

## Comment on “surface characterization of cerium oxide catalysts using deep learning with infrared spectroscopy of CO”

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### ABSTRACT

We demonstrate that the predicted distribution of ceria facets in CeO<sub>2</sub> nanorods, derived from the analysis of the measured IR spectrum of CO by fitting it using experimentally or DFT(HSE) calculated CO vibrational frequencies collected on all three low-index ceria surfaces, does not align with that derived using deep learning methods [1]. The latter utilizes a dataset based on extensive DFT(PBE) + U calculations, which are erroneous and have thus been scaled to the experimental values.

To gain detailed insight into the nature and orientation of the exposed facets of cerium dioxide (CeO<sub>2</sub> or ceria) nanoparticles, carbon monoxide (CO) can serve as a probe molecule. However, in infrared (IR) spectroscopy, peak assignments pose challenges due to complex IR spectra and lack of accurate reference data. Ensuring consistency between reliable reference experimental and theoretical data obtained from first principles density functional theory (DFT) calculations for CO adsorbed on model ceria systems is crucial for characterizing the surface of ceria nanoparticles, even under operando conditions, where changes in particle shape and faceting might occur [1]. Achieving this consistency for CO adsorption on oxide surfaces is challenging, as demonstrated by the notorious example of CO on MgO, which took approximately fifty years to resolve inconsistencies in the values of the adsorption energy [2,3]. The main reason is that theoretical methods, largely depending on DFT, have been lagging behind in accurately describing the small shift of the C–O stretching frequency induced by its weak interaction with the oxide surface. Moreover, claiming a good agreement between theory and experiment requires both to be reliable, ensuring that what has been computed corresponds to what has been measured, specifically regarding surface orientation, presence of oxygen vacancies, CO coverage, etc. It is important to note that the lateral interactions between adsorbed CO molecules (CO dipole-dipole coupling and substrate-mediated static interactions), when CO is bound to oxide surface and coverage increases, influence the vibrational frequencies [4, 5]. Recently, it has been established that only results obtained with the hybrid-DFT HSE06 functional [6] and at full CO coverage (1 monolayer,

ML) are in good agreement with infrared reflection absorption spectroscopy (IRRAS) data [7,8] and reproduce the experimentally observed blue-shifted frequencies of all CO species adsorbed on the three low-index oxidized and reduced ceria surfaces (Fig. 1) [9–11]. On all oxidized surfaces, distinct CO species atop formally Ce<sup>4+</sup> cations are observed. Additionally, for the oxidized (110) and (100) surfaces, tilt and bridge configurations, respectively, have been identified. The identification of these species has facilitated the accurate interpretation of the experimentally observed frequency shifts for CO adsorption on these surfaces and the reinterpretation of the spectra of the reduced (100) surface [8].

Not considering the experimental CO coverage, but a lower one in the DFT simulations, and using the commonly applied DFT(PBE) + U methodology would have led to erroneous results [8]. The most dramatic consequence corresponds to a predicted large red shift of up to 23 cm<sup>−1</sup>, instead of the observed blue-shift in IRRAS (see Fig. 1a), for the tilt configurations on the oxidized CeO<sub>2</sub>(110) surface at 1 ML coverage. Moreover, considering the DFT(PBE) + U at 1/4 ML, one would have mistakenly believed that CO could be used to probe the subsurface nature of the oxygen vacancy sites in the reduced (111) surface [8].

CeO<sub>2</sub> is an insulator with Ce atoms in a tetravalent 4f<sup>0</sup> configuration. In partially reduced ceria, some cerium atoms adopt a trivalent configuration (4f<sup>1</sup>), and the insulating character of the ground state arises from Coulomb repulsion between the *f* electrons, forcing them to localize in atomic-like orbitals. The DFT(PBE) approach, based on the generalized gradient approximation (GGA) for the exchange-correlation energy, is

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known to inadequately describe the ground state properties of both oxidized and reduced ceria [12–14]. Specifically, reduced ceria is predicted to exhibit conductivity. In contrast, the DFT(PBE) + U approach includes a term  $U$  to describe the Coulomb repulsion between  $f$  electrons responsible for the localization, providing a computationally convenient means for improved calculations of the electronic structure of ceria systems. Regarding the electronic structure of adsorbed CO, the HOMO–LUMO gap of CO is approximately 30% smaller, and the CO  $\rightarrow$  surface (electron donation) and surface  $\rightarrow$  CO (back-donation) charge transfers are larger with DFT(PBE) + U than with HSE06, making DFT(PBE) + U inherently unsuitable [8]. The HSE06 method addresses the shortcomings of the DFT(PBE) + U for describing CO bound to oxide surfaces, and it has helped resolve the puzzle regarding the adsorption site of CO on Pt(111) [15].

