

Consequences of Overtones in Raman Spectra for Assigning Nickel Anode Surface Structures as NiO₂ during Alkaline Electrolysis

Corresponding Author: Dr Albert Engstfeld

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In this work, Leist et al report an operando/in-situ SERS of Ni(OH)₂ under alkaline water electrolysis conditions. They argue that the common region that is frequently attributed to superoxides or peroxides can instead be explained by overtone and combination bands and that the surface is effectively more deprotonated and behaves more like NiO₂ at high overpotentials like 1.54V vs RHE and they perform DFT computed Raman spectroscopy as well to support their conclusions. They also explicitly state that prior computational studies of NiOOH exist but haven't explicitly shown computed Raman spectra to motivate this work. I appreciate the authors' thoroughness with respect to the walking the readers through each aspect of development in the literature and then comparing it with their insight and interpretation making it a comprehensive work that highlights key developments in the literature for NiOOH and how their work can supplement some of the missing interpretation and further promote inverse design of PGM-free alkaline water electrocatalysts. I do have some comments and concerns that I have described below that I recommend the authors address.

Major:

1. In their CVs, the authors show Au@Ni as their primary catalyst. While this is fairly common, by carefully examining the CV I see there is a little uptick around 1.1-1.2V which typically we don't see in bulk Ni catalysts. The CV remains more-or-less featureless till the oxidation bump comes. I wonder if that is the enhanced effect from the gold underlayer? Could the authors expand on this? Since they are proposing something deviating from what the literature has been postulating, it would make the manuscript more robust if they can do a comparison CV with and without gold underlayer. There are known ligand and strain effects from underlayer for thin-film Ni catalysts and that could be contributing to their conclusions.

2. It is interesting to see that the authors don't see more commonly reported features that the literature sees. Could the authors explain why they think in Fig 2A they don't observe any ClO₄⁻ adsorption? Also, in the discussion and the caption they say that Fig 2A is reported at an applied potential of 1.54V is that vs Ag/AgCl or vs RHE? If it is RHE then I understand you wouldn't see the effect of pH as the conversion scale from Ref to RHE takes care of (at least) the intensity offset. It is unclear what scale it is and would help the reader if the authors could explicitly mention it. Additionally, what is their reasoning behind not seeing any pH effects with the peak shift? The authors note that it is different from several studies but they do not explain why.

a. Probing further on the no-pH effect and no ClO₄⁻ adsorption seen, it currently reads as anecdotal/observational statements without any mechanism. The authors should provide a rationale for the ClO₄⁻ suppression despite prior reports. Do they have high surface hydroxylation, different facets exposed, are there strong local field/roughness effects in play here, or is it the way the intensities are scaled?

b. I strongly recommend the authors separate two important distinctions 1) no pH effect on the peaks and their positions. And 2) no pH effect on structure. Because 1 is a spectral observation and 2 is an interpretation and should be presented with appropriate caution.

3. The authors do mention that for DFT they omit U because the NiOOH geometry is not affected by it and use DFT D3 for dispersion. This is one rationale among many to choose the approach of one's liking and currently is not very convincing. Raman frequencies and intensities can be sensitive not only to the geometry but also to the electronic structure and U can affect force constants via bonding character. Why do the authors think the Raman-relevant phonons are robust enough to the U omission? Likewise, Pourbaix diagram for why a fully deprotonated surface is expected at 1.54V vs RHE under their conditions would help the readers connect thermodynamics to the DFT model of choice like they have highlighted in many works. Here are a few examples: DOI: 10.1021/acs.jpcc.4c06788, 10.1088/1361-648X/aa9140

4. Looking at Fig 4, it appears to me that a combination of computational results from 4A and 4B explain the experimental results of the Raman spectra. I agree that NiO₂ shoulder features match more with the experimental. However, the computed NiO₂ doesn't show the region II. Which is covered by NiOOH. The authors partially resolve this by selection rules and overtone discussion but they still overstate DFT completely explains this. Additionally, when they agree with the literature

findings that have an average oxidation state ranging between 3-3.7 they imply the presence of +4 oxidation state and the presence of the superoxide. While that is a mathematically plausible statement, it also implies that there are some +3 species (previously identified NiOOH) present as well. So there is some degree of coexistence that may likely be occurring in this complex system. I suggest author frame the article and its core message as lessons learned from the literature and how their method and rationale is a promising candidate among the existing ones and offers a different perspective.

5. Because the authors note that region II has been previously linked to superoxide/peroxides but also that it appears before OER and remains unclear of its origins, it may be worth explicitly stating that their overtone explanation does not exclude reactive oxygen species under some conditions and that it only shows that region II is not unambiguous evidence.

Minor:

1. Figures in the supporting information, in some instances, do not correspond to what is mentioned in the manuscript.
2. Figures S2 and S3 are reported V vs Ag/AgCl, but for the sake of consistency, it would help to have additional graphs showing V vs RHE like the other CVs.
3. Ref 96 in the bibliography still have LaTeX formatting that needs to be typeset properly.
4. The table says "my work" for their calculations. Perhaps "this work" would be more appropriate?

Reviewer #2

(Remarks to the Author)

This manuscript employs in-situ Surface-Enhanced Raman Spectroscopy (SERS) and Density Functional Theory (DFT) to re-examine the vibrational signatures of nickel hydroxide catalysts during the oxygen evolution reaction (OER). The authors argue that peaks traditionally assigned to superoxide species (NiO_2^-) in the 900 cm^{-1} to 1200 cm^{-1} and 1400 cm^{-1} to 1800 cm^{-1} ranges are actually overtone and combination bands. This work addresses a critical potential pitfall in the interpretation of in-situ Raman data for OER mechanisms.

However, in its current form, the study's scope is somewhat narrow, focusing on a single material system ($\text{Ni}(\text{OH})_2$). While the correction of spectroscopic assignments is valuable, the manuscript lacks the broader impact typically expected for Nature Catalysis. The significance is further dampened by the fact that the oxidation of Ni^{2+} to Ni^{4+} at OER potentials is already well-supported by other techniques, such as X-ray Absorption Spectroscopy (XAS). Crucially, while the authors challenge existing peak assignments, they do not offer a definitive alternative strategy for identifying elusive surface intermediates, which limits the mechanistic utility of the work. Furthermore, some specific details need clarification, as follows:

1. To elevate the impact, the authors should investigate whether these overtone/combination phenomena are universal across other OER-active oxides (CoOx , RuOx , IrOx , etc.). Demonstrating this would transform the paper from a specific case study into a foundational guide for the electrocatalysis community.
2. The paper identifies a problem (misassignment) but stops short of providing a "solution." Can the authors propose a robust protocol—perhaps combining SERS with specific isotope labeling or advanced deconvolution—to distinguish between these overtones and actual reactive oxygen species?
3. The authors attribute potential- and pH-dependent shifts to the Vibrational Stark Effect. To strengthen this claim, I suggest investigating a broader range of alkali metal cations (e.g. Li^+ , Na^+ , K^+ , Cs^+). Since cation identity significantly modifies the double-layer electric field, this would provide much stronger evidence than the current Li^+/K^+ comparison.
4. The abstract states, "We question the presence of NiOOH upon electrochemical oxidation..." However, the discussion on page 11 (lines 675-676) suggests NiOOH may still partially exist. The abstract should be revised for consistency with the text to reflect that NiOOH may coexist with NiO_2 .
5. What is the estimated detection depth of the SERS configuration used? In Figure 4, there are clear discrepancies between surface and bulk spectra for NiOOH and NiO_2 . How were these differences accounted for during the peak deconvolution presented in Figure 5?
6. Beyond the Stark effect, could the subtle Raman shifts in Figure 6 be attributed to changes in the bulk valence state or variations in the surface coverage of adsorbed intermediates?
7. In Figure 6, the I3 peak intensity increases with potential. Please clarify the physical origin of this trend and discuss whether a corresponding change is observed in Region II.
8. In Figure 6b, were the ionic strengths kept constant across different pH values? If the ionic intensities differ, it is difficult to isolate the Stark effect from other interfacial changes. Have the authors tested solutions with identical ionic strengths at varying pH to confirm the results?
9. The subtitles in the "Results and Discussion" section (e.g., Raman Spectroscopy, Density Functional Theory, Overtone and combination modes, Vibrational Stark effect) are too generic. They should be more descriptive of the specific scientific findings contained within each subsection.

Reviewer #3

(Remarks to the Author)

See the attached file.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

I'm satisfied by the corrections made to the manuscript per my comments.

Reviewer #2

(Remarks to the Author)

The author further provided many experiments and DFT calculations to address the concerns raised by the reviewers. I am convinced that the second region is attributed to overtones and combination bands. Although the authors' revisions have resolved most of the technical issues, the following two more fundamental concerns continue to affect my overall assessment of the impact of this paper.

1. The authors propose that SERS probes a surface termination layer that is pure NiO₂, while the bulk could remain as NiOOH. The core of this structural model rests on the experimental observation that "SERS probes only the outermost few monolayers." However, the authors do not provide structural evidence independent of Raman spectroscopy, with comparable surface sensitivity, to verify this NiO₂ termination layer.

