

Supplementary information (ESI)

to

**Acetone and the precursor ligand acetylacetone:
Distinctly different electron beam induced decomposition? †**

Jonas Warneke^a, Willem F. Van Dorp^b, Petra Rudolf^b, Michal Stano^c, Peter Papp^c,
Stefan Matejcik^c, Tobias Borrmann^a, Petra Swiderek^{a*}

*a University of Bremen, Institute of Applied and Physical Chemistry,
Fachbereich 2 (Chemie/Biologie), Leobener Straße / NW 2,
Postfach 330440, D-28334 Bremen, Germany*

*b Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, NL-9747
AG Groningen, The Netherlands*

*c Department of Experimental Physics, Comenius University Mlynska dolina F2, 84248
Bratislava, Slovakia*

*Corresponding author. Email: j.warneke@uni-bremen.de

S1. Coverage-dependent TDS

The molecular film thickness used in the TDS and ESD experiments was estimated from the amount of vapour leaked from a small calibrated volume onto the polycrystalline Au sheet held at 35-38 K. This amount of vapour was determined from the drop in pressure in the calibrated volume as measured in units of mTorr with a capacitance manometer. In the case of acetone, a good correlation between the leaked amount of vapour and the area under the characteristic desorption peak was obtained. As seen in Fig. S1, the acetone desorption data for 43 amu show a weak but characteristic peak between 150 and 220 K which rapidly saturates and is therefore ascribed to the monolayer. A second peak with maximum at 140 K starts to increase upon saturation of the monolayer peak and is hence attributed to the successive layers no longer in contact with the substrate. In all experiments, multilayer films with thickness between 6 and 15 layers were prepared.

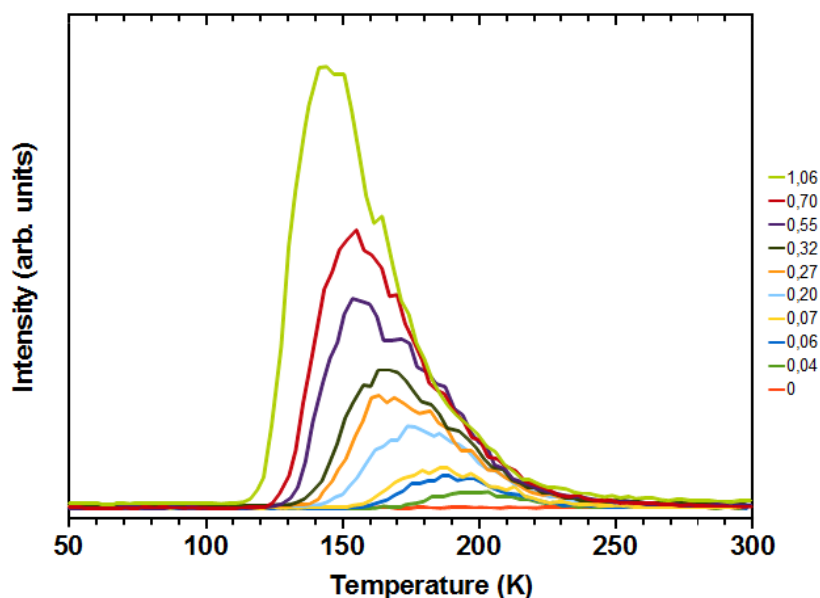


Figure S1: TDS curves for acetone measured at $m/z = 43$ after deposition by leaking into the main chamber variable amounts of vapour as stated in units of mTorr (see legend at right axis).

For acetylacetone, the integrated desorption peaks did not correlate well with the leaked amounts of vapour indicating that deposition with reproducible thickness was not achieved. This is due to strong adsorption of the vapour in the inlet system and vacuum chamber. However, for small amounts of vapour, desorption peaks with variable maximum shifting between 170 K and 240 K were obtained as characteristic of the monolayer regime while larger amounts of vapour produced films which revealed a well-defined and constant position of the desorption peak maximum near 170 K as characteristic of multilayer coverages (Fig. S2). All experiments reported in this work were performed in the latter regime.

