

Supplemental Material for calculating the frequencies and intensities of strongly anharmonic modes of adsorbates on surfaces: a low-cost but accurate computational approach

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SUPPLEMENTAL MATERIAL

Structural coexistence in TPA on Cu(100)

To understand the intensity mismatch discussed in the main text, we refer to the literature. At submonolayer coverages, the TPA molecules prefer to form commensurate (3×3) islands [1–3]. However, more recent investigations have reported on the existence of other metastable phases [4]. The coexistence of various structures must affect the relative intensity of the bands, since: (i) changes in coverage can modify the metal-adsorbate interactions (e.g. different adsorption sites) and (ii) the intermolecular interactions are usually different from one structure to the other.

In order to prove the existence of a direct correlation between relative vibrational intensities and coverage, we calculated the adsorption of TPA when forming a hypothetical (4×4) structure. In this structure the molecules are also adsorbed preferentially on hollow sites. This means that the major contribution to changes in frequencies and intensities comes from varying the intermolecular interactions with respect to the previous (3×3) structure (see Figure 1a). The resulting calculated spectra for TPA at 3×3 and 4×4 coverages are shown in Figure 1b. Here we clearly observe that the overestimated signal of the γ_{CH} at $\sim 850\text{ cm}^{-1}$ is quenched from the (3×3) to the (4×4) coverage. This is mainly attributed to weaker [CH \cdots O] interactions at (4×4) than at (3×3) coverage (schematically represented in Figure 1a). This effect is observed for the spectra obtained using the harmonic correction, and also for those resulting from applying anharmonic corrections. The coexistence of diverse structures could explain the mismatch between the calculated and experimental intensities of the γ_{CH} signal.

Choice of density functional

To assess the importance of the functional of choice in predicting accurate vibrational intensities and frequencies, we compare the simulated spectra obtained using PBE and optPBE-vdW for each of the previous systems. No significant differences between the PBE and optPBE-

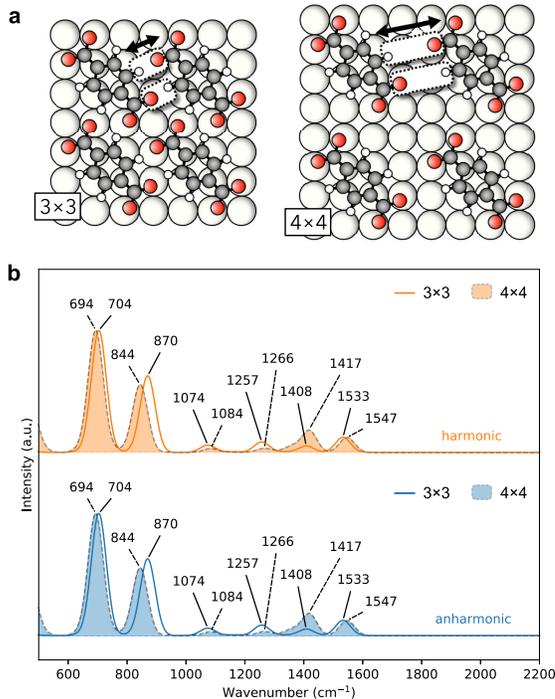


Figure 1. Models of the (a) (3×3) and (b) (4×4) structures of TPA on Cu(100). Boxes are included to highlight the different [CH \cdots O] interactions for the (3×3) and (4×4) coverages. Calculated harmonic (in orange) and harmonic including anharmonic corrections (in blue) HREEL spectra for TPA at these two coverages: (3×3), represented with solid lines, and (4×4), represented by the shaded areas. Frequency values are included for the most relevant bands (in cm^{-1}) for the (3×3) and the (4×4) (dashed lines) structures.

