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REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The manuscript reports the detection of carbon dioxide and hydrogen peroxide on Charon using data from JWST. Spectral modeling indicates that the CO₂ is crystalline, and possibly layered on top of crystalline water ice. The detections of CO₂ and H₂O₂ are robust, and well-supported by the presented data. The hypothesis that the crystalline CO₂ is layered is plausible, but by no means certain. However, the authors are suitably cautious in their presentation of this theory. I recommend publication with only some minor revisions, detailed below.

1. Line 168: "The JWST spectral aligns remarkably well..." "Remarkably" is a bit too strong here. The alignment is good, certainly, but I don't think that it's remarkable.
2. Lines 435-439. The laboratory experiments use a 2% CO₂ in H₂O film. What drove this choice of concentration? Also, two irradiation fluences were used. What drove the choice of these fluences? Can you comment on how these fluences relate to irradiation timescales on Charon?
3. Lines 619-624. The implantation of C⁺ ions into water ice with subsequent formation of CO₂ from the Solar wind is invoked as a possible contribution to the observed CO₂. Given the low flux of C⁺ in the Solar wind, and the low yield of CO₂ in this reaction, is this really a significant source of CO₂ on Charon? Some back of the envelope calculations could be made to see if this is worth mentioning as a possible contributor.
4. Line 642: "The radiolytic yield for each interface is modest, around 0.05-0.1 CO₂ molecules for every incoming proton, and the utmost quantity produced doesn't surpass approximately a few 10¹⁵ CO₂ molecules cm² per interface (due to CO₂ shielding the carbon from water and the destruction of CO₂ by incident ions)." This sentence requires a reference.
5. Line 719: The presence of amorphous water ice is explained through radiation-induced amorphization. Are there other processes that could lead to amorphous surface ice as well? For instance, re-deposition of water (generated from an impact, say) at Charon surface temperatures would likely also lead to amorphous ice.

6. Lines 829-849: Step two of the data reduction procedure describes the removal of flux from Pluto from the Charon spectra. Can you give a quantitative estimate of the contribution of flux from Pluto prior to removal? A figure showing the contamination spectrum, the initial Charon spectrum, and the result of the subtraction would be useful.

7. Line 905-926; Were the laboratory spectra taken in a reflection-absorption configuration? Can you comment on how this configuration compares to the diffuse reflectance spectra of Charon?

8. Line 1086. The ammonia concentration is given as approximately 1%. This seems like a useful result that should be incorporated into the main text, rather than buried in the Methods section.

9. Figure 1: The caption refers to the 2.2 μm feature as due to "NH₃-bearing species," while the figure labels the feature as "NH₃:H₂O." This is inconsistent and a bit confusing.

10. Figure 2: In the lower left panel, the Europa spectrum is not shown, while it is shown in the lower right panel. I suggest you include it, since there is a noticeable CO₂ peak in the Europa spectrum, and the comparison is informative. Additionally, in the lower two panels, the order of comparison spectra is different. The figure would be easier to read if the order were consistent between the two panels.

Reviewer #2 (Remarks to the Author):

Dear Editor,

Please find my review for "Discovery of Carbon Dioxide and Hydrogen Peroxide on Charon's Stratified Surface with JWST" by Protopapa et al. below. I enjoyed reading the manuscript and liked that observational and laboratory experts worked together on this, as I think it made the manuscript more thorough and identifications more convincing. Most of my suggestions are on clarity of presentation, as I do think the identifications made in this paper are reasonable and worthy of publication in a journal of this quality. Please have the authors prepare a point by point response to my comments below and show in the revised version where they addressed the comments (bold, italics, etc.).

Two broad points, which are reiterated below:

1) For the discussion section, the pieces are there but it is a bit hard to follow. I made some recommendations below to hopefully help make this clearer but I would encourage the authors to clearly read over the discussion, consider adding some subsections and check that it is not too repetitive. I think this would go a long way in improving this section.

2) For the results/discussion about CO₂ and its possible environments/modeling efforts, please double check the wording to make sure it is consistent throughout the text and methods section. I have made multiple notes below where the wording appears to be contradictory and did not realize until I read the last part of the methods that CO₂ is modeled with crystalline H₂O in the bottom layer of the ice.

Specific points

Line 64/65 – add keywords

Line 151 – “The Charon spectra” – does this mean the albedo or the absorption features/depths?

Figure 1 – top. The “Obs #” is a bit squished in a few cases. Perhaps only list the “Obs #” at the top and remove the three “Obs #” below, keeping the actual numbers by the spectra (106, 103, 005, 004).

Figure 2 – bottom left, is the data from Europa missing here? Is there data from Europa? Please clarify.

Line 212 – “Irradiation ...” – this refers to a previous work? Please clarify.