2. The authors recognize that "our work does not primarily aim at providing direct insights into the OER mechanism on Ni," and emphasize that "detailed insights into the surface structural properties of a catalyst material are equally important." I agree with this view – resolving ambiguities in structural assignment before mechanistic studies indeed has significant foundational value. However, the current discussion in the manuscript stops at "the surface is NiO₂," with insufficient exploration of the catalytic mechanistic implications of this structural correction. As a reader of Nature Catalysis, I would expect at least a preliminary discussion of the following topics:

If the active surface is NiO₂ (rather than the widely assumed NiOOH (valence state ~3.7)), what impact does this have on the widely discussed debate between the adsorbed oxygen mechanism (AEM) and the lattice oxygen mechanism (LOM) in OER? Is the reaction path or reaction intermediates' formation energy on the NiO₂ surface fundamentally different from that on the NiOOH surface? Can the existing DFT calculations provide some initial insights? Does the exploration of the electronic structure of the NiO₂ surface suggest reactivity characteristics fundamentally different from those of NiOOH (e.g., distribution of surface states)?

I recognize that some of these questions may exceed the scope of the current DFT calculations, but providing a forward-looking qualitative analysis in the discussion section would significantly enhance the appeal of this work to readers in its core catalysis field.

Minor comments:

1. In Figure 7, the potentials for 0.1 M, 0.01 M, 0.001 M KOH electrolyte are 1.6, 1.64 and 1.58 VRHE. However, in the main text, it is 1.6 VRHE on page 15.

2. On page 6, the author said "hence keeping the total ion concentration in the solution constant with respect to the 0.01 M KOH solution (pH = 12, black spectrum), did not reveal any measurable changes in either region I or II". While there is minor changes in the position of Peak I1 and I2, the peak intensity of I2 still can see comparable changes. The author should rewrite the above sentence to ensure its accuracy

Reviewer #3

(Remarks to the Author)

The authors have addressed the previous comments appropriately, and the revised manuscript has improved. However, direct theoretical support for the catalytic activity of NiO₂ toward the OER is still lacking. Therefore, a DFT reaction profile confirming the OER activity of NiO₂ is needed.

Version 2:

Reviewer comments:

Reviewer #2

(Remarks to the Author)

I have no further question. The authors have addressed all my comments properly.

Open Access This Peer Review File is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

In cases where reviewers are anonymous, credit should be given to 'Anonymous Referee' and the source.

The images or other third party material in this Peer Review File are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this license, visit <https://creativecommons.org/licenses/by/4.0/>

Response to Reviewers' comments on manuscript NATCATAL-25112577

“Consequences of Overtones in Raman Spectra for Structural Assignment of Nickel Anodes during Alkaline Electrolysis”

by J. Leist et al.

To assist in using this document, we have colored our **responses to the reviewers'** comments in **blue** and any **text from the manuscript in red**.

General comments to the Editor and Reviewers:

First, we want to thank the Editor and especially all Reviewers for their time reviewing our manuscript and their comments which we found were useful to improve the quality of our manuscript. We want to address some general aspects raised by individual reviewers that we consider of general concern, before proceeding with responses to the Editors' comments from the decision letter and those from the Reviewers'.

A crucial aspect is related to the direction of the paper, i.e., Reviewer 1 (comment 4) suggested to frame the article more toward “... lessons learned from the literature ...,” while Reviewer 2 (general comment) suggested the work should provide “... a definitive strategy for identifying elusive surface intermediates, ...”. Our initial version leaned in the direction of Reviewer #1's suggestion, and we remained with it, also because the aim of this paper was not to present a definitive strategy for identifying surface intermediates for Ni during the OER specifically (see also answer to Comment B of the Editor below).

Based on comment 9 of Reviewer #2, we adopted less generic Section headings. Furthermore based on the discussion to the general statement by reviewer #2, we decided to change the title to “**Consequences of Overtones in Raman Spectra for Structural Assignment illustrated for of Nickel Anodes during Alkaline Electrolysis**”. The word “*illustrate*” was nevertheless already used in the original submission in the abstract and introduction, since Ni studied under OER conditions is a perfect model system for this study, while simultaneously providing a contrasting view on the current understanding of this particular system. The inclusion of additional Raman spectra for Co and Mn based oxides (suggested by Reviewer #2), further broadens the relevance of our findings to catalyst systems beyond the OER or communities interested in layered materials properties.

With our changes made to the manuscript, we hopefully address all issues raised by the reviewers, which make our article suitable for publication in Nature Catalysis.

Editor:

A) To unambiguously demonstrate that the observed surface transformation is a general behavior of Ni catalysts under OER relevant conditions. Any potential revision must rule out other possible explanations, surface models or

spurious contributions, and ideally support the assignment with additional techniques.

To illustrate that the Ni catalyst under OER conditions is a suitable model system for this work, we included numerous new experiments and especially DFT calculations (see also comment C below) requested by the reviewers, which are now discussed more extensively in the manuscript as well as the supporting information. We also carefully screened the literature and have included a substantial number of new relevant references, especially for structural data (including data from XAS, XRD, and HAXPES), which are added to the manuscript and SI. Further, all Raman spectra (from the original submission and those requested by the Reviewers) recorded in different electrolytes and on substrates with different bulk or subsurface compositions, look almost perfectly identical. Hence, if impurities are present in either the electrolytes or the electrode, they do not seem to have a measurable effect on the Raman bands in this work. Overall, these new results further strengthen our conclusions on the assignment of the DFT models to the experimental Raman spectra proposed in our initial submission.

B) Both NiOOH and NiO₂ would seem to co-exist, contradicting a main statement in the Abstract. This apparent inconsistency needs to be resolved. It has been demonstrated before that NiOOH is catalytically active, but no actual proof of NiO₂ being catalytically active has been provided. A revision must include a DFT reaction profile showing the reaction's feasibility on a NiO₂ surface. If both NiOOH and NiO₂ co-exist and NiOOH is more active than NiO₂, the relevance of the latter for catalysis would be unclear.

We apologize for the somewhat unfortunate phrasing from our side in the original submission of the manuscript, which may have led to a misunderstanding. With regard to the specific structural assignment of Ni, we intended to convey that, at the onset and during the OER, the surface is exclusively terminated by NiO₂ and can therefore be considered the only active phase rather than NiOOH. We perfectly agree that the bulk can have a different composition or structure, which is, however, not accessible with SERS. Now, we provide a discussion on the probing depth of SERS (Request by Reviewer 2.5), including additional experiments to estimate the probing depth for our system including a comparison to other suggested values in the literature, to strengthen our assignment. Both aspects (surface vs. bulk structure and probing depth) are included in the manuscript where applicable, with a consolidated discussion in the Section "*Near Surface Structure of Ni at high overpotentials*".

Regarding the construction of a reaction profile, with this work we provide a crucial component in constructing such a profile (the structural properties of the substrates surface under reaction conditions). However, any further analysis of the exact OER mechanism requires detailed and careful knowledge of possible reaction intermediates which are unambiguously identified by a combined experimental and theoretical effort and certainly more details on the reaction kinetics. Considering the various extensive studies that have already been performed on understanding the OER reaction mechanisms (see similar works performed on the OER mechanism on NiOOH (<https://doi.org/10.1021/acscatal.7b00999>) or IrO₂(100) (<https://doi.org/10.1038/s41467-025-61367-z>)), we believe that resolving the reaction mechanism with the required accuracy and care is certainly far beyond the scope of this

work. However, as mentioned above our work already provides a crucial step in this direction by suggesting that NiO_2 is the only active phase.

C) In addition, the reviewers raised comments regarding the appropriateness of the DFT methods of choice, the inclusion of a Pourbaix diagram or conducting a broader investigation of the proposed assignment.

We appreciate the Reviewers suggestions and have performed additional tests and calculations using different methods. Adding these to the manuscript and SI led to a major extension of the DFT part in the manuscript, further confirming our initial conclusions. The Figure with computed Raman spectra has been updated and several Tables have been included in the manuscript and the SI. The text was adapted and we deliberately omitted a detailed listing of the peak positions in the text (now included in comprehensive Tables, of which some were moved into the Zenodo repository). In addition, we briefly comment on the usefulness of density of states (DOS) calculations (which seem to be reported also rather inconsistently in the experimental literature and thus an extensive discussion is added in the SI) and a more careful comparison of computed structural data with results from the literature (DFT, EXAFS, and XRD). These comparisons revealed some interesting discrepancies in the catalysis (OER) literature which are discussed. Aside from that, during this revision process we also found some rather informative works on NiO_2 from the battery community, studying Li intercalation in NiO_2 . Computed interatomic distances and Raman spectra of NiO_2 from these studies (only showing region I of our spectrum) perfectly support our structural assignment. Details on the considered computation models, their choice and respective results are included in the responses to the Reviewers below.

