

Reply to: On the role of metal cations in CO₂ electrocatalytic reduction

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Reply to: On the role of metal cations in CO₂ electroreduction

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Federico Dattila¹, Mariana C. O. Monteiro^{2,3}, Marc T. M. Koper³✉
& Núria López⁴✉ Check for updatesREPLYING TO: D. Le et al. *Nature Catalysis* <https://doi.org/10.1038/s41929-022-00876-2> (2021)Q1 Q2
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In our recent publication¹, we demonstrate the absence of CO₂ electroreduction on copper, gold and silver electrodes without alkali metal cations in solution through unequivocal experimental evidence. Additionally, we propose a mechanism for CO₂ electroreduction in which the metal cation is key to stabilizing CO₂ adsorption, thus enabling its activation and reduction. This last finding is supported by ab initio molecular dynamics (AIMD) simulations on Au/solvent/cation/CO₂ supercells. In their Matters Arising², Le and Rahman point out a constraint included in our computational setup, suggesting that it may affect our main conclusions. We here confirm that, although our computational framework was minimal, it is robust enough to support the proposed mechanism and thus our main conclusions.

In our study¹, we carried out density functional theory (DFT) simulations to compare the thermodynamic, structural and electronic properties of an activated CO₂ molecule on Au(111) with and without metal cations in solution (Fig. 7a,b in ref. ¹). At that stage, we primarily aimed at investigating whether metal cations enable the electrochemical reduction of CO₂ on polycrystalline copper, gold and silver, as found in our experiments. We did this by following a divide-and-conquer approach, where different degrees of complexity are included in the simulations step by step. First, we focused on the effect of short-term interactions by alkali metal cations on the activation of CO₂, disregarding concurrent effects by mean electric field and surface charging. We employed a minimal computational setup to tackle our research question, highlighting the need to further improve the model. To allow other researchers to build upon our study¹, we provided full open access to the DFT datasets generated². We very much appreciate the efforts by Le and Rahman in this direction and we hope that future datasets related to the topic will be equally made available, as we typically do for all our DFT datasets through the ioChem-BD repository³.

Our initial setup included no electric field, low cation coverage, a neutral solvation layer, an alkali cation, a compensating hydroxide and the Au(111) supercell. During the AIMD simulations, we fixed the C–Au surface distance ($d_{\text{Au-C}}$) to a value of 2.16 Å to prevent CO₂ from desorbing, as evident from the supplementary videos¹ and open-access DFT

datasets² related to the study. Le and Rahman suggest that this last assumption was instrumental to our conclusions since they could not reproduce cation–CO₂ coordination nor CO₂ activation when allowing the carbon atom to move. In fact, AIMD simulations on Au(111) with explicit solvation and a K⁺ cation confirmed desorption of CO₂ within less than 100 fs if the C–Au distance was not fixed. Besides, they performed an ionic optimization of the initial bidentate $\eta_{\text{C,O}}^2\text{CO}_2$ configuration (without explicit solvation and cation), which equally desorbs. In this regard, the key message of our study¹ is indeed that CO₂ activation does not occur without the presence of a metal cation on gold, thus the instability of CO₂ on Au without cation is consistent with our findings. We note that ΔG for CO₂ chemisorption is around 1 eV in the absence of a metal cation¹, and the optimized structure is typically achieved by converging CO₂H and removing the H with the C fixed⁴. Allowing the O–C–O angle to bend to 120° without electron transfer or any external support by cations requires more than 3 eV (ref. ⁵). Thus, it is not surprising that the ionic optimization or AIMD simulation of such an endergonic structure is difficult and requires electric field, excess electrons and cations to prevent desorption of a fully relaxed CO₂. In our original work¹, we fixed the C–Au distance to compute the thermodynamics of CO₂ activation in the absence and presence of cations and compare both cases. Such a comparison would have been impossible without fixing such a distance, as, in line with our main conclusions, CO₂ activation does not occur unless a cation is present. Finally, by highlighting the limitations of our approach, the authors indicate that more accurate modelling protocols must include electrode potential (grand-canonical DFT) with excess electrons within the simulation cell⁶. In a successive study published at the end of last year⁵, we included explicit electric field effects and higher cation concentrations. In this short reply, we demonstrate that the minimal setup employed in our original study¹ was sufficiently accurate to support our previous conclusion: without metal cation, CO₂ activation does not occur. We have run additional simulations that support this conclusion⁷, which are freely and openly accessible in the ioChem-BD database³.

