CO Adsorption on Au(332): A Combined Infrared Spectroscopy and Density Functional Theory Study

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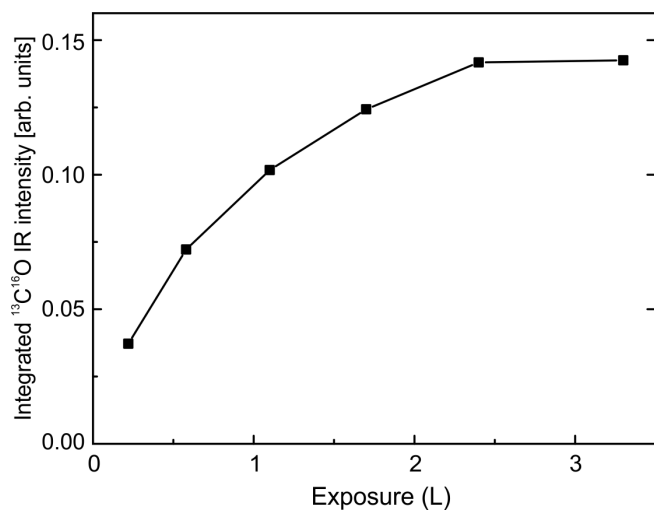[c] *Institut für Chemie, Carl von Ossietzky Universität Oldenburg, 26129 Oldenburg, Germany*

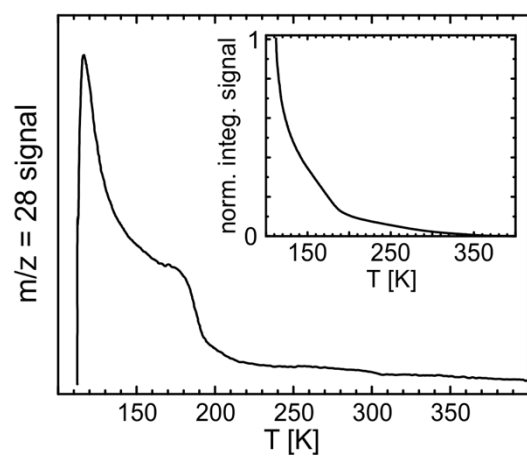Figure S1: IR intensity of the coverage series shown in Figure 2.

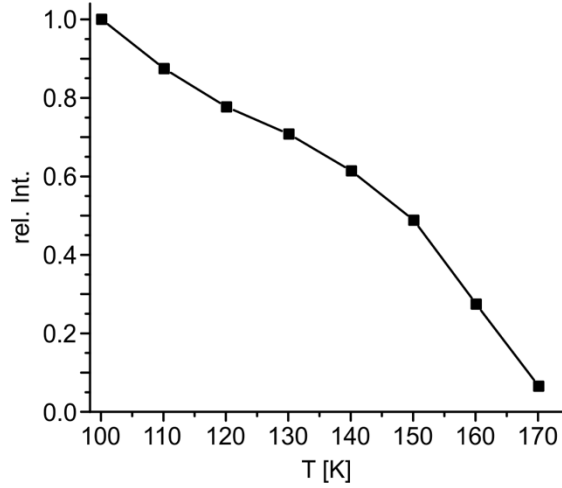Figure S2: CO-TPD spectrum (m/z = 28) of a pristine Au(332) surface using a heating rate of 2 K/s.

Figure S3: IR intensity of the annealing series shown in Figure 3.

Adsorption positions and adsorption energies of CO on Au(332) and Au(321)

To investigate favorable co-adsorption positions of CO two energetic criteria are used. The first is the average adsorption energy E_{av}, which is calculated as E_{ads} (see Eq. 1 manuscript) divided by the number of CO molecules n adsorbed in a (4×1) surface cell.

$$E_{av} = \frac{E_{ads}}{n} \tag{S1}$$

If two or more CO molecules are co-adsorbed at different adsorption sites, E_{rel} gives the average adsorption energy of the k CO molecules adsorbed at the site with the weakest binding and is calculated according to Eq. S2

$$E_{rel}\left(\frac{E_{sub}}{eV}\right) = \frac{E_{ads} - (n-k)E_{sub}}{k} \tag{S2}$$