Other General changes:

- Some wavenumbers and potentials given in the manuscript and the SI were updated, which now correspond consistently to the background subtracted data shown in the graphs. The values only change slightly and have no impact on the interpretations or conclusions drawn.
- Based on the minor comment by Reviewer #1, we changed the SI Figure labels, such that they contain the SI Section number, such as Figure S4.1. We hope this change will improve the cross referencing between the manuscript and the SI.
- Parts of the SI were reorganized, to meet the new structure of the manuscript.
- After suggesting at the end of the DFT Section that the Raman spectrum at high overpotentials corresponds to that of NiO_2 , we replaced NiOOH with NiO_2 in the following sections in the manuscript to hopefully mitigate further confusion. Also in the SI we consistently use NiO_2 , instead of NiOOH for the surface. NiOOH is only used when this phase is explicitly mentioned in cited works or when describing the bulk.
- Long tables initially placed in the SI and newer ones related to the DFT calculations were moved from the SI to the Zenodo repository (<https://doi.org/10.5281/zenodo.19439352>).

- A recently published extensive review on SERS from the SERS community has been added to the introduction, substantiating our claim that overtones might have been neglected by the community (<https://doi.org/10.1039/D4CS00883A>)

Reviewer #1:

In this work, Leist et al report an operando/in-situ SERS of Ni(OH)₂ under alkaline water electrolysis conditions. They argue that the common region that is frequently attributed to superoxides or peroxides can instead be explained by overtone and combination bands and that the surface is effectively more deprotonated and behaves more like NiO₂ at high overpotentials like 1.54V vs RHE and they perform DFT computed Raman spectroscopy as well to support their conclusions. They also explicitly state that prior computational studies of NiOOH exist but haven't explicitly shown computed Raman spectra to motivate this work. I appreciate the authors' thoroughness with respect to the walking the readers through each aspect of development in the literature and then comparing it with their insight and interpretation making it a comprehensive work that highlights key developments in the literature for NiOOH and how their work can supplement some of the missing interpretation and further promote inverse design of PGM-free alkaline water electrocatalysts. I do have some comments and concerns that I have described below that I recommend the authors address.

We thank the Reviewer for his or her kind words. Regarding the comment on the computed Raman spectra of NiOOH, we are not quite sure whether this was a typo, since both the spectra of the NiOOH surface and bulk were included in Figure 4a of the original submission. We hope that with the additional DFT results provided and changes made to the text in the revised manuscript, we could clarify this issue.

Major Issues:

1. In their CVs, the authors show Au@Ni as their primary catalyst. While this is fairly common, by carefully examining the CV I see there is a little uptick around 1.1-1.2V which typically we don't see in bulk Ni catalysts. The CV remains more-or-less featureless till the oxidation bump comes. I wonder if that is the enhanced effect from the gold underlayer? Could the authors expand on this? Since they are proposing something deviating from what the literature has been postulating, it would make the manuscript more robust if they can do a comparison CV with and without gold underlayer. There are known ligand and strain effects from underlayer for thin-film Ni catalysts and that could be contributing to their conclusions.

Indeed there is a small uptick in current before the large oxidation peak O, and we apologize that we did not mention this feature so far. Based on the literature, this peak apparently is not consistently observed for polycrystalline and single crystal electrodes (pure Ni). Similarly, we also observe a small shoulder, although slightly shorter, after potential cycling pure Ni electrodes into the OER region. We agree that the shoulder in the

Au@Ni samples could also be associated with subsurface oxidation of Au. Nevertheless, we do not see any peaks related to Au in the Raman spectra in the $\text{Ni}(\text{OH})_2$ region (where peaks related to Au, should appear at different wavelengths. In the NiO_2 region (higher potentials), the possible Au peaks would overlap with those of NiO_2 . However, rescaled Raman spectra recorded on pure Ni and Au@Ni samples are almost perfectly identical. Therefore we suggest that possible subsurface structural changes do not have an effect on the vibrational properties of the surface structures probed by Raman. These aspects are only briefly mentioned in the manuscript and are more extensively discussed in the SI in Section S3, including additional CVs and Raman spectra.

2. It is interesting to see that the authors don't see more commonly reported features that the literature sees. Could the authors explain why they think in Fig 2A they don't observe any ClO_4^- adsorption? Also, in the discussion and the caption they say that Fig 2A is reported at an applied potential of 1.54 V is that vs Ag/AgCl or vs RHE? If it is RHE then I understand you wouldn't see the effect of pH as the conversion scale from Ref to RHE takes care of (at least) the intensity offset. It is unclear what scale it is and would help the reader if the authors could explicitly mention it. Additionally, what is their reasoning behind not seeing any pH effects with the peak shift? The authors note that it is different from several studies but they do not explain why.

This comment is separated in i) ClO_4^- adsorption, ii) reference scales, and iii) pH effect.

i) The peak related to ClO_4^- feature depends on its concentration in the electrolyte and is also not observed in reported Raman spectra, such as in <https://doi.org/10.1039/C5SC04486C>. The concentration effect (peak appears clearly at higher concentration) is now shown in Section S9 of the SI, comparing Raman spectra of Ni electrodes recorded in 0.1 and 0.01 M KClO_4 solutions, as well as a Raman spectrum of the solution only. Note that the position of the ClO_4^- peak is identical in the Raman spectrum recorded on the Ni sample and that recorded for the electrolyte, which suggests that ClO_4^- is likely not adsorbed on the surface (and should possibly also appear at different wavenumbers). Furthermore, an adsorbed species could in principle induce a distortion of the surface oxide lattice by forming an adsorption complex, which could lead to a shift in the fundamental modes of the lattice (which we do not observe either). Since the ClO_4^- concentration is low in our experiments (0.01 M) and no significant contributions are observed in the Raman spectra, we consider a possible effect negligible.

ii) We apologize for the unclear presentation of the potential scales, which is now explicitly mentioned on each occasion in the manuscript (and SI), such as 1.54 V_{RHE}.

iii) The effect of the pH is addressed both in the discussion to Fig. 2 and Fig. 7 (former 6) and was possibly not perfectly clear. In the case of Fig. 2 we keep the total ion concentration constant upon varying the pH (compensated by the addition of KClO_4 at low pH), while in Fig. 7 we simply change the pH without keeping the total ion concentration constant. In the discussion to Fig. 2 we now refer to the Section on the vibrational Stark effect, including a more extensive discussion on the role of pH and total ion concentration. In combination, the results suggest that the changes observed in the SER spectra are only related to the changes of the electric field at the electrode interface, which can be modulated simply by varying the potential or by changing the total ion concentration in the

solution (no changes are observed for constant total ion concentration). In the cited works, the pH dependence was mostly discussed based on changes in intensity of the bands (regions I and II). Considering (based on our data) that region II is related to overtones of the fundamental modes, we now believe that these formerly reported changes are simply related to changes in intensity of the fundamental modes (region I), which are directly reflected in the intensity of the overtone modes (region II). Therefore, we suggest that differences should be discussed based on scaled spectra, rather than absolute intensities which can change depending on the experimental conditions.

a. Probing further on the no-pH effect and no ClO₄ adsorption seen, it currently reads as anecdotal/observational statements without any mechanism. The authors should provide a rationale for the ClO₄ suppression despite prior reports. Do they have high surface hydroxylation, different facets exposed, are there strong local field/roughness effects in play here, or is it the way the intensities are scaled?

The role of ClO₄ is addressed in the previous comment and is thus, as explained, not an effect of the way how the intensities are rescaled.

Furthermore, surface hydroxylation can be excluded due to the lack of a Deuterium shift in the Raman spectrum in isotope labeled experiments. The role of electric fields, discussed in the original version of the manuscript, is now more extensively covered in the Section *“Influence of the Vibrational Stark Effect”*, which both depends on the total ion concentration and the applied potential. Since roughened Au substrates are required to perform SERS measurements, the deposited film is without a doubt polycrystalline. Hence, the surface exposes a mixture of crystallographic orientations (and possibly also numerous grain boundaries). Since we do not observe differences between Raman spectra between different measurements (and measurement conditions), we do not expect that small variations in the crystallographic orientation of the surface plays a significant role.

b. I strongly recommend the authors separate two important distinctions
1) no pH effect on the peaks and their positions. And 2) no pH effect on structure. Because 1 is a spectral observation and 2 is an interpretation and should be presented with appropriate caution.