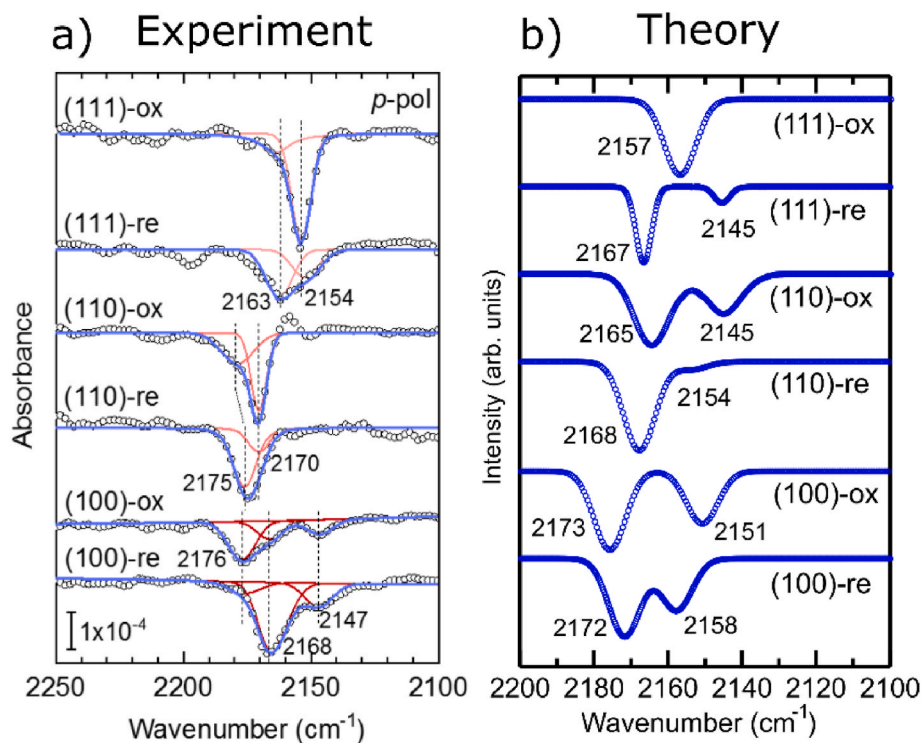
In the context of surface characterization of ceria catalysts with IR spectroscopy of CO, the goal of computer simulations is to provide means for a correct interpretation of the experimental spectra as well as an understanding of the binding of CO to the oxide surface. However, achieving this goal using the DFT(PBE) + U methodology alone is not feasible. To assess if the reference experimental and HSE06 data for CO on the three low-index  $\text{CeO}_2$  surfaces can help in the interpretation of real-world spectra of CO adsorbed on ceria nanoparticles, we used them to fit the experimental spectrum of CO on  $\text{CeO}_2$  nanorods. Notably, in these nanorods, the (110) surface has been observed to partially restructure, exposing (111) nanofacets [10].

Fig. 2a shows the results of fitting the central part of the experimental spectra within the  $2200\text{--}2115\text{ cm}^{-1}$  range, using eight bands with a Gaussian lineshape applied. The fit, employing the experimentally determined bands (cf. Fig. 1), predicts approximately 34 % of oxidized (110) exposed facets (top + tilt), along with 27% and 27% of oxidized (111) and (100) facets (top + bridge), respectively (Table 1). The proportion of reduced (110), (111) and (100) facets is approximately 6%, 4% and 1%, respectively. Therefore, the existence of (111) facets is revealed, aligning with experimental observations. The results of the fit using the HSE06-determined bands (Fig. 1) are consistent with