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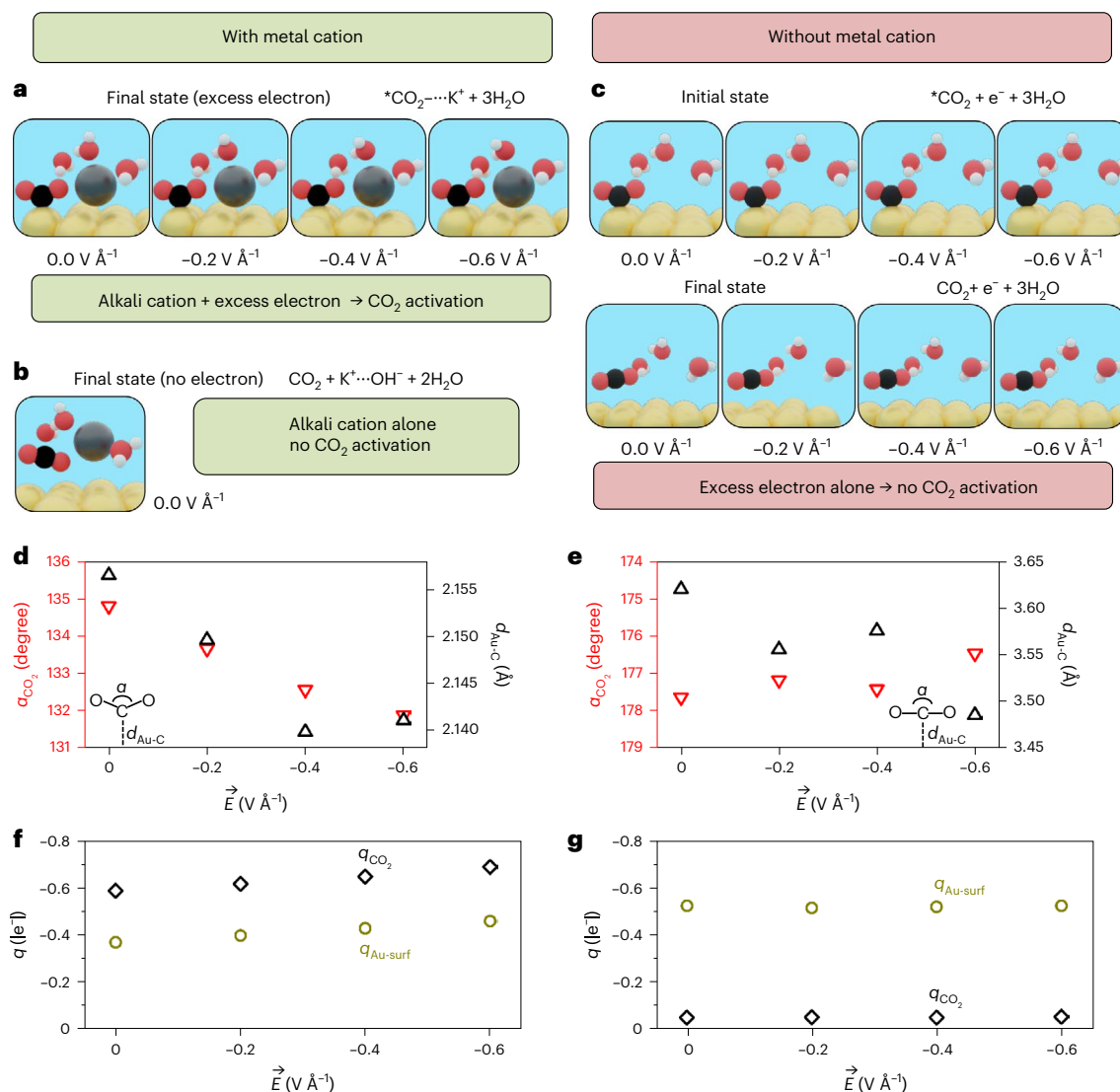


Fig. 1 | CO₂ activation with and without alkali cations and excess electrons. **a–g**, Ionic optimization of adsorbed CO₂ on Au(111) (3 × 3) with (**a, b, d, f**) and without (**c, e, g**) metal cation K⁺. α_{CO_2} corresponds to the activation angle; q_{CO_2}

and $q_{\text{Au-surf}}$ stand for the Bader charges of CO₂ and the first Au surface layer and all of them are presented as a function of the external electric field, \vec{E} .