The reviewer addresses important correlated aspects, which we think are directly coupled, but should in principle be discernable. If the pH would induce a significant structural change (such as a phase transformation), we would expect significant changes in the vibrational properties, i.e., formation of bands at different positions. According to Fig. 2, we conclude with high certainty that a phase transition (or change in structural properties) does not take place upon changing the pH over almost four decades (between 8.5 to 12) and keeping the total ion concentration constant, since these changes do not lead to any changes in the SER spectra. Possible dissolution processes will not be captured, since the removal of parts of the oxide will not change the chemical composition of the layers probed by Raman. If we change the pH without keeping the total ion concentration constant in Fig. 7b (former 6b), subtle changes are observed in the peak positions, which are rationalized by the vibrational stark effect. The aspects on varying the pH and the role of the total ion

concentration are now more carefully discussed (specifically in the section “*Influence of the Vibrational Stark Effect.*”)

3. The authors do mention that for DFT they omit U because the NiOOH geometry is not affected by it and use DFT D3 for dispersion. This is one rationale among many to choose the approach of one's liking and currently is not very convincing. Raman frequencies and intensities can be sensitive not only to the geometry but also to the electronic structure and U can affect force constants via bonding character. Why do the authors think the Raman-relevant phonons are robust enough to the U omission? Likewise, Pourbaix diagram for why a fully deprotonated surface is expected at 1.54V vs RHE under their conditions would help the readers connect thermodynamics to the DFT model of choice like they have highlighted in many works. Here are a few examples: DOI: 10.1021/acs.jpcc.4c06788, 10.1088/1361-648X/aa9140

We separate the comment in i) DFT functionals and ii) Pourbaix Diagrams.

i) This comment also relates to comments from Reviewer 3. We initially chose the PBE+D3 approach for phonon calculations in our draft, since, even though this method has its limitations in describing the electronic structure, it yields reliable geometries, which are essential for accurate phonon calculations. We further agree and now show that employing additional computational approaches provides a more comprehensive basis for supporting our DFT-based conclusions. Summarizing, we performed and included calculations using the DFT+U approach. In addition, bulk structures of Ni(OH)₂ were calculated using both the D3 dispersion correction and the +U approach. To validate the computational methodology, we now cover all possible Ni-oxy-hydroxides (Ni(OH)₂, NiOOH, and NiO₂) relevant for the discussion on the structural assignment in this work. For all bulk structures, densities of states (DOS) and band gaps were calculated to evaluate the representation of the electronic structure. Additionally, hybrid functional calculations (B3LYP, HSE06, and PBE0) were performed to determine both the geometry and the electronic structure. For all structures we included a table summarizing interatomic distances (Ni-Ni and Ni-O) of the various structures inferred from different experiments (reported in the literature) in the manuscript and more elaborate tables in the SI. Overall, the calculated interatomic distances for bulk NiO₂ are in good agreement with experimental values, largely independent of the computational approach used. Furthermore, the experimental SER spectrum is reproduced reasonably well with the calculation of NiO₂ using both the D3-corrected and +U approaches (except for the missing overtone region II). The experimental Raman spectrum of crystalline Ni(OH)₂ reported in the literature can only be reproduced using the +U approach.

In contrast, the computed Raman spectra and interatomic distances for NiOOH are not consistent with either our experimental Raman spectra nor previously reported interatomic distances for this material. Note that our computed values of NiOOH are similar to other reported computed values. The differences between the DFT approaches and a thorough interpretation of the structural assignment of NiOOH is provided in the manuscript. This thorough comparison reveals that the reported interatomic distances of NiOOH are very similar to the values for NiO₂ (and in some cases also Ni(OH)₂). Since our DFT results almost perfectly reproduce the experimental NiO₂ Raman spectrum and isotope-labeling

reveals an absence of hydrogen, we conclude that the surface is terminated by NiO₂, while mixed phases in the bulk can not be ruled out.

Finally, Section S13 has been added in the SI, showing and discussing the DOS, band gaps and interatomic distances of all calculated structures.

ii) We thank the reviewer for highlighting these important references that we overlooked while writing our initial submission. We perfectly agree that a discussion on Pourbaix diagrams makes a nice addition to the manuscript. Especially, since these diagrams support our claim that the final oxidation state at high overpotentials is indeed NiO₂. The reported potential for the transition between the NiOOH and NiO₂ phase seems to be predicted at higher potentials to those reported in our work. However, this can be rationalized as the Pourbaix diagrams present thermodynamic bulk structures and do not necessarily reflect the potential-dependent changes on the surface of a material. References to Pourbaix diagrams are now included in the introduction and included in the discussion in the Section *“Near Surface Structure of Ni at high overpotentials”*.

4. Looking at Fig 4, it appears to me that a combination of computational results from 4A and 4B explain the experimental results of the Raman spectra. I agree that NiO₂ shoulder features match more with the experimental. However, the computed NiO₂ doesn't show the region II. Which is covered by NiOOH. The authors partially resolve this by selection rules and overtone discussion but they still overstate DFT completely explains this. Additionally, when they agree with the literature findings that have an average oxidation state ranging between 3-3.7 they imply the presence of +4 oxidation state and the presence of the superoxide. While that is a mathematically plausible statement, it also implies that there are some +3 species (previously identified NiOOH) present as well. So there is some degree of coexistence that may likely be occurring in this complex system. I suggest author frame the article and its core message as lessons learned from the literature and how their method and rationale is a promising candidate among the existing ones and offers a different perspective.

We agree with the reviewer that conclusions can not solely be drawn from theory. We now address this aspect more carefully with the new DFT results and a detailed comparison of structural data with experimental findings. Nevertheless, our initial suggestion that region II is not related to OH bending vibrations can still be discarded, since we do not observe a deuterium shift in the isotope labelled experiment. Most importantly overtones (region II) are not exclusive to NiO₂, but also appear for Ni(OH)₂ (Fig. 1) and in the newly added potential-dependent Raman spectra for Co and Mn based-oxides in Fig. 6 (see Reviewer #2.1). Furthermore, region III in Fig. 1 (which can not be assigned by any DFT approach) can to this point only be rationalized by overtones.

We agree with the reviewer on the possible presence of mixed phases. This aspect was unfortunately not presented perfectly clear in the manuscript. Most importantly we conclude that mixed phases do not exist on the surface at high overpotentials (which is terminated by NiO₂), while the bulk composition can be different. This is now discussed more extensively in the section *“Near Surface Structure of Ni at high overpotentials”* and the comparison of Raman spectra recorded on β/γ-NiOOH in the SI (see Reviewer #3.3). A key aspect is that

discrepancies between reported structures from experimental approaches and thus the assignment of oxidation states possibly relate to the probing depth of the respective methods. We suggest that Raman (based on additional measurements, see Reviewer #2.4) probes only the near surface region and is insensitive to the structural properties in the bulk, while EXAFS usually always provides information on the bulk and the surface.

5. Because the authors note that region II has been previously linked to superoxide/peroxides but also that it appears before OER and remains unclear of its origins, it may be worth explicitly stating that their overtone explanation does not exclude reactive oxygen species under some conditions and that it only shows that region II is not unambiguous evidence.

We agree with the reviewer, that in principle overtones and superoxide peaks can fall in the same region, but could also appear elsewhere in the spectrum. This was indeed indicated in the initial version of the manuscript, where we noted that SERS bands related to these species were observed at around 1130 cm^{-1} (and 830 cm^{-1}) were reported to appear as sharp peaks in the work by Pushkarev et al. (<https://doi.org/10.1021/jp0311254>) studying O_2 adsorption on CeO_2 . These measurements were performed under different conditions, i.e., a temperature controlled gas flow reactor. Since this aspect was maybe overlooked by the reviewer and the wording was a bit unclear in our manuscript, we made several changes in the manuscript. We also note now more clearly, that these species are either not present under our experimental conditions or can for unexpected reasons not be resolved with SERS measurements.

Minor:

1. Figures in the supporting information, in some instances, do not correspond to what is mentioned in the manuscript.

All references to the SI have been updated. We also use new SI Figure labels, such that the figure number contains the Section Number in the SI, such as Figure S4.1. We hope this change will improve the cross referencing between the manuscript and the SI.

2. Figures S2 and S3 are reported V vs Ag/AgCl, but for the sake of consistency, it would help to have additional graphs showing V vs RHE like the other CVs.

We agree, and we now report all potentials on the RHE (see comment 2ii above).

3. Ref 96 in the bibliography shall have LaTeX formatting that needs to be typeset properly.

The issue with reference 96 (now 131) has been fixed.

4. The table says “my work” for their calculations. Perhaps “this work” would be more appropriate?

We thank the reviewer for the suggestion and made replacements accordingly.

Reviewer #2:

This manuscript employs in-situ Surface-Enhanced Raman Spectroscopy (SERS) and Density Functional Theory (DFT) to re-examine the vibrational signatures of nickel hydroxide catalysts during the oxygen evolution reaction (OER). The authors argue that peaks traditionally assigned to superoxide species (NiO_2^-) in the 900 cm^{-1} to 1200 cm^{-1} and 1400 cm^{-1} to 1800 cm^{-1} ranges are actually overtone and combination bands. This work addresses a critical potential pitfall in the interpretation of in-situ Raman data for OER mechanisms.

However, in its current form, the study's scope is somewhat narrow, focusing on a single material system ($\text{Ni}(\text{OH})_2$). While the correction of spectroscopic assignments is valuable, the manuscript lacks the broader impact typically expected for Nature Catalysis. The significance is further dampened by the fact that the oxidation of Ni^{2+} to Ni^{4+} at OER potentials is already well-supported by other techniques, such as X-ray Absorption Spectroscopy (XAS). Crucially, while the authors challenge existing peak assignments, they do not offer a definitive alternative strategy for identifying elusive surface intermediates, which limits the mechanistic utility of the work. Furthermore, some specific details need clarification, as follows:

We thank the reviewer for the detailed comments, and address separately the three critical points: i) potential narrow scope, ii) significance of the work, and iii) limits in mechanistic utility.

i) In the initial submission, the title and the data presented may give the impression that the study primarily addresses the structural assignment of the widely discussed Ni phases during the OER. However, our primary aim is to address the broader and more general issue of overtone formation and its relevance for structural assignment, particularly in combination with isotope labeling and DFT. In this context, we have chosen Ni anodes, as we consider it to be a highly relevant system, for which, based on a detailed evaluation of the previously unassigned overtone Raman bands, we demonstrate that the surface structure of the Ni electrode is terminated by NiO_2 rather than NiOOH . This finding serves as a clear proof of concept for our approach, which relies on a careful analysis combining DFT calculations with an extensive comparison to the literature, now significantly expanded relative to previous reports on this class of materials. Consequently, the OER on Ni represents an ideal model system for this study, while at the same time providing a contrasting perspective on the current understanding of this system.