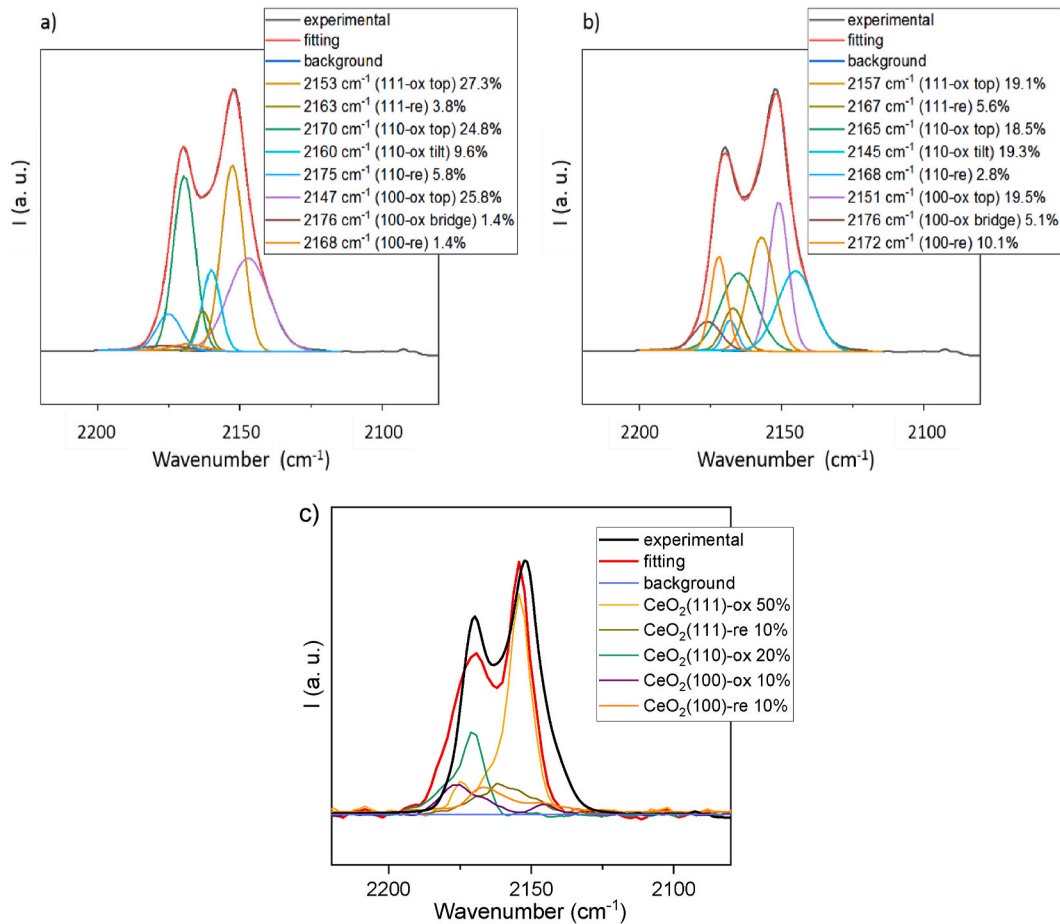
those employing the experimentally determined ones, revealing approximately 38% of oxidized (110) exposed facets, along with 19% and 25% of oxidized (111) and (100) facets, respectively (Fig. 2b–Table 1).

At this stage, we conclude that reliable experimental and theoretical data for CO adsorbed on model systems are essential for interpreting complex IR spectra of CO adsorbed on oxide nanocrystals with varied morphologies.

In recent years, the combination of machine learning (ML) techniques with first principles density functional theory (DFT) calculations has gained popularity for the interpretation of spectroscopic data (see Ref. [16] and references therein). Yu et al. in their recent publication [16] have utilized this combination for the characterization of  $\text{CeO}_2$  surfaces with IR spectroscopy of CO. While the concept of having a computationally affordable methodology for the interpretation of complex IR spectra is appealing, in the case of CO adsorbed on oxide surfaces, establishing a high-quality DFT-based database for machine learning presents challenges, as discussed above. Yu et al. established a database encompassing frequencies and intensities derived from DFT(PBE) + U calculations, taking into account five adsorption configurations (top cerium cations as well as bicarbonate, bidentate, bridge, and polydentate carbonate) at a low coverage of  $1/4\text{ ML}$ . Despite recognizing the limitations of DFT(PBE) + U in precisely characterizing CO interactions with oxide surfaces, Yu et al. opted for a frequency scaling procedure proposed in the literature [17]. However, even with the scaling, the frequencies for the top configuration on the oxidized ceria (111), (110) and (100) surfaces exhibit deviations from experimental values of up to  $33\text{ cm}^{-1}$  (cf.  $2164$ ,  $2180$ , and  $2180\text{ cm}^{-1}$  compared to  $2154$ ,  $2170$ , and  $2147\text{ cm}^{-1}$ , respectively, as shown in Fig. 1). Similar deviations were noted for the reduced surfaces (cf.  $2160$ ,  $2126$ , and  $2204\text{ cm}^{-1}$  for the reduced ceria (111), (110) and (100) surfaces compared to  $2163$ ,  $2175$ , and  $2168\text{ cm}^{-1}$  in Fig. 1). Furthermore, critical factors such as different CO adsorption configurations (e.g., tilt and bridge for the (110) and (100) surfaces) essential for accurately interpreting the IR spectra of the single crystal surfaces, as well as the effect