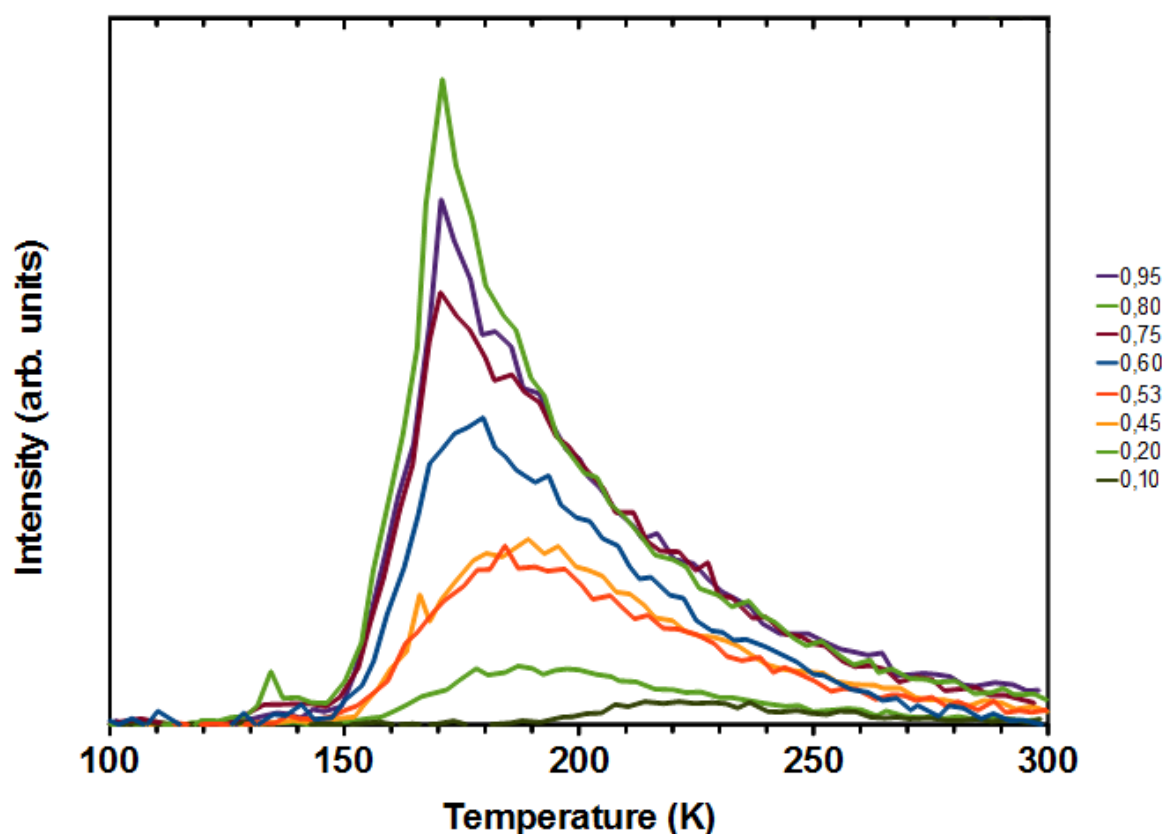


Figure S2: TDS curves for acetylacetone measured at $m/z = 43$ after deposition by leaking into the main chamber variable amounts of vapour. Peak areas do not correlate directly with the leaked amount of vapour but a multilayer film yielding a peak maximum at 165 K is obtained for sufficiently large vapour dosages.

S2. O1s XPS data

In addition to the C1s XPS data described in detail in Section 3.1, O1s data are included here (Fig. S3). They clearly show a much stronger loss of oxygen in the case of electron exposure of acetone layers than for acetylacetone. The remaining signal in the case of acetone can at least in part be traced back to residual water that deposited on the sample from the chamber.