Beyond this important finding, we broaden the scope of the work by including additional potential-dependent Raman spectra of Co- and Mn-based systems (both widely discussed for catalytic applications) in Fig. 6. These data support our conclusions (see comment 1 below) and highlight how overtone analysis in Raman spectroscopy enables differentiation between rigid oxide and layered oxide structures. In light of these additions, and consistent with the wording in the abstract and introduction, where we already state that Ni is used to “*illustrate*” the challenges of structural assignment, we have revised the title to “Consequences of Overtones in Raman Spectra for Structural Assignment **illustrated for** Nickel Anodes during Alkaline Electrolysis”.

ii) Regarding the XAS data, we agree with the referee that previous works reported already on oxidation states +II and +IV, which was also mentioned in our initial work, though admittedly without explicitly addressing the key findings of these studies. We now extended this discussion significantly (by including numerous new references) also in relation to the newly added DFT results. However, none of these works unambiguously assign the +IV state to NiO_2 and still denote the catalyst structure as NiOOH . We now suggest that the surface is terminated exclusively by NiO_2 and other phases may exist in the bulk, which do not have an effect on the surface structural properties (see Reviewer #1.1 and 3.3).

iii) Regarding the mechanistic implications we disagree with the reviewer that our work “limits the mechanistic utility”, even though our work does not primarily aim at providing direct insights into the OER mechanism on Ni (which we think is also a very domain specific question and is beyond the scope of this work). To those expecting additional insights in possible reaction intermediates, the work might seem a bit unsatisfying. However, detailed insights into the surface structural properties of a catalyst material (here NiO_2) are equally important since the surface also plays a crucial role in the steps of an electrocatalytic cycle (here the OER), which therefore inevitably has direct mechanistic implications and is thus highly important for further studies.

1. To elevate the impact, the authors should investigate whether these overtone/combination phenomena are universal across other OER-active oxides (CoOx , RuOx , IrOx , etc.). Demonstrating this would transform the paper from a specific case study into a foundational guide for the electrocatalysis community.

We agree with the reviewer that such measurements are highly valuable to the community. Thus we added Raman spectra for Mn and Co recorded under similar conditions than Ni (alkaline electrolyte but different oxidation potentials). The spectra are now included in the section “*Overtone and combination band formation in Raman spectra*” in Fig. 6, both showing overtones. Specifically, the layered CoOOH shows a clear overtone band, while the rigid Co_3O_4 does not. Similarly, MnO_2 displays an overtone band (which can consist of multiple phases including layered structures), while in the rigid Mn_3O_4 structure the intensity of the bands are significantly lower. In combination with the non-oxide layered materials referred to in the manuscript (MoS_2 , WS, graphene oxide, and LiCoO_2) and these new measurements on Mn and Co, it seems that overtones are indeed generally likely to appear in many non-rigid, layered materials. Due to the complex Raman spectra of Co and Mn oxides (with possible overlapping peaks of multiple phases), a detailed discussion is beyond the scope of this work and must be addressed for these systems individually in the future. Note that these materials were investigated at potentials below the onset of the OER (to rule out superoxide formation). While this is not directly relevant for the OER, it also shows that this aspect should not be neglected in other reactions studied at potentials outside the potential region of the OER.

2. The paper identifies a problem (misassignment) but stops short of providing a “solution.” Can the authors propose a robust protocol—perhaps combining SERS with specific isotope labeling or advanced deconvolution—to distinguish between these overtones and actual reactive oxygen species?

We agree with the reviewer that protocols to distinguish between overtones and bands related to intermediates would be beneficial to the community. But this is only possible if the spectra show peaks, which can be unambiguously addressed to such intermediates. In our case, *“region II consists of a rather broad band, which is somewhat unexpected for superoxide systems, which, for other systems such as CeO₂ and Pt oxides, usually consist of fewer and sharper peaks (see <https://doi.org/10.1021/jp0311254> or <https://doi.org/10.1038/ncomms12440>) is stated in our initial submission.* Furthermore, superoxide assignment requires bands, which do not fit or cannot be deconvoluted with the position of overtone or combination modes for at least a single isotope. If these conditions are met, reactive species can be identified which has now been incorporated into the discussion. We are confident that this work will i) help in preventing the propagation of errors in data analysis and ii) help in differentiating individual case peaks related to overtones and others related to adsorbed species (not only during the OER), which (as pointed out by the reviewer) should then be possible to probe with isotope labeled measurements. Further assignment will then require a combination of additional experimental and computational methods, to draw unambiguous conclusions as presented in this work.

3. The authors attribute potential- and pH-dependent shifts to the Vibrational Stark Effect. To strengthen this claim, I suggest investigating a broader range of alkali metal cations (e.g. Li⁺, Na⁺, K⁺, Cs⁺). Since cation identity significantly modifies the double-layer electric field, this would provide much stronger evidence than the current Li⁺/K⁺ comparison.

We agree with the reviewer that this is a particularly interesting point. We now performed additional SERS measurements using Na⁺ and Cs⁺ containing electrolytes (in addition to the previously presented K⁺ and Li⁺ measurements). The data are included in Fig. 2 and the new Figure S7.1. In summary, we do not see any changes in the Raman bands, except for a small shift for the Cs⁺ containing electrolyte (about 2 cm⁻¹), which has been reported previously by other authors but for higher concentrations. Based on these reports using higher concentration variations in peak intensity and position seem to be more pronounced. Related works and findings are now included in the description of the new data.

4. The abstract states, "We question the presence of NiOOH upon electrochemical oxidation..." However, the discussion on page 11 (lines 675-676) suggests NiOOH may still partially exist. The abstract should be revised for consistency with the text to reflect that NiOOH may coexist with NiO₂.

We sincerely apologize that this unclear statement led to confusion. We address this crucial aspect in the general part of this report, on multiple occasions in this report and now hopefully clarified this aspect consistently across the manuscript. In total, we suggest that the surface is terminated by NiO₂ while the bulk can have different structures, hence the surface does not consist of co-existing phases.

5. What is the estimated detection depth of the SERS configuration used? In Figure 4, there are clear discrepancies between surface and bulk spectra for

NiOOH and NiO₂. How were these differences accounted for during the peak deconvolution presented in Figure 5?

We separate this comment in i) detection depth and ii) peak deconvolution.

i) The referee raises an important question. To the best of our knowledge there are no reports dealing explicitly with the question how many layers are probed by SERS (or from which depth the scattered signal originates) for solid materials presented in this work. Information on the probing depth of solid materials are scarce and seem to strongly depend on the material.

For example, Chanet al. (<https://doi.org/10.1021/jp983787c>) reported values of 4 nm, by following the electrooxidation of Cu on a Au SERS substrate. Conversely, the penetration for non-surface-enhanced Li_xNiO₂ samples have been suggested to be between 100 to 200 nm (<https://doi.org/10.1021/acsenergylett.4c00360>).

Considering this discrepancy in numbers, we tried to assess the probing depth for our in situ SERS measurements, by following the evolution of the Raman signal during the growth of the oxide layer on the Ni anode (similar to the experiment by Chatenet et al.). The temporal evolution of the Ni oxide growth has been studied by Alsabeth et al. (<https://doi.org/10.1007/s12678-013-0172-z>), who showed that the oxide layer thickness increases from approximately 3.2 nm after 20 s to slightly above 4.5 nm after 10 min, corresponding to roughly 6.6 to 9.3 monolayers (data for less than 20 s were not reported by the authors). Our Raman measurements show that the Raman spectrum is fully evolved after 1 s of electrode polarization and remains unchanged over a time of 10 minutes. Hence, we suggest that the probing depth in our case must be equal or smaller than 6.6 monolayers (the thinnest layer determined by Alsabet et al. after 20 s polarization). We included values for the probing depth in the manuscript and the detailed experimental insights on the oxide growth are presented in the new Section S16 in the SI. A more extensive discussion on the consequences of different probing depths of various methods is now included in the manuscript in the Section “*Near Surface Structure of Ni at high overpotentials*”.

ii) We apologize if this aspect has been presented in a misleading way. The peak deconvolution in Fig. 5 is based on the experimentally observed fundamental modes, and not on the DFT calculations. The positions of overtones and combination bands are simply determined by doubling or summing the peak positions of the experimentally observed fundamental modes. We clarified the procedure in Section “*Overtone and combination band formation in Raman spectra*”.

6. Beyond the Stark effect, could the subtle Raman shifts in Figure 6 be attributed to changes in the bulk valence state or variations in the surface coverage of adsorbed intermediates?

Regarding the reviewer's comment on the “changes of the bulk valence state” we are not confident what the reviewer is referring to. We hope that with the numerous changes made to the manuscript we provide a conclusive answer.