Here E_{sub} is the average adsorption energy (E_{av}) for the reduced system with $(n-k)$ CO molecules adsorbed to the sites with the higher (in absolute value) adsorption energy. In the following, E_{rel} is accompanied by a value given in parentheses $\left(\frac{E_{sub}}{eV}\right)$, which is the average adsorption energy of the reduced system. For example, in case of two CO molecules adsorbed at 6-fold and 7-fold coordinated sites, E_{ads} of the CO adsorbed at the favorable position (6-fold), is subtracted from E_{ads} of the co-adsorbed species. Or in case of three CO molecules adsorbed at 6-fold, 7-fold, and 8-fold coordinated sites, two times E_{av} of the reduced system with two CO molecules (one at a 6-fold and one at a 7-fold coordinated site) adsorbed has to be subtracted from the total adsorption energy E_{ads}.

Figure S4: Favorable adsorption and co-adsorption positions of CO at different coverages on Au(332). E_{av} and E_{rel} are calculated according to Eq. S1 and S2, respectively. The values of E_{sub} (Eq. S2) used to calculate E_{rel} are given in parentheses.

a) $E_{av} = -0.83$ eV

b) $E_{av} = -0.45$ eV

c) $E_{av} = -0.56$ eV

d) $E_{av} = -0.82$ eV

e) $E_{av} = -0.82$ eV

f) $E_{av} = -0.61$ eV E_{rel} (-0.83) = -0.39 eV

g) $E_{av} = -0.63$ eV E_{rel} (-0.83) = -0.44 eV

h) $E_{av} = -0.81$ eV

i) $E_{av} = -0.71$ eV E_{rel} (-0.81) = -0.31 eV

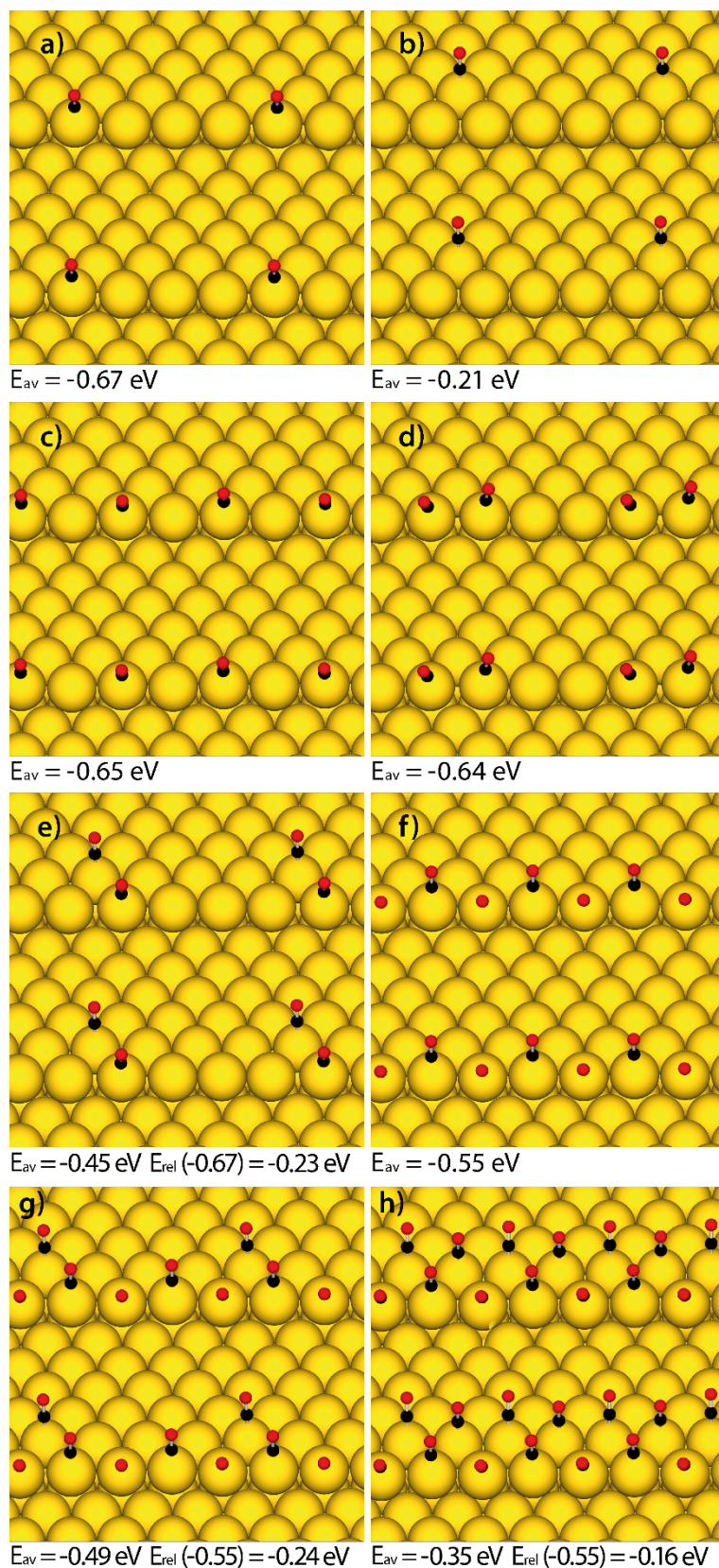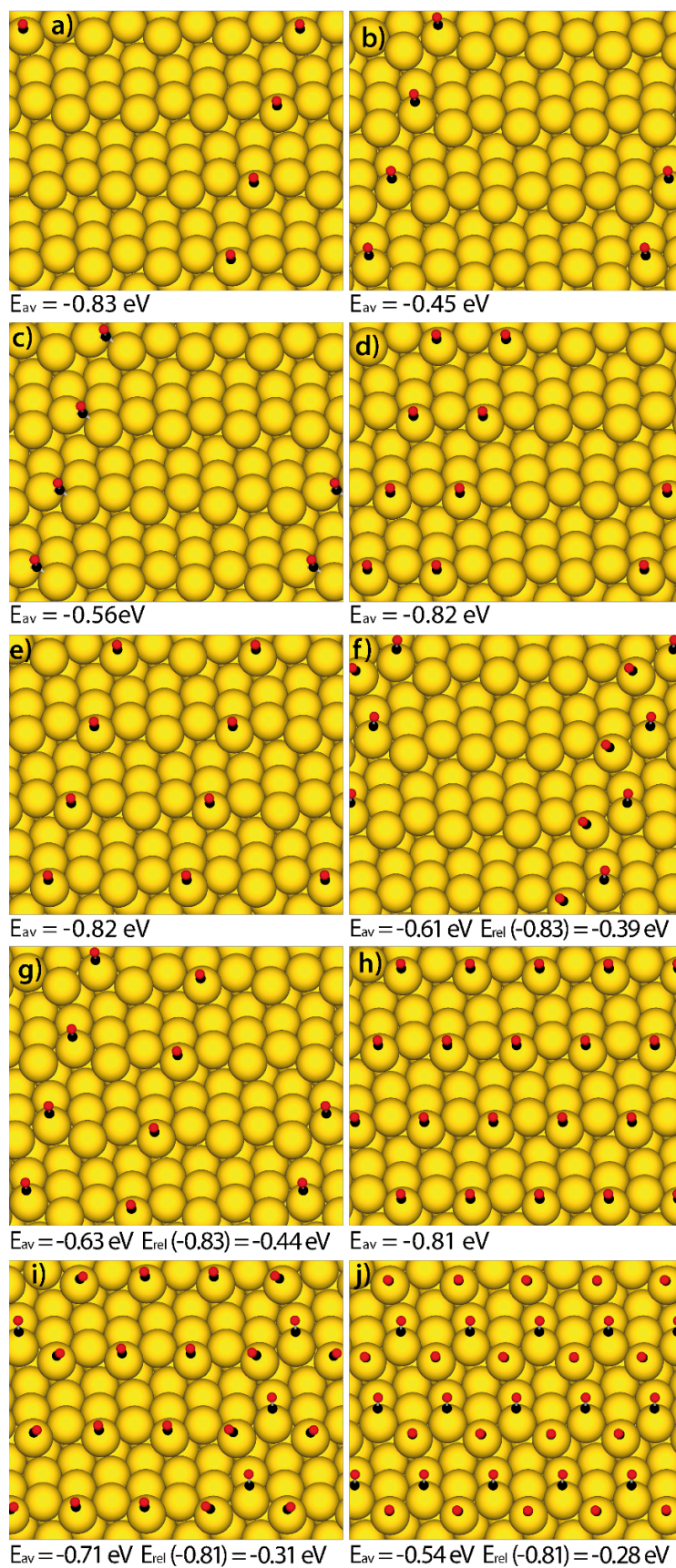**j)** $E_{av} = -0.54$ eV E_{rel} (-0.81) = -0.28 eV