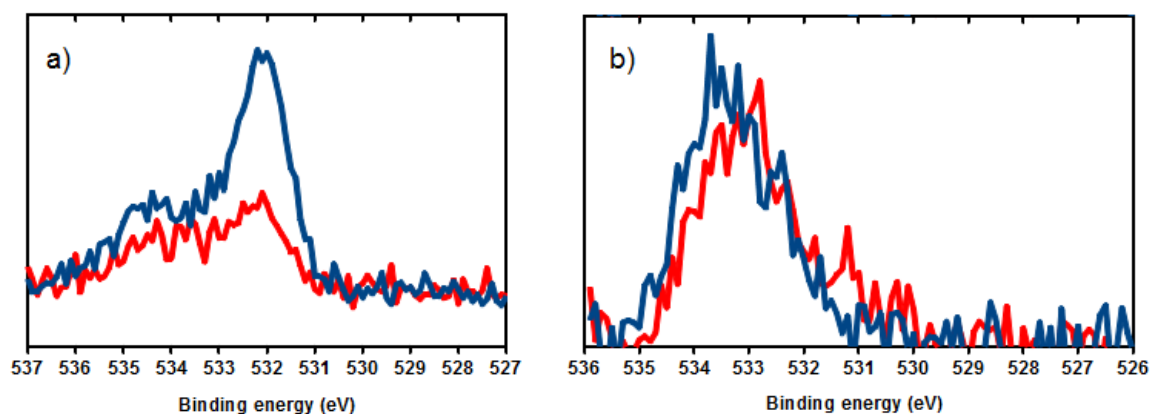


Figure S3: O1s core level region of the XPS spectra of acetone (a) before (blue) and after (red) electron exposure of 0.1 C at $E_0 = 500$ eV and of acetylacetone (b) before (blue) and after (red) electron exposure of 0.4 C at $E_0 = 500$ eV. The multilayer films were deposited and measured at 110 K.

S3. Calculated energies

The difference in energy between reactants and products regarding methyl addition to acetone and acetylacetone as well as different fragmentation reaction steps in the two compounds were calculated at the B3LYP/6-311+G(d,p) level. The particular reactions as well as their energetic are summarized in Fig. S4.

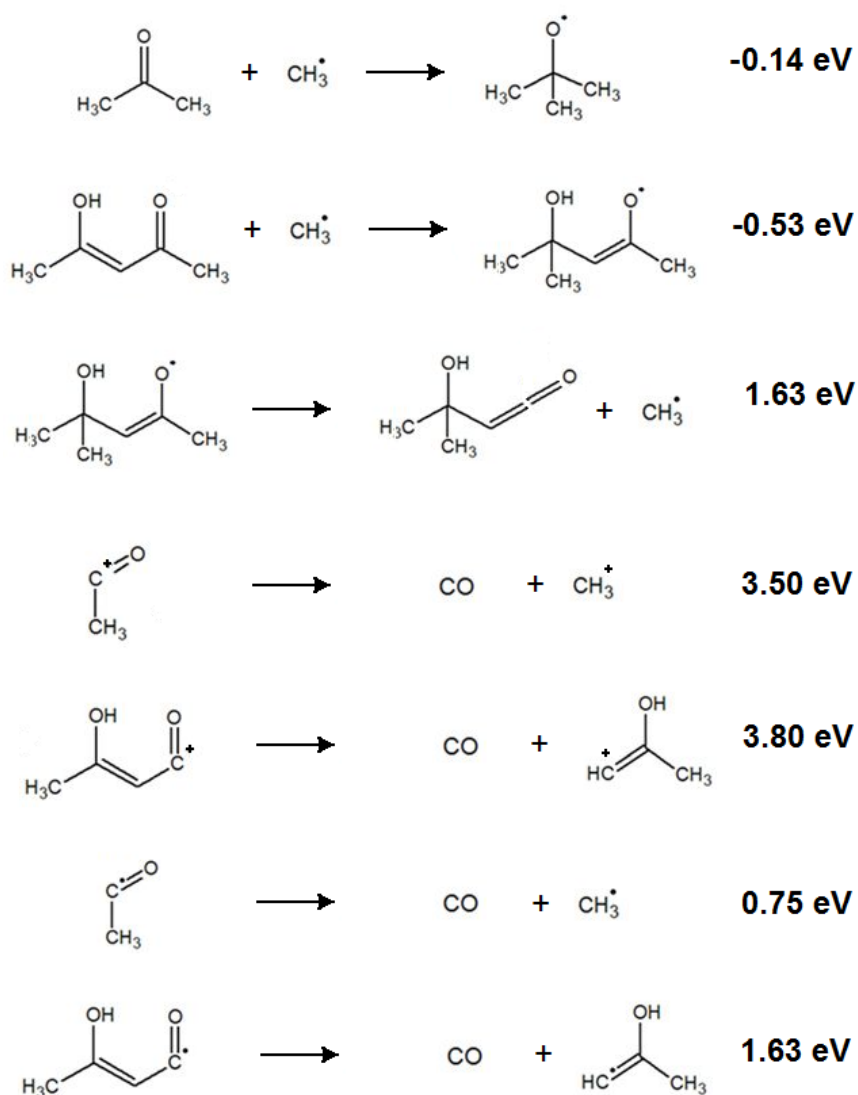


Figure S4: Reaction energies predicted at the B3LYP/6-311+G(d,p) level.