**Fig. 1.** a) Polarization-resolved IRRAS data of  $1\text{ ML}$  CO adsorption on the oxidized (ox) and reduced (re) (111), (110), and (100) ceria surfaces at  $75\text{ K}$ . b) HSE06 calculated IR spectra of  $1\text{ ML}$  CO adsorption on the same surfaces, for which a Gaussian broadening of  $10\text{ cm}^{-1}$  has been used [8].



**Fig. 2.** Predicted facets of CeO<sub>2</sub> nanorods using the (a) experimentally and (b) HSE06-determined bands of CO on oxidized (110) CeO<sub>2</sub> (top and tilt configurations), oxidized (111) CeO<sub>2</sub> (top), oxidized (100) CeO<sub>2</sub> (top and bridge), as well as the three reduced facets. (c) Fitted data derived from the experimental spectra of CO on indicated ceria surfaces and using facet proportions predicted by the ML model [16].

**Table 1**

Predicted percentages of CeO<sub>2</sub> facets on CeO<sub>2</sub> nanorods according to a fit using the experimental IR frequencies of CO on the three oxidized and reduced low-index surfaces [8], the DFT(HSE) calculated values [8], and the ML model [16].

	111_ox top	111_re	110_ox top	110_ox tilt	110_ox total	110_re	100_ox top	100_ox bridge	100_ox total	100_re
Fit Exp.	27.3	3.8	24.8	9.6	34.4	5.8	25.8	1.4	27.2	1.4
Fit HSE06	19.1	5.6	18.5	19.3	37.8	2.8	19.5	5.1	24.6	10.1
ML model	50	10			20	0			10	10

of CO coverage, were not considered for the construction of the database.

Given that incorrect data can lead to erroneous model predictions and missing data can compromise the accuracy of ML models, we conducted a comparison for the CeO<sub>2</sub> nanorods. Specifically, we assessed the predicted percentages of CeO<sub>2</sub> facets using the ML model (Fig. 2c) and contrasted them with those derived from fitting experimental IR frequencies of CO on the three oxidized and reduced low-index surfaces, as well as DFT(HSE)-calculated values presented in Table 1. The comparison reveals noticeable differences. For instance, the ML model predicts about approximately 20% of oxidized (110) exposed facets, along with 50% and 10% of oxidized (111) and (100) facets, respectively (Table 1). The proportion of reduced (110), (111) and (100) facets is 0%, 10% and 10%, respectively. Consequently, the presence of (111) facets is notably accentuated, while that of (100) facets is diminished, compared to the fit based on the experimental data. The fitted spectrum, obtained from the experimental spectra of CO on different ceria facets (Fig. 1) and utilizing ML-derived facet fractions, distinctly deviates from the IR spectrum of CO measured on ceria nanorods (Fig. 2c).

In conclusion, it is advised against using DFT(PBE) + U data, even when combined with ML models, for the interpretation of IR spectra of CO adsorbed on oxide surfaces. Generally, interpreting such spectra poses significant challenges, and it is imperative to ensure that the computed data used for generating databases accurately corresponds to what has been experimentally measured for model systems. Additionally, a caveat regarding the performance of hybrid functionals is warranted, as adjusting the amount of Fock exchange may be necessary to achieve agreement with experiment for certain oxide systems [18].

#### CRediT authorship contribution statement

**M. Verónica Ganduglia-Pirovano:** Writing – original draft, Investigation, Conceptualization. **Arturo Martínez-Arias:** Writing – review & editing, Validation, Investigation. **Shuang Chen:** Validation, Investigation. **Yuemin Wang:** Writing – review & editing, Validation, Investigation. **Pablo G. Lustemberg:** Writing – review & editing, Validation, Investigation, Formal analysis, Data curation.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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