Figure S5: Favorable adsorption and co-adsorption positions of CO at different coverages on Au(321). E_{av} and E_{rel} are calculated according to Eq. S1 and S2, respectively. The values of E_{sub} (Eq. S2) used to calculate E_{rel} are given in parentheses.

a) $E_{av} = -0.77$ eV

b) $E_{av} = -0.63$ eV

c) $E_{av} = -0.42$ eV

d) $E_{av} = -0.77$ eV $E_{rel} (-0.77) = -0.77$ eV

e) $E_{av} = -0.59$ eV $E_{rel} (-0.77) = -0.41$ eV

f) $E_{av} = -0.69$ eV $E_{rel} (-0.77) = -0.62$ eV

g) $E_{av} = -0.58$ eV $E_{rel} (-0.69) = -0.35$ eV

h) $E_{av} = -0.56$ eV $E_{rel} (-0.72) = -0.31$ eV

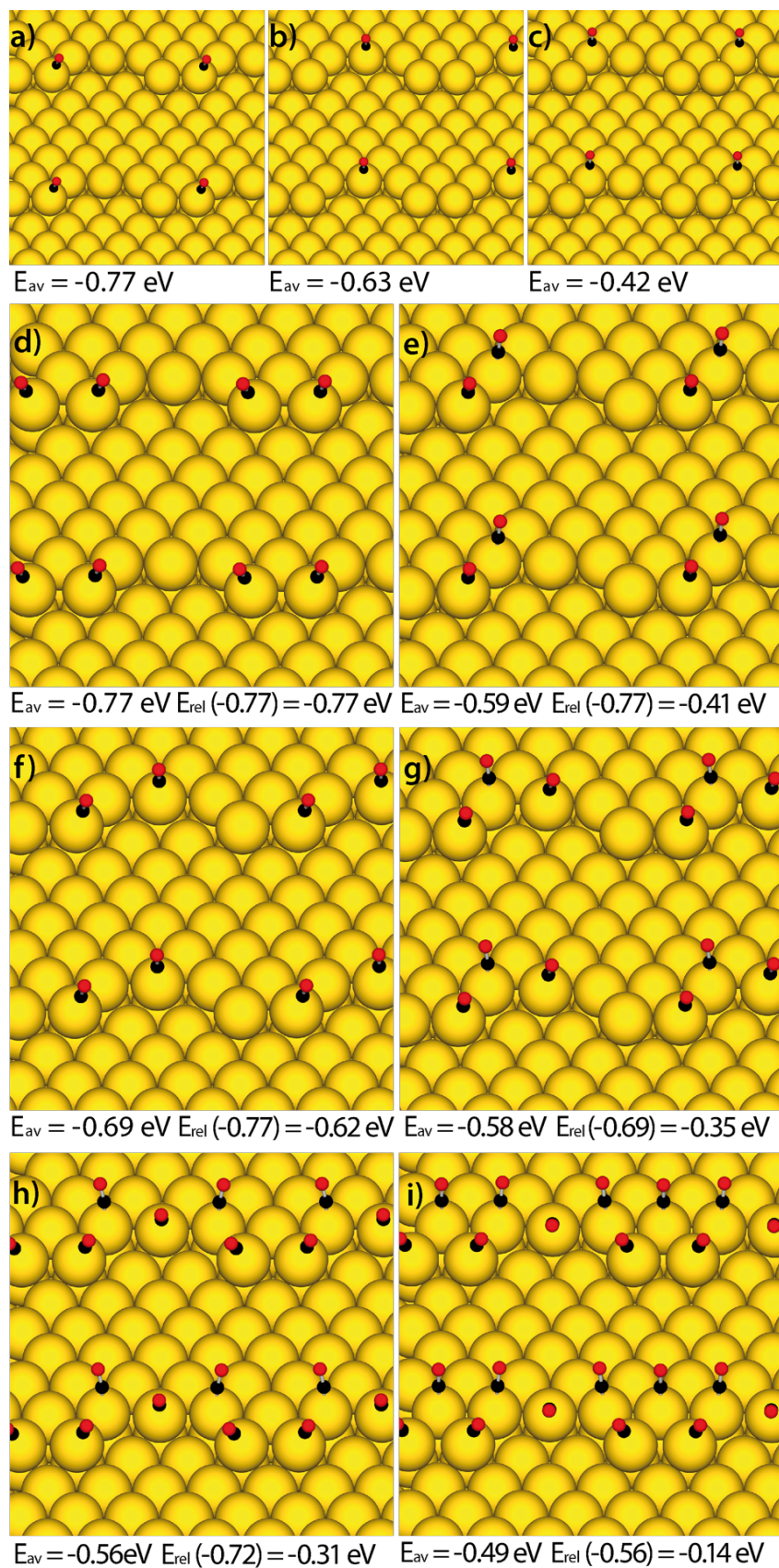i) $E_{av} = -0.49$ eV $E_{rel} (-0.56) = -0.14$ eV