vdW values (frequencies and intensities) are found for the two chemisorbed systems, ethynidyne on Rh(111) and benzene/CO on Rh(111). PBE and optPBE-vdW provide the same poor results when using the harmonic approximation (orange dashed and solid lines in Figure 2). For both methods the intensities of the overestimated bands associated to the C–C (for the ethynidyne system) and C–O stretching (for benzene/CO system) are significantly improved when using anharmonic corrections (dashed and solid blue lines in Figure 2). In contrast, for TPA on Cu(100), large differences in intensities are found

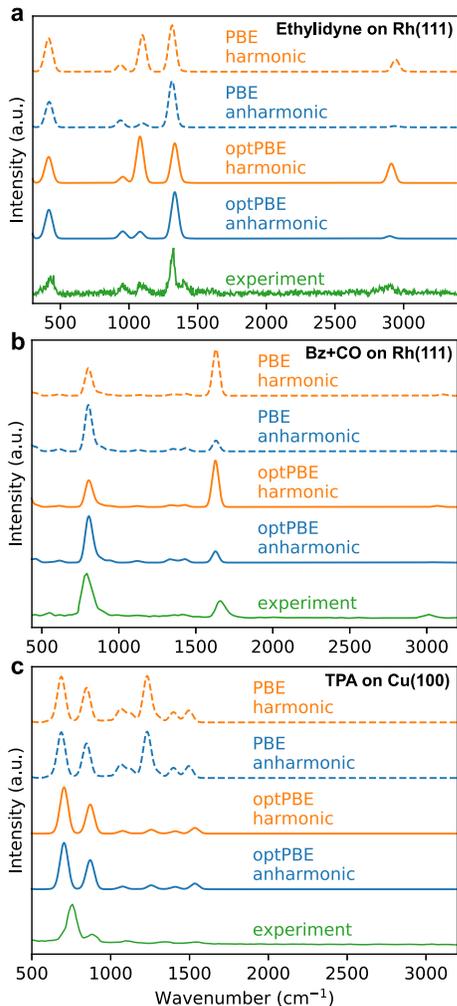


Figure 2. Experimental and theoretical spectra calculated using the PBE (dashed lines) and optPBE-vdW (solid lines) functionals for (a) (2×2) -(C_2H_3) on Rh(111), (b) $c(2\sqrt{3} \times 4)$ rect- C_6H_6 +CO on Rh(111) and (c) (3×3) -TPA on Cu(100).

between PBE and optPBE-vdW (Figure 2c). When comparing with the experiments we notice that the optPBE-vdW functional seems to provide an accurate description of the intensities. This is not the case for PBE for which we find a large overestimation of the intensity of the band of the carboxyl C–C stretching (ν_{CC}) at $\sim 1230 \text{ cm}^{-1}$ (even when applying anharmonic corrections). This suggests that PBE is not accurate enough to provide a good description of this system. This is expected since DFT-GGA methods (such as PBE) poorly describe the adsorption of aromatic molecules on weakly interacting substrates [5–8].

A good description of the geometries is required in order to obtain accurate spectra. A comparison between the geometries obtained when using PBE and optPBE-vdW is included in Table I. Here we notice that the geometry values for the chemisorbed systems obtained with

PBE and optPBE-vdW correspond to each other and also are in agreement with the experimental values reported in the literature [9, 10]. All calculated distances and angles for the ethylidyne on Rh(111) system are within the experimental uncertainties (Table I). For the benzene/CO on Rh(111) system the highest discrepancies between experiment and theory are 0.065 Å for PBE and 0.051 Å for optPBE-vdW. This correlates the excellent match between theoretical and experimental geometries with the high accuracy of the calculated spectra.

Table I. Calculated distances (in Å) and angles (in degrees) using the PBE and optPBE-vdW functionals. Atom labels are defined in Figure 3. Geometry difference values between the PBE and optPBE-vdW are calculated in percentage. Experimental values are taken from Refs. 9 and 10.

