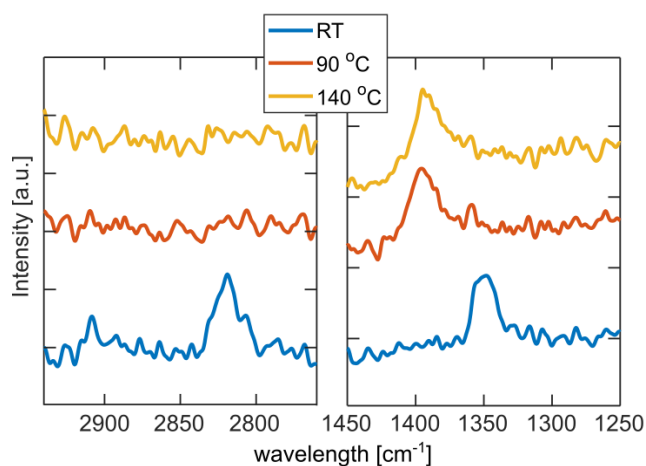


Figure S8 – PM-IRRAS spectra from Ag(111) at RT in the presence of 10 mbar of ambient air. While at RT the surface is covered with formate, carbonate forms due to CO_2 oxidation and replaces the formate at 90 °C and 140 °C. Formate produces two prominent peaks roughly at 1350 cm^{-1} and 2820 cm^{-1} due to its C-O and C-H stretching frequencies, whereas polydentate carbonate produces one peak at around 1400 cm^{-1} due to its C-O stretching frequency.