The reviewer's comment on attributing possible changes to surface coverage of adsorbed species is indeed an interesting point. A key problem is that an unambiguous statement can only be made if such intermediates can be resolved (for which we do not have any evidence). We would, however, expect that the specific adsorption of intermediates would lead to the formation of an adsorption complex, which should significantly change the vibrational properties of the fundamental modes of the lattice or lead to the appearance of additional modes (see sharp band formation for adsorbed oxygen on CeO₂ in <https://doi.org/10.1021/jp0311254>, mentioned in our work). We added a comment in the Section "*Influence of the Vibrational Stark effect*".

7. In Figure 6, the I₃ peak intensity increases with potential. Please clarify the physical origin of this trend and discuss whether a corresponding change is observed in Region II.

We agree with the reviewer that this aspect should be explained more carefully. We extended the discussion in the manuscript and added a new Section in the SI, which also shows the overtone region with a higher magnification. In that figure we included positions for possible overtones of the I₃ mode and corresponding combination modes with I₁ and I₂. Furthermore, based on the DFT calculations, we attribute the I₃ mode to the Raman-inactive (but IR-active) A_{2u} vibration. We propose that this mode becomes Raman-active due to the broken symmetry at the surface and the influence of the vibrational Stark effect. In addition, we now also address the possible activation of the second DFT-predicted IR-active mode, E_u (appearing between peaks I₁ and I₂), which might be related to potential-dependent changes observed in the SER spectrum in region I (Fig.7a former 6a).

8. In Figure 6b, were the ionic strengths kept constant across different pH values? If the ionic intensities differ, it is difficult to isolate the Stark effect from other interfacial changes. Have the authors tested solutions with identical ionic strengths at varying pH to confirm the results?

This aspect has probably been written in the manuscript in a misleading way. We actually show in Fig. 2 the effect, when the ionic strength is kept constant upon changing the pH (12 and 8.5). Here the SER spectra remain unchanged. In Figure 7b (formerly 6b), the pH (or total ion concentration) is varied without keeping the total ion concentration constant. This leads to changes in the SER spectra, caused by changes in the interfacial electric field induced by the different ion concentrations. We hope that the rewording of the descriptions of Fig 2 and Fig 7b (former 6b) resolves this aspect.

9. The subtitles in the "Results and Discussion" section (e.g., Raman Spectroscopy, Density Functional Theory, Overtone and combination modes, Vibrational Stark effect) are too generic. They should be more descriptive of the specific scientific findings contained within each subsection.

Our idea was to separate methods and effects that are primarily discussed in these sections. However, we agree that the section titles were likely too generic and did not accurately reflect their content. We hope that the new less generic section titles are also acceptable for the editor and other reviewers.

Reviewer #3:

In this paper, the authors use operando/in situ SERS (including H/D isotope tests) together with DFT-calculated Raman spectra to reassess the surface structure of oxidized nickel (oxy)hydroxide catalysts under OER-relevant conditions. They argue that spectral features commonly assigned to NiOOH and to adsorbed superoxide-like intermediates are better explained by a NiO₂ (Ni(IV)) near-surface phase, and that several “extra” bands (regions II/III) arise from overtone/combination modes rather than distinct reaction intermediates. The work further proposes that reported potential- and pH-dependent band shifts can be largely rationalized by a vibrational Stark effect, implying that parts of the Raman-based mechanistic literature may require reinterpretation. Although the results are interesting, in its current format and level of supporting evidence I cannot recommend publication.

We thank the reviewer for finding the results interesting and hope that with the additional measurements and calculations we can provide sufficient evidence for the conclusions drawn in this work.

Below are my comments:

1-Since Ni is a 3d transition-metal ion and the manuscript focuses on nickel (oxy)hydroxide/oxide phases (e.g., NiOOH and NiO₂), a more reliable description of the ground state typically requires treating on-site correlation (e.g., DFT+U) and/or hybrid functionals. I recommend that the authors recalculate the key Raman predictions using PBE+U (and, if feasible, benchmark with a hybrid functional for at least one representative structure) to demonstrate that the central spectral assignments and conclusions are robust to the exchange–correlation treatment.

We thank the reviewer for the comment and performed additional calculations for NiOOH and NiO₂ structures and their Raman spectra using DFT+U, where the spectra are now included in an updated version of Figure 4 (and full spectra in Fig. S12.1). Still, none of the NiOOH spectra match the experimental findings, as supported by the absence of a deuterium shift in the isotope labeled experiment. In contrast, independent from the choice of the computational approach all spectra for NiO₂ look rather similar with small changes in peak intensity ratios and position, thus now providing a more reliable set of data for comparison. DOS were inferred from the calculations but were not perfectly conclusive, especially since reported experimental values on band gaps show strong discrepancies (see next comment 2). We also provide a more detailed discussion in the manuscript of the interatomic distances (Ni-Ni and Ni-O) of the materials in comparison with experimental values, which finally contribute to the discussion of the actual structural properties of the Ni anodes on the surface and the bulk.

The robustness of our computational approach is now also emphasized by performing additional similar calculations for Ni(OH)₂ (D3, Hubbard correction or hybrid functionals). Using DFT+U, previous theoretical and experimental results, including interatomic

distances, band gaps, and the Raman spectra of crystalline $\text{Ni}(\text{OH})_2$ could be reproduced (See section S12 and forward).

We further calculated the geometry and density of states of NiOOH and NiO_2 using Hybrid functionals (PBE0, HSE06, and B3LYP), showing similar lattice parameters. Resulting band gaps are addressed in the next comment. Due to computational limitations, Raman spectra using hybrid functionals were not calculated. It should be also noted that hybrid functionals may not necessarily be the most suitable approach for the electronic structure of Ni(hydr)oxides, as they significantly overestimate the band gap of $\text{Ni}(\text{OH})_2$ (see Section S13 for our values or <https://doi.org/10.1021/acscatal.1c04647> and <https://doi.org/10.1021/acs.jpcc.5b08481>) compared to DFT+*U*.

2-Please include the density of states (DOS) and/or band structures for the relevant structures computed with PBE and PBE+*U* (either in the main text or the Supplementary Information). This would allow readers to assess whether the predicted ground state changes (e.g., metal vs insulator) upon applying *U*, and would strengthen confidence that the chosen electronic-structure setup is appropriate for these Ni-based materials.

We thank the reviewer for these suggestions. We now included the DOS in the SI (Fig. S13.1 to S13.8) for all calculated bulk structures (including the newly studied $\text{Ni}(\text{OH})_2$ structures). The DFT and DFT+*U* calculations predict NiOOH to be metallic. Only hybrid calculations open up a direct bandgap (2.24 to 3.27 eV depending on method). On the other hand, non metallic direct band gaps are predicted for NiO_2 with all methods (PBE+D3: 0.95 eV, PBE+*U*: 1.58 eV and hybrid: 2.88 to 3.58 eV). Similar varieties in numbers were reported in the literature for computed band gaps as well as experimentally reported band gaps (1.7 - 3.75 eV). Considering these discrepancies of experimentally reported values, which we briefly mention in the manuscript and describe in more detail in Section S13 in the SI, we are hesitant in drawing any definitive conclusion on the robustness of the theoretical methods to describe DOS. However, the interatomic distances are almost unaffected from the choice of the DFT approach and thus serve as a more reliable descriptor for comparison with experimental results from the literature (see comment 3), which in combination with experimental results (Raman spectroscopy and isotope labeled experiments) provide a good agreement between experiment and theory.

3- The central conclusion—that the active near-surface structure under OER conditions is predominantly NiO_2 (Ni(IV)) rather than NiOOH , and that the additional bands arise from overtone/combination modes—rests heavily on Raman/SERS assignments and DFT spectral matching. To make this claim compelling for Nature Catalysis, the authors should provide independent operando evidence for Ni(IV)/ NiO_2 formation (or clearly rule out NiOOH), for example via operando XAS (XANES/EXAFS), complementary XPS (with careful consideration of surface sensitivity), or another orthogonal probe. At minimum, the manuscript should include a more quantitative discussion of alternative structural models (β/γ - NiOOH , defected/hydrated phases, intercalated $\text{K}^+/\text{H}_2\text{O}$, surface hydroxylation) and demonstrate that the key spectral conclusions remain unchanged across these plausible scenarios.

We separate this comment in i) operando XAS and complementary XPS, and ii) β/γ -NiOOH.

i) We agree that XAS measurements are beneficial, however, such measurements require beamline access (including the design of an appropriate setup) and can not be performed within the timeframe of the reviewing process. Fortunately, numerous EXAFS/XANES measurements have already been reported in literature (see also reviewer #2), which we now discuss in detail in the Section “DFT-guided Assignment of Raman Spectra”, primarily to compare computed and reported interatomic distances and structural parameters of NiO_2 , NiOOH , and Ni(OH)_2 . Comparisons for Ni(OH)_2 and NiO_2 are rather consistent in contrast to NiOOH . Oxidation states between 3 and 4 have been reported for NiOOH , and indeed reported bond lengths seem to correspond to those of Ni(OH)_2 and NiO_2 , suggesting a mixed structure. We now illustrate more clearly that SERS only probes the surface terminating NiO_2 layer(s), as discussed in Section “*Differences Between Surface and Bulk Structure*” (which includes a comparison of the surface sensitivity of SERS in contrast to XAS methods that usually probe both the surface and the bulk).