Line 204 – Paragraph beginning here - the wording is a bit awkward. Initially it is stated that the band profile matches crystalline CO₂. Then it lists all the other possibilities that do not work and then it is restated that it matches crystalline CO₂ again. Perhaps make this a bit more streamlined or direct, saying the figure shows a number of different environments and then saying which is best.

Line 241 – “triple” perhaps “three-component” is better?

Line 267 – please clarify the difference between “solid-state” and “crystalline” CO₂ mentioned earlier, as this seems contradictory. For CO₂ to be crystalline, it would have to be in the solid state and in precipitates, right?

Line 278 – Please clarify what is meant by “short wavelength absorption bands”.

Line 279 – Please clarify what is meant by “the layer”. Is this different than the depth below the surface or the penetration depths mentioned a few lines up?

Line 275- 280 – it seems the authors are saying two things regarding the CO₂, that it is less abundant than on other satellites but also that it is not below the surface layer. This could be true but this sounds contradictory. First, it is stated that low wavelengths are not observed, so it is not abundant. Next, it is stated low wavelengths are not observed because of the remote sensing depth. Please clarify.

Figure 2 – it would be easier to read if the spectra in 2c and 2d were stacked the same. It looks like they are in a different order. Please modify.

Line 322 – if CO₂ were embedded in H₂O-ice, the band should be asymmetric, and this is not the case. Please clarify.

Line 352 – Please clarify what is meant by “complexed CO₂”.

Line 355 – Starting here, I would clarify that the possibility being considered is that there are not actually two peaks but there is a Fresnel peak in the middle.

Line 377 – 389 – This explanation is reasonable and think it should be highlighted a bit more in that one could say there really is not a good lab fit to the lower wavelength peak, even though a number of environments have been considered. I would also clarify the layers the authors are considering. The way the text is written gives the impression that there is a crystalline layer of H₂O devoid of CO₂

and a thin layer of amorphous H₂O+CO₂ that has been formed by amorphization. However, in the methods section CO₂ is in the crystalline H₂O layer. Please clarify.

Figure 3b –The Charon spectrum looks worse than Figure 2b. Is that the same data? Please clarify.

Line 466 – Is there a hypothesis for the longer wavelength feature – carbonic acid, methanol?

Line 474 – if this spectrum is in good agreement with lab experiments with CO₂ and H₂O, then is there a shoulder in the Charon spectrum? Please clarify.

Line 481 – 485 – Is the structure apparent in both the NIMS feature as well as the JWST? Please clarify.

Line 480ish – the Europa data from JWST has structure that looks similar to an irradiated pure H₂O ice sample that has been cooled (see Figure 8 in Loeffler 2006). I am not saying that is what the structure is but interestingly it is in about the same spot.

Line 487 – can the authors give an approximate abundance?

Line 491 – H₂O₂ and ammonia are both detected on the surface, yet H₂O₂ and NH₃ have been shown to react thermally (Loeffler Hudson 2015), perhaps comment on the possibility of spatial variations that could be observed in future studies. Also, thermal reactions between these species may explain the lower abundances of H₂O₂ detected even though the temp is lower than on Europa; this should be considered in the text.

Line 536 – 7 – Please clarify how it is concluded that amorphous H₂O is in a thin surface layer. I believe I understand that it is in comparison to the near-IR data but I don't think this is clear as is written. I do see text following this that explains the reasoning but perhaps this can be tweaked a bit to make it more clear.

Line 535 – 549 – Is a grain size being assumed here? Please clarify.

Line 578 – pure CO₂ is segregated – is this contradictory with the modeling which shows crystalline H₂O and amorphous CO₂ mixed with amorphous water

Line 599 and below – “ly-alpha” should be “lyman-alpha”, right?

Line 629 – the statement that many lab experiments match the Lorentzian peak seems to contradict what is said earlier about the CO₂ band simply being altered from Fresnel reflection. Please clarify.

Line 635 – it seems this paragraph is intended to say CO₂ formed at the interface could explain the 2.7 micron feature. However, it does not actually link the previous paragraph to the next paragraph and so the authors’ intentions/argument are not clear. Also, wouldn’t the interfacial CO₂ have to diffuse and aggregate to make the 2.7 micron feature. Thousands of single ML layers of CO₂ that are separated probably would not have the appearance of polycrystalline CO₂. Please consider/clarify.

Line 668 – perhaps a subsection here.

Line 695 – this is the first time electrons are mentioned in the manuscript but it is possible they also play a role. Perhaps they should be mentioned earlier?

Line 696 – it is unclear whether the SW ions and electrons are only impinging on the sunlit hemisphere. Please clarify.

Line 703-5 – please add a reference for the gardening

Line 706-708 – please add a reference

Line 714 – 5 “Charon’s...” – this sentence seems out of place here. Perhaps rework this paragraph to be more concise.

Line 734 – Please clarify different radiation environments means – this might require invoking some timescale arguments.

