

# *A combined experimental and theoretical study of methyl acetoacetate adsorption on Ni{100}*

Article

Supplemental Material

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## Supporting Information

# A Combined Experimental and Theoretical Study of Methyl Acetoacetate Adsorption on Ni{100}

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This document contains:

- NEXAFS fitting and determination of tilt angle with respect to the surface plane
- XPS data of the NEXAFS layers (**Figure S1**)
- Initial configurations of MAA on Ni{100} (**Figure S2, Table S1**)
- Core-level shift calculations of C 1s for the most stable *bidentate deprotonated* configuration (**Table S2**) and comparison with experimental data (**Figure S3**)

# NEXAFS

## Data Analysis

The NEXAFS were fitted using an equation which consist of a linear background, a step function and several Gaussian functions depending on the number of resonances (eq. 1):

$$I(E) = B_0 + B_S(E - S_P) + S_H \left[ \frac{1}{\pi} \arctan \left( \frac{E - S_P}{0.2 * S_W} \right) + \frac{1}{2} \right] + \sum_i G_{i,H} \exp \left[ -4 \ln 2 \frac{(E - G_{i,P})^2}{G_{i,W}^2} \right] \quad (1)$$

Where  $B_0$  is the offset at the point of the adsorption step,  $B_S$  is the slope of the linear background,  $S_P$  is the step position,  $S_H$  is the step height,  $S_W$  is the width of the step, and  $G_{i,H}$ ,  $G_{i,P}$  and  $G_{i,W}$  are the height, position and full width at half maximum of the  $i$ th resonance.

The tilt angles with respect to the surface plane,  $\alpha$ , corresponding to each resonance were obtained by fitting the intensity of the peak as function of the angle of incidence  $\theta$  using the following equation <sup>1</sup> for surfaces with 4-fold symmetry:

$$I(\gamma) = \frac{I_\alpha}{3} \left[ 1 + \frac{1}{2} (3 \cos^2(90^\circ - \theta) - 1) (3 \cos^2 \alpha - 1) \right] \quad (2)$$

## XPS data for layer studied by NEXAFS

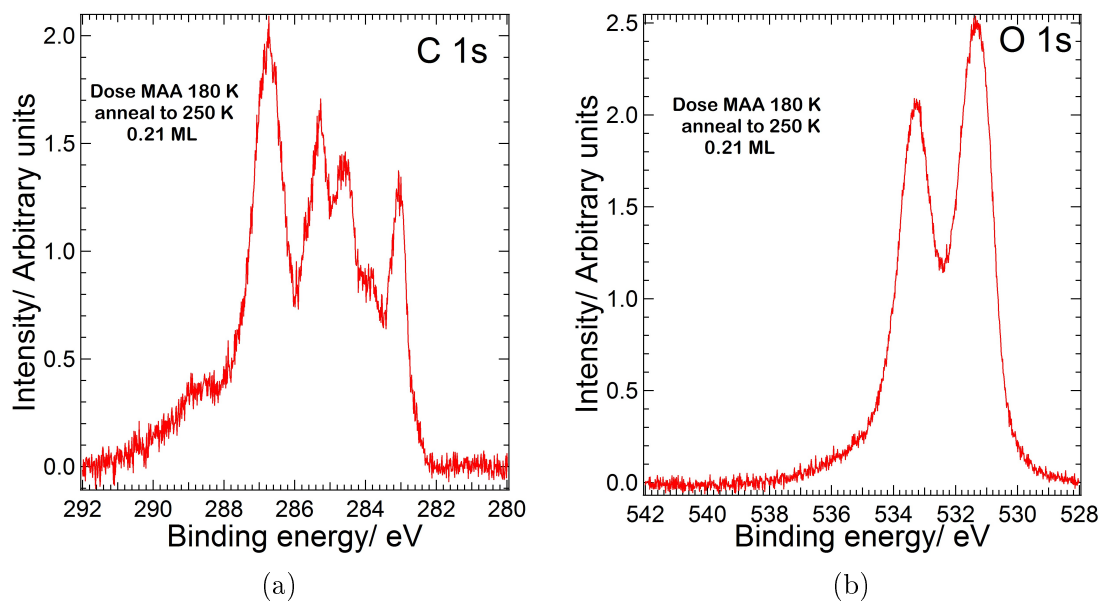


Figure S1: XPS data of the MAA layer used for the NEXAFS study. (a) C 1s region ( $h\nu = 400$  eV) and in the (b) O 1s region ( $h\nu = 650$  eV)

## DFT Modelling

Figure S2 shows the start geometries for all configurations tested by DFT modelling. Table S1 lists the adsorption energies of the optimised configurations. After relaxation, *flat-enol top I* (*top II*) converged to *4-hollow I* (*4-hollow II*). Regarding the *bidentate deprotonated enolate* candidates, the molecular plane in *O-bridge 1 row* remained perpendicular with respect to the surface whereas it tilted in the case of *O-bridge 2 rows*. Configurations with diketo MAA are far less stable than those discussed in the main section.