There exist already numerous XPS measurements in the literature of Ni anodes prepared in alkaline electrolytes. However, none of these works reported on NiO_2 (for example <https://doi.org/10.1016/j.elspec.2012.06.008>, <https://doi.org/10.1116/1.1247756>), most likely since this structure is considered rather unstable under ambient conditions or contact with water (<https://doi.org/10.1002/zaac.19502610103>) and thus likely decomposes during the transfer into the UHV chamber. In contrast, XPS measurements of Li_xNiO_2 (studied in the battery community and which we only found recently during the reviewing process), including $\text{Li}_{0.01}\text{NiO}_2$ prepared under inert atmosphere, have been reported (<https://doi.org/10.1021/acseenergylett.4c00360>), and show clear differences compared to Ni hydroxides studied in the aqueous electrocatalysis community (<https://doi.org/10.1016/j.elspec.2012.06.008>). Furthermore, even under their conditions, the surface of $\text{Li}_{0.01}\text{NiO}_2$ was reported to be reduced to Ni^{2+} according to XPS measurements. Only by employing synchrotron-based HAXPES measurements, the authors were able to detect Ni^{4+} in lower-lying layers with a probing depth of up to 34 nm. This particular work also reported Raman spectra, which they estimated to have a penetration depth of 100-200nm in their setup, and which resembles the spectrum for NiO_2 presented in our work. Furthermore they report on Ni–Ni interatomic distances inferred from XRD measurements, (Fig. S15 and Tab. S1 in <https://doi.org/10.1021/acsenergylett.4c00360>) which also fit well with our theoretical data. These aspects are now included in the discussion of our work.

ii) We agree with the reviewer that addressing the possible presence of β/γ -NiOOH and intercalated species might be relevant, as it is widely discussed in the community. We include in Section S4 SER spectra recorded on β/γ -NiOOH electrodes (prepared according to procedures reported in the literature). Despite significant changes in the redox peaks in the CV, the SER spectra do not show any measurable differences. Based on a more detailed discussion on the probing depth of SERS we conclude that these processes take place in the bulk and not the electrode surface.

Furthermore, according to Fig. 2 (now including data for LiOH, NaOH, KOH, and CsOH), possible intercalation of cations of various sizes does not have an effect on the SER

spectra (for 0.01 M solutions). These observations are consistent with works on the intercalation of Li into NiO₂ layers, where no significant changes in interatomic distances or Raman spectra were observed with Li loadings of 10% (<https://doi.org/10.1021/acsenenergylett.4c00360>) or 30% (<https://doi.org/10.1039/B003377O>).

Finally, these results show that the structural properties of the surface terminating layer (NiO₂) seems largely independent from possible phase transformations in the bulk and changes in the NiO₂ interlayer spacing due to intercalation processes in the near surface or regions below.

4 In Section S9 (“Computational method”), the authors state that a plane-wave cutoff of 500 eV for bulk and 600 eV for slab calculations was used, and that phonons were calculated with a 600 eV cutoff. Please explicitly justify why two different cutoffs were chosen for the wavefunction expansion (bulk vs. slab), and provide a simple convergence check (e.g., total energy and forces) demonstrating that these choices are sufficient for the reported results.

We thank the reviewer for the comment and agree that using a uniform cutoff of 600 eV provides a cleaner treatment. Accordingly, we have recalculated all structures with a 600 eV cutoff for improved comparison. Furthermore, the requested convergence check is provided in Tab. S10.1.

5- The computational workflow appears to assume only a ferromagnetic (FM) spin configuration for the Ni-based phases (e.g., NiOOH/NiO₂). Given that Ni 3d oxides/oxyhydroxides can favor antiferromagnetic (AFM) or more complex spin orderings depending on structure and oxidation state, restricting the study to FM may bias the predicted electronic structure and phonon/Raman properties. I recommend that the authors test at least a small set of plausible AFM configurations (and report relative energies and magnetic moments) to confirm that the FM ground state is energetically favorable

We agree with the reviewer that testing different spin configurations makes sense for the present system. Indeed the spin ordering is not conclusive in literature. Thus we calculated the bulk structure of Ni(OH)₂ and NiOOH in its AFM configuration with PBE+D3, PBE+*U*, and hybrid functionals. The magnetic moments for Ni atoms for Ni(OH)₂ and NiOOH bulk structure are provided in Tab. S11.2. The resulting energy, geometry and Raman spectra are only slightly affected by using this spin configuration. Similar conclusions are drawn from calculating an AFM arrangement for the NiOOH surface using PBE+D3 and PBE+*U*. Most significant changes are prominent in the DOS, which present a problem of its own as discussed in the reviewers comment 2 and in Section S13 in the SI.

Response to Reviewers' comments on manuscript NATCATAL-25112577A

Consequences of Overtones in Raman Spectra for Structural Assignment illustrated for Nickel Anodes during Alkaline Electrolysis

by J. Leist et al.

To assist in using this document, we have colored our **responses to the reviewers' comments in blue** and any **text from the manuscript in red**.

General comments to the Editor and Reviewers:

Comment from the editor: You will see that while think that the work has improved upon revision, they have raised points that need to be addressed before we can make a decision on publication. In particular both Reviewers 2 and 3 consider that the reaction mechanism should be studied to confirm that the proposed surface is catalytically active.

We would like to thank the Editor and all Reviewers for the time and effort devoted to evaluating our manuscript.

As discussed internally during the last revision and now suggested by Reviewer #2.2, we agree and follow his or her recommendation, to include a forward-looking discussion on the reaction mechanism in a new Section "Mechanistic Implications" at the end of the article.

The question whether the proposed surface is active is somewhat philosophical. The activity of the material is well established in the community, which found a consensus that the catalytically active surface consists of that specific phase (NiOOH). Based on the findings in our work it seems now very likely that the structure was misinterpreted. So, in principle the material did not change only the interpretation of the structure. Furthermore, we found one study on the OER activity for a free-standing NiO₂ sheet using DFT (albeit without inclusion of the electrolyte and using lattice parameters of γ -NiOOH), suggesting a lower overpotential for the OER than on NiOOH. (<https://doi.org/10.1002/celc.201700445>) We fully agree that further DFT calculations (as requested by Reviewer #3) will still be relevant to verify the claims from this previous work. However, considering the ongoing debate in literature and the discussion provided in our previous report, a rigorous and accurate DFT study on the reaction mechanism would be too extensive as it would require considering various possible mechanisms (each including a possible LOM or AEM mechanism) on pristine and defective surfaces with different orientation. In addition, besides coverage and co-adsorbate effects it would require a rigorous treatment of the electrode potential, solvation effects from the electrolyte, and thermochemical contributions. This is also elaborated in the revised version of the manuscript now.

Reviewer #1:

I'm satisfied by the corrections made to the manuscript per my comments.

We thank the Reviewer for the careful revision of our manuscript and for the positive feedback.

Reviewer #2:

The author further provided many experiments and DFT calculations to address the concerns raised by the reviewers. I am convinced that the second region is attributed to overtones and combination bands. Although the authors' revisions have resolved most of the technical issues, the following two more fundamental concerns continue to affect my overall assessment of the impact of this paper.

We thank the reviewer for the comments and are pleased with the reviewers evaluation of the overtones.

Major Issues:

1. The authors propose that SERS probes a surface termination layer that is pure NiO₂, while the bulk could remain as NiOOH. The core of this structural model rests on the experimental observation that "SERS probes only the outermost few monolayers." However, the authors do not provide structural evidence independent of Raman spectroscopy, with comparable surface sensitivity, to verify this NiO₂ termination layer.

With the techniques available to us, the combination of SERS, isotope labeled experiments, and DFT calculations is the only approach for *operando* characterization of the electrode material, providing a high level of consistency. Any *ex situ* technique, such as XPS, would lead to the decomposition of the material, which was discussed in our previous report to the reviewers. Hence to date, the only *in situ* and *operando* techniques, providing a similar level of detail are based on synchrotron measurements. These are, however, not readily available and are not feasible during the revision of the manuscript and, thus, in our opinion beyond the scope of this work (setting aside the fact that a model system and a specific electrochemical cell must be designed, which provide a comparable situation to that in our SERS experiments). However, as shown in our revised version (and the discussion in our previous responses) numerous results are available in literature already, which have been carefully summarized in tables and discussed in the Section "Differences Between Surface and Bulk Structures" in the revised version of our manuscript, to support our assignment. To clarify this aspect more explicitly, we highlight the issue of decomposing electrodes during *ex situ* characterization (including Refs. <https://doi.org/10.1039/d3cy00674c> and <https://doi.org/10.1002/zaac.19502610103>) and the role of synchrotron-based techniques in the the Section "Differences Between Surface and Bulk Structures".