Line 752 – 754 – I may have missed something but this seems to be the first time endogenous source has been used to explain what is found on Charon. According to the text, there is a pure crystalline h₂O layer with a layer of amorphous H₂O/CO₂ on the surface. Please clarify as this seems contradictory. Note the first line of the discussion says CO₂ came from a number of sources.

Line 928 – I only saw 5 keV electrons in the paper, were 10 keV electrons also used? Please clarify.

Line 1030 – 1035 – I don't think this is clearly stated in the manuscript. Please double check this.

Also, in this multilayer model, please clarify how thick the layers being modeled are.

Reviewer #3 (Remarks to the Author):

The manuscript presents very interesting observational results obtained with the NIRSPEC JWST instrument for Pluto's moon Charon. The observational data are thoroughly analyzed, and the conclusions are well supported by the analysis of the observations and lab experiments. The main content of the paper suits Nature Communications very well.

However, the paper is not focused on the main topic, announced in the title. It is organized rather eclectically, mixing the analysis of the main results with other topics that makes it hard to read and hard to detach the crucial information from the unnecessary details or details which are of interest only to the readers specializing in planetary spectrometry.

I suggest a significant editing of the paper to make it focused on the main results: discovery of the CO₂ and H₂O₂ spectral features and possible formation of the carbon dioxide and hydrogen peroxide in the surface layers of Charon.

Specifically, I am concerned about the following parts of the paper, which contain details not necessary for understanding the main results of the paper but divert the readers from the main topic of the paper:

- Section "Compositional Inventory" and related to it subsection of Methods "Ammoniated Species." They contain information that is not required for understanding the main results of the paper. It would be better to write a separate paper, focused on the ammonia-related bands in the Charon's spectrum.

- Subsection "Spectral modeling" in "Methods." It looks as if its results either duplicate the results from the lab measurements reported in the main body of the paper or fail to reproduce the spectra as it is in the case of H₂O₂ feature. Thus, this subsection contains information that is not very helpful, but it significantly complicates the paper.

- Also, I would remove supplementary figures. I have found that in many cases the paper refers to them together with the reference to a figure in the main body of the paper or together with references to other papers. Supplementary figures 2 and 4 might be OK for an astronomical paper, but the information they provide is too special to be in a paper in Nature Communications. Thus, it looks as if the supplementary figures contain some specific details but are not crucial for the paper. At the same time, they are very busy and complicated and contain very long and hard-to-comprehend captions.

As I said above, those parts of the paper are not wrong, but they make the paper loose and do not let the readers grasp the main reported achievements: the discovery of CO₂ and H₂O₂ on Charon, the mechanism of their formation, and the possible structure of the upper layers of Charon's surface.

The paper is also overwhelmed with the details of the data analysis which are not necessary but make it difficult to read the paper. Examples of such unnecessary details are: the mentioning of the opposition effect on page 5; the discussion on the bands around 2 microns and comparison with the Uranian satellites on page 6; the discussion that refers to Supplementary Figure 3b on page 7; details in the selection of the polynomial fit on pages 9-10, including the unproved influence of CH₃OH, and many smaller pieces of unnecessary information which I have not mentioned. Specifically, I would recommend removing numerous cases where the authors discuss some details of the spectra or their interpretation ending up with a conclusion "this is not clear," "this may be a result of the uncertainties..." Such statements are often not related to the main topic of the paper but reduce confidence in the results.

The abstract and Conclusions should be updated correspondingly. For example, I suggest, in Conclusions, changing the emphasis by moving the H₂O₂ discussion closer to the beginning of the section and a more hypothetical result on a layer of crystalline CO₂ closer to the end. Also, I strongly recommend removing the two last sentences in this section. I think Nature Journals' mission is to report outstanding scientific results, not possible plans for future research.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The manuscript reports the detection of carbon dioxide and hydrogen peroxide on Charon using data from JWST. Spectral modeling indicates that the CO₂ is crystalline, and possibly layered on top of crystalline water ice. The detections of CO₂ and H₂O₂ are robust, and well-supported by the presented data. The hypothesis that the crystalline CO₂ is layered is plausible, but by no means certain. However, the authors are suitably cautious in their presentation of this theory. I recommend publication with only some minor revisions, detailed below.

We appreciate the reviewer's insightful feedback. Our responses are highlighted in blue, and the text modifications made in the revised manuscript are also highlighted in blue and boldface for clarity.

1. Line 168: “The JWST spectral aligns remarkably well...” “Remarkably” is a bit too strong here. The alignment is good, certainly, but I don’t think that it’s remarkable.

The adjective 'remarkably' has been removed.

2. Lines 435-439. The laboratory experiments use a 2% CO₂ in H₂O film. What drove this choice of concentration? Also, two irradiation fluences were used. What drove the choice of these fluences? Can you comment on how these fluences relate to irradiation timescales on Charon?

The reviewer's feedback has been taken into consideration, and the text has been revised accordingly to address their