Figure S6: Adsorption positions of CO on a defected Au(332) surface. The defected surfaces have been created by removing two Au atoms at the step edge of the p(4×1) supercell. The values of E_{sub} (Eq. S2) used to calculate E_{rel} are given in parentheses.

Convergence tests

We tested the dependence of adsorption energies of small species, like CO, O_2 and atomic O, on the number of Au layers in the slab,[1] and on the thickness of the vacuum region[2] in our previous studies. The present model showed average deviations for adsorption energies of no more than 0.06 eV from benchmark models with a larger vacuum region of more than 20 Å. We ensured convergence with respect to the chosen size of k-point mesh (3×3×1) for the Au(332)-(4×1) unit cell by calculating CO adsorption energies in selected adsorption geometries using a larger 5×5×1 k-point mesh. We computed E_{ads} = -0.65 eV for one CO molecule adsorbed at the step edge of Au(332) and an average adsorption energy of -0.54 eV for four CO molecules adsorbed at the step edge using the 5×5×1 k-point mesh, which is very close to -0.67 eV and -0.55 eV, respectively, calculated using k-point mesh of 3×3×1 chosen in the present work. The deviations are within 0.02 eV; hence, the 3×3×1 k-point mesh ensures sufficient accuracy.

Similarly, we ensured the convergence with respect to the chosen size of k-point mesh (3×5×1) for the Au(321)-(4×1) unit cell by calculating CO adsorption energies in selected adsorption geometries using a larger 5×7×1 k-point mesh. We computed E_{ads} = -0.78 eV for one CO molecule adsorbed at the 6f-Au at the step edge of Au(321) and an average adsorption energy of -0.77 eV and -0.54 eV for four and eight CO molecules adsorbed at the step edge using the 5×7×1 k-point mesh, which should be compared to -0.83 eV, -0.81 eV and -0.54 eV, respectively, calculated using k-point mesh of 3×5×1 chosen in the present work. The deviations are within 0.05 eV; hence, the 3×5×1 k-point mesh ensures sufficient accuracy for the Au(321)-(4×1) unit cell.

Increasing the energy cut-off from 415 to 515 eV and the kinetic energy cut-off from 645 to 745 eV leads to virtually identical energies as those calculated using the presently adopted cut-offs on both Au(332)-(4×1) and Au(321)-(4×1) surfaces.