Ethylidyne on Rh(111)				
	PBE	optPBE	Diff.(%)	Exp. [9]
$d(\text{C}_1\text{-H})$	1.103	1.104	-0.10	–
$d(\text{C}_1\text{-C}_2)$	1.495	1.498	-0.24	1.48 ± 0.04
$d(\text{C}_2\text{-Rh})$	1.994	2.003	-0.44	2.06 ± 0.10
$\angle(\text{C}_1\text{-C}_2\text{-Rh})$	127.2	127.0	-0.10	129 ± 2
Benzene/CO on Rh(111)				
	PBE	optPBE	Diff.(%)	Exp. [10]
$d(\text{C}_1\text{-H}_1)$	1.093	1.092	0.09	–
$d(\text{C}_1\text{-C}_2)$	1.432	1.434	-0.14	1.46 ± 0.15
$d(\text{C}_2\text{-C}_3)$	1.461	1.463	-0.14	1.58 ± 0.15
$d(\text{C}_4\text{-O})$	1.218	1.219	-0.01	1.21 ± 0.05
$d(\text{C}_1\text{-Rh}_1)$	2.207	2.213	-0.26	2.20 ± 0.05
$d(\text{C}_4\text{-Rh}_2)$	2.055	2.069	-0.69	2.16 ± 0.04
TPA on Cu(100)				
	PBE	optPBE	Diff.(%)	
$d(\text{C}_1\text{-H})$	1.092	1.091	0.14	
$d(\text{C}_1\text{-C}_2)$	1.404	1.404	0.01	
$d(\text{C}_2\text{-C}_3)$	1.439	1.419	1.43	
$d(\text{C}_3\text{-C}_4)$	1.491	1.512	-1.43	
$d(\text{C}_4\text{-O})$	1.293	1.288	0.39	
$d(\text{O-Cu})$	2.017	2.058	-1.95	

One the other hand, some of the calculated geometric values for TPA using PBE are very different to those obtained when using optPBE-vdW. The largest differences are found for the $\text{C}_3\text{-C}_4$ ($\sim 1.43\%$) and O-Cu ($\sim 1.95\%$) bonds. This would explain the large intensity difference between PBE and optPBE-vdW for the peak associated with the carboxyl C–C stretching (ν_{CC}). The accuracy of these methods cannot be directly evaluated, since no experimental geometry has been reported yet for TPA on Cu(100).

However, one would expect PBE to be less accurate than the optPBE-vdW method, since the latter accounts for vdW interactions. In any case, the spectra obtained using the more sophisticated method (optPBE-vdW) are in agreement with the experiments, whilst the PBE seems to provide a large overestimation of some bands. These

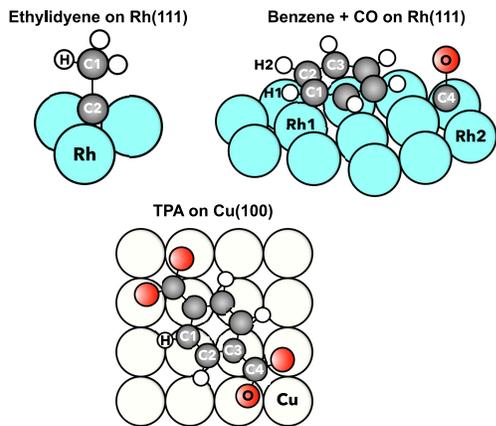


Figure 3. Definition of the atom labels used in Table I.

results suggest that the origin of the erratic values obtained for TPA on Cu(100) must be related to a bad description of the PBE geometries. These results are of relevant interest for two reasons. First, they demonstrate that the choice of functional can affect the quality of the spectra. Therefore, the functional has to be chosen wisely in order to obtain accurate spectra. Second, these results open the question of whether simulation of spectra can be used to indirectly assess the quality of the functionals. For example, optPBE-vdW spectra are in good agreement with the experiments for the three systems, whilst PBE seems to fail to describe the spectra of the TPA sys-

tem. Since the quality of the spectra is directly related to the quality of the geometries, the comparison between experiments and theory could serve as a diagnostic tool to evaluate how good or bad a method is for describing a given system.

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