In Fig. 1 we report the structural and electronic properties of a CO₂ molecule adsorbed on Au(111) (3 × 3) at different external electric fields in the presence of a partially solvated K⁺ with three H₂O molecules in its solvation shell (Supplementary Methods). As shown in Fig. 1a, CO₂ does adsorb on Au(111) in a bent configuration with or without applied electric field, provided that the alkali metal donates its extra electron to the surface. Instead, if we impose charge neutrality (as in our original AIMD simulations), CO₂ desorbs towards the non-activated, linear configuration (Fig. 1b). Thus, increasing charge separation through excess electrons within the simulation cell (and thus the cation-induced local electric field) is crucial for the accurate assessment of cation effects in CO₂ activation. By contrast, excess electrons or an external electric field alone does not enable CO₂ activation if K⁺ is absent (Fig. 1c). Remarkably, CO₂ activation angles (α), C–Au distances and CO₂ Bader charges for optimized $^*\text{CO}_2$ (* indicates adsorption) configurations in the presence of K⁺ are in line with the ones achieved in our previous AIMD study (Fig. 1d, f). All these parameters confirm that, without a metal cation, even an initially activated CO₂ molecule deactivates towards the linear configuration (Fig. 1c, e). As shown in Fig. 1g, although the extra electron increases the excess electronic density at the surface

($q_{\text{Au-surf}}$), the electron transfer to CO₂ does not occur without metal cation ($q_{\text{CO}_2} \sim 0$ |e|). Thus, CO₂ activation on Au(111) does not occur without a metal cation, even if an excess electron is added to the system.

Taking all the previous considerations into account, the complementary findings that we report here highlight that our previous insights on thermodynamic, structural and electronic properties of CO₂ activation with and without a metal cation in solution hold true for more accurate simulations including electrode charging through excess electrons and electric field (as shown independently in ref.⁸). Additionally, we observe that an external homogeneous electric field up to -0.6 V Å⁻¹ (-1.6 V vs SHE, Supplementary Methods) does not enable CO₂ activation alone, since to increase charge separation through excess electrons and high cation-induced electrostatic fields are needed to assist the electron transfer to adsorbed CO₂. Thus, although higher level (grand canonical) modelling approaches are desirable to achieve realistic modelling of cation effects, simplified simulations without applied electric potential may be representative enough under specific and well-motivated assumptions. This is the case of our original study¹, where we showed that alkali cations

enable adsorption of short-lived CO₂ species on Au(111) prone to fast desorption or protonation. We highlight that modelling choices should be validated by robust experimental evidence, as we exercise in our studies^{1,5}.

We agree with Le and Rahman that a generalized protocol to fully assess cation effects in electrochemical CO₂ reduction should include electrode charging through excess electrons and electric field, but also mass transfer effects, as shown recently⁹. Indeed, the state of the art is evolving fast in this research area (see the very recent work on CO₂ activation and C₂ selectivity⁸). As a last remark, we call the community for a shared effort toward the development of an ultimate protocol to assess cation effects in electrochemical CO₂ reduction and other electrocatalytic reactions. Such a protocol should integrate electrode potential and excess charge, cation accumulation, local pH, local solvent structure, mass transfer effects and their mutual dependences¹⁰. All the data and models related to them should be open to ensure that all researchers can validate and reuse them, as it was in our original study.

Data availability

Computational details are available in the Supplementary Information. The new datasets generated through DFT simulations and analysed during the current study are available in the ioChem-BD database³ at <https://doi.org/10.19061/iochem-bd-1-243>.

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Author contributions

All authors contributed to this study (PLACEHOLDER).

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Competing interests

The authors declare no competing interests.

Additional information

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