2. The authors recognize that "our work does not primarily aim at providing direct insights into the OER mechanism on Ni," and emphasize that "detailed insights into the surface structural properties of a catalyst material are equally important." I agree with this view – resolving ambiguities in structural assignment before mechanistic studies indeed has significant foundational value. However, the current discussion in the manuscript stops at "the surface is NiO₂," with insufficient exploration of the catalytic mechanistic implications of this structural correction. As a reader of Nature Catalysis, I would expect at least a preliminary discussion of the following topics: If the active surface is NiO₂ (rather than the widely assumed NiOOH (valence

state 3.7)), what impact does this have on the widely discussed debate between the adsorbed oxygen mechanism (AEM) and the lattice oxygen mechanism (LOM) in OER? Is the reaction path or reaction intermediates' formation energy on the NiO₂ surface fundamentally different from that on the NiOOH surface? Can the existing DFT calculations provide some initial insights? Does the exploration of the electronic structure of the NiO₂ surface suggest reactivity characteristics fundamentally different from those of NiOOH (e.g., distribution of surface states)? I recognize that some of these questions may exceed the scope of the current DFT calculations, but providing a forward-looking qualitative analysis in the discussion section would significantly enhance the appeal of this work to readers in its core catalysis field.

During our last revision we indeed internally discussed on whether or not to include a section on the implications on the OER mechanism. We agree with the reviewer, and reconsidering our last decision, that at least a forward-looking discussion on the implications of our findings for the reaction mechanism would be of interest to the readers of Nature Catalysis. Thus, as requested, we now added a brief forward-looking Section "Mechanistic Implications" at the end of the manuscript focusing on the, in our opinion, most crucial aspects, including work using DFT calculations to study the OER on NiO₂ sheets as also noted in the comment to the editor (<https://doi.org/10.1002/celc.201700445>). We also highlighted this section with a sentence in the Abstract and the Introduction. A more extensive discussion will require a much more expanded addition to the already comparably lengthy new Section. We are looking forward reading dedicated extensive articles on the reaction mechanism in the future, which provide such detailed insights.

Minor Issues:

3. 1. In Figure 7, the potentials for 0.1 M, 0.01 M, 0.001 M KOH electrolyte are 1.6, 1.64 and 1.58 VRHE. However, in the main text, it is 1.6 VRHE on page 15.

We thank the reviewer for highlighting this inconsistency, which has now been fixed.

4. 2. On page 6, the author said "hence keeping the total ion concentration in the solution constant with respect to the 0.01 M KOH solution (pH = 12, black spectrum), did not reveal any measurable changes in either region I or II". While there is minor changes in the position of Peak I1 and I2, the peak intensity of I2 still can see comparable changes. The author should rewrite the above sentence to ensure its accuracy

The sentence has been rewritten to include this observation.

Reviewer #3:

The authors have addressed the previous comments appropriately, and the revised manuscript has improved. However, direct theoretical support for the catalytic activity of NiO₂ toward the OER is still lacking. Therefore, a DFT reaction profile confirming the OER activity of NiO₂ is needed.

The question of whether NiO_2 is the active surface has been addressed in the general comment to the editor.

As indicated in our previous report, we omitted a DFT-based reaction profile because a detailed mechanistic investigation would require extensive calculations which, we still believe, are beyond the scope of this work. Maybe this aspect was not perfectly clear in our previous report since we only mentioned one work on NiOOH and one on IrO_2 . Focusing on NiOOH , several groups tried in dedicated studies to elucidate mechanistic details over the past years (<https://doi.org/10.1021/jacs.9b13708>, <https://doi.org/10.1021/acscatal.7b00999>, <https://doi.org/10.1021/ja511559d>, <https://doi.org/10.1021/acscatal.1c04647>, <https://doi.org/10.1021/cs401245q>, <https://doi.org/10.1021/acs.jpcc.6b07931>, to name a few). Based on these studies one would have to consider different active sites, including the (001) surface and various edge and defect sites, as well as multiple reaction pathways, such as adsorbate-mediated and lattice-oxygen mechanisms each involving several possible elementary steps. Furthermore, the effects of the applied potential and the electrical double layer structure has to be considered as well as the effects of the different geometry, magnetization, and oxidation state. Furthermore, possible edge and defect structures must be reevaluated (and possibly supported by additional model catalysis studies) as the higher oxidation state of Ni could suppress oxygenated edge terminations.

We actually started looking into this aspect already several months back. This ongoing work did, however, not provide any conclusive answer yet. The key challenge is the large effort required to ensure for a representative catalyst model as well as an accurate computational treatment, which is further slowed down by inconsistencies in literature that we found during our previous revision between reported experimental band gaps, which have been addressed in our previous report, the manuscript, and the supporting information. As mentioned above, just recently we found a work from 2017, dealing with the activity of an isolated single layer NiO_2 sheet for the OER (however, outside of electrolyte and with lattice constants of NiOOH instead of NiO_2). The authors reported on very low overpotentials for this material, suggesting that it is active. (Again this article substantiates that an extensive DFT study is beyond the scope of our work) In total, we therefore rather follow the suggestion by Reviewer #2.2, to include a qualitative forward-looking discussion on this mechanistic aspect (including works using DFT).

Further Changes:

- A somewhat duplicate sentence in the introduction has been removed and a follow up sentence has been adapted.
- In the chapter "Differences Between Surface and Bulk Structure" we now properly differentiate between EXAFS and XANES in the two marked cases.
- Added missing transparent raw noise signal to Figure 6.
- Several grammatical mistakes were fixed.
- We double-checked every value in each table and noticed a few typographical errors. These corrections do not affect the interpretation of the results. To ensure accuracy, we replaced the manual comparison of tables against the data with a Python-based validation.

- During double-checking for errors, we identified discrepancies in the SI of Zaffran et al. (<https://doi.org/doi/10.1021/acs.jctc.6b00657>) between their raw data and their tabulated lattice parameters. All values reported in Tab. S11.1 were therefore taken from the raw data, which is now noted in the caption.
- For clarity the vacuum distances reported in the SI and the manuscript are now given as the total separation distances between layers across the vacuum region.

In this paper, the authors use operando/in situ SERS (including H/D isotope tests) together with DFT-calculated Raman spectra to reassess the surface structure of oxidized nickel (oxy)hydroxide catalysts under OER-relevant conditions. They argue that spectral features commonly assigned to NiOOH and to adsorbed superoxide-like intermediates are better explained by a NiO₂ (Ni(IV)) near-surface phase, and that several “extra” bands (regions II/III) arise from overtone/combination modes rather than distinct reaction intermediates. The work further proposes that reported potential- and pH-dependent band shifts can be largely rationalized by a vibrational Stark effect, implying that parts of the Raman-based mechanistic literature may require reinterpretation. Although the results are interesting, in its current format and level of supporting evidence I cannot recommend publication.

Below are my comments:

1-Since Ni is a 3d transition-metal ion and the manuscript focuses on nickel (oxy)hydroxide/oxide phases (e.g., NiOOH and NiO₂), a more reliable description of the ground state typically requires treating on-site correlation (e.g., DFT+U) and/or hybrid functionals. I recommend that the authors recalculate the key Raman predictions using PBE+U (and, if feasible, benchmark with a hybrid functional for at least one representative structure) to demonstrate that the central spectral assignments and conclusions are robust to the exchange–correlation treatment.

2-Please include the density of states (DOS) and/or band structures for the relevant structures computed with PBE and PBE+U (either in the main text or the Supplementary Information). This would allow readers to assess whether the predicted ground state changes (e.g., metal vs insulator) upon applying U, and would strengthen confidence that the chosen electronic-structure setup is appropriate for these Ni-based materials.

3- The central conclusion—that the active near-surface structure under OER conditions is predominantly NiO₂ (Ni(IV)) rather than NiOOH, and that the additional bands arise from overtone/combination modes—rests heavily on Raman/SERS assignments and DFT spectral matching. To make this claim compelling for *Nature Catalysis*, the authors should provide independent operando evidence for Ni(IV)/NiO₂ formation (or clearly rule out NiOOH), for example via operando XAS (XANES/EXAFS), complementary XPS (with careful consideration of surface sensitivity), or another orthogonal probe. At minimum, the manuscript should include a more quantitative discussion of alternative structural models (β/γ -NiOOH, defected/hydrated phases, intercalated K⁺/H₂O, surface hydroxylation) and demonstrate that the key spectral conclusions remain unchanged across these plausible scenarios.

4-In Section S9 (“Computational method”), the authors state that a plane-wave cutoff of 500 eV for bulk and 600 eV for slab calculations was used, and that phonons were calculated with a 600 eV cutoff. Please explicitly justify why two different cutoffs were chosen for the wavefunction expansion (bulk vs. slab), and provide a simple convergence check (e.g., total energy and forces) demonstrating that these choices are sufficient for the reported results.

4- The computational workflow appears to assume only a ferromagnetic (FM) spin configuration for the Ni-based phases (e.g., NiOOH/NiO₂). Given that Ni 3d oxides/oxyhydroxides

can favor antiferromagnetic (AFM) or more complex spin orderings depending on structure and oxidation state, restricting the study to FM may bias the predicted electronic structure and phonon/Raman properties. I recommend that the authors test at least a small set of plausible AFM configurations (and report relative energies and magnetic moments) to confirm that the FM ground state is energetically favorable.