Adsorption energies for selected structures using D3 dispersion correction

In an earlier study we compared CO adsorption energies on coinage metal nanoparticles at the PBE level of theory with CCSD(T) and found that PBE functional without dispersion correction gives results in good agreement with CCSD(T) or even overestimates the binding energy of CO on small nanoparticles.[3] Additionally, we found that D3-corrected[4] binding energies are even more overestimated compared to CCSD(T) values than those calculated at

the uncorrected PBE level.[5] In another study, we calculated the adsorption energy of O_2 on Au(321) with and without dispersion correction and found that O_2 binding energies might be overestimated as well.[2] Therefore, in the current study we chose to use uncorrected PBE energies. Nevertheless, for test purposes selected structures have been calculated using D3 dispersion correction[4] (one and four CO molecules adsorbed at the step edge of Au(332)). The optimized structures are virtually identical to those calculated without dispersion correction. Binding energies (the negative of adsorption energy) are larger when calculated using dispersion corrections. Specifically, we calculated E_{ads} = -0.89 eV for one CO molecule at the step-edge of Au(332) and an average energy of -0.80 eV for four CO molecules at the step-edge. In both cases the magnitude of E_{ads} exceeds by ~ 0.2 eV the uncorrected PBE values. We calculated E_{ads} = -1.01 eV for one CO molecule at the 6f-Au of Au(321) and average energies of -0.99 eV and -0.78 eV for four or eight CO molecules at the step edge of Au(321). Here again E_{ads} exceeds by ~ 0.2 eV the uncorrected PBE values. Thus, the usage of D3 correction shifts the energies systematically towards stronger binding but is not expected to affect the overall trend of the findings of this work and are therefore not considered for all structures.
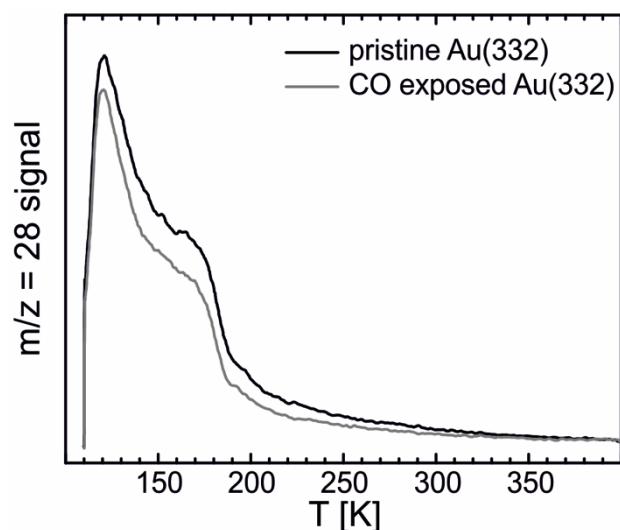

Figure S7: Comparison of TPD spectra taken for a pristine Au(332) surface and a Au(332) surface exposed to CO for a prolonged time (see text for details). The heating rate was 2 K/s.
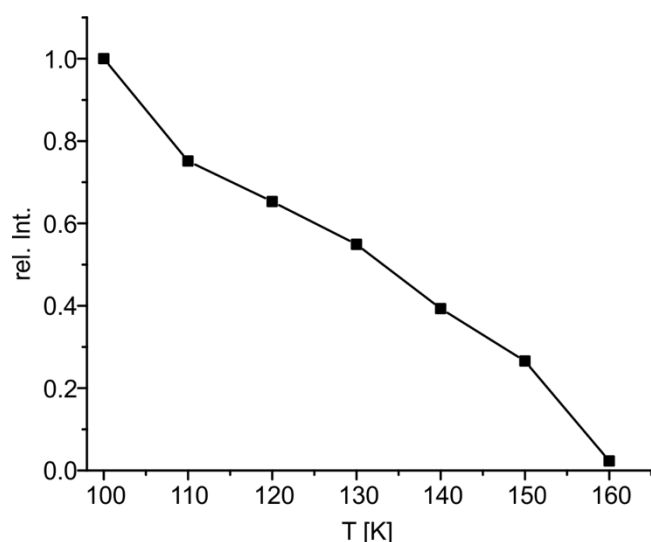
Figure S8: IR intensity of the annealing series shown in Figure 5.

References:

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5. Arrigo, R.; Badmus, K.; Baletto, F.; Boeije, M.; Brinkert, K.; Bugaev, A.; Bukhtiyarov, V.; Carosso, M.; Catlow, R.; Chutia, A., et al. Theory as a Driving Force to Understand Reactions on Nanoparticles: General Discussion. *Faraday Discussions* **2018**, 208, 147-185.