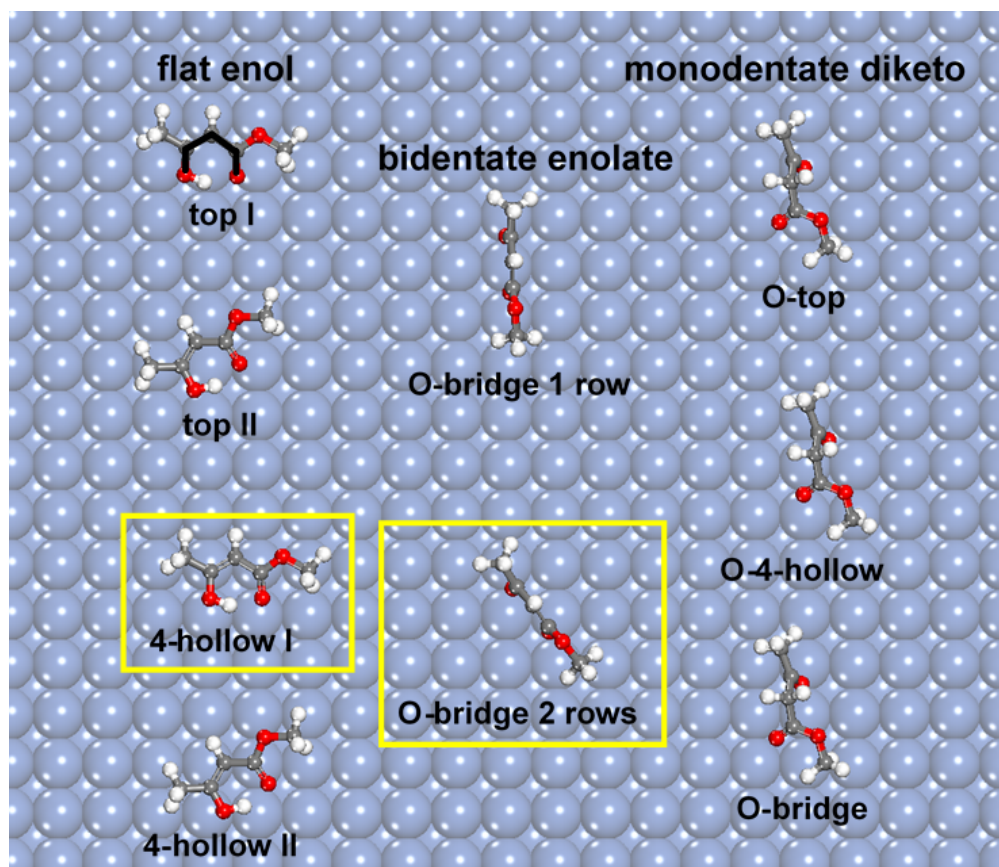


Figure S2: Initial configurations of MAA on the Ni{100} surface considered in the present study. To facilitate visualization, the O-CCC-O chain is highlighted and the dissociated H removed. The candidates discussed in the main section are indicated by yellow rectangles.

Table S1: Adsorption energies of the optimised configurations shown in Figure S2.

Start Configuration	$E_{\text{ads}}$
flat-enol	
top I (converged to 4-hollow I)	−1.91 eV
top II (converged to 4-hollow II)	−1.69 eV
4-hollow I	−1.91 eV
4-hollow II	−1.69 eV
bidentate deprotonated enolate	
O-bridge 1 row	−1.78 eV
O-bridge 2 rows	−1.82 eV
monodentate diketo	$> -0.95$ eV

## XPS: C 1s core level shifts

Table S2: Core-level shift values for the C 1s photoemission of the *bidentate deprotonated* configuration according to DFT. For numbering, refer to Figure 1 in the main section.

Atom numbering	$\Delta BE$ (eV)
C1	0.00
C2	3.00
C3	1.56
C4	2.29
C5	0.83

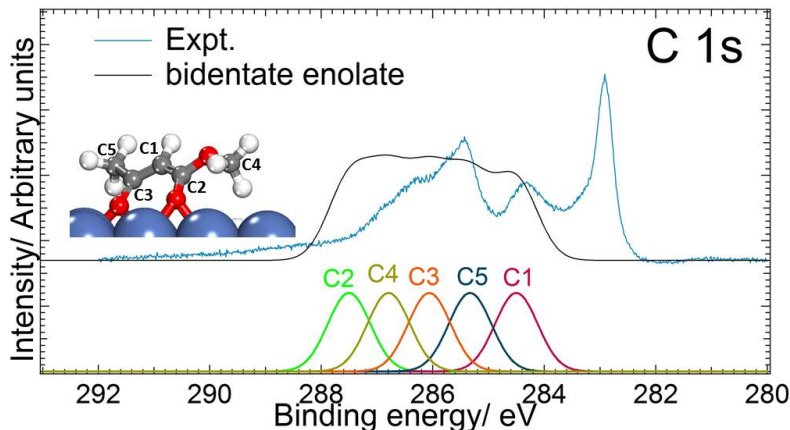


Figure S3: Top panel: Comparison of experimental C 1s XPS spectrum obtained upon annealed the MAA layer to 340 K (0.16 ML) with modelled XPS spectrum of the *bidentate deprotonated*. Bottom panel: individual Gaussian peaks of FWHM 0.9 eV placed at the core-level shift positions of Tab. S2.

## References

- (1) Stöhr, J.; Outka, D. A. Determination of molecular orientations on surfaces from the angular dependence of near-edge X-ray-absorption fine-structure spectra. *Phys. Rev. B* **1987**, *36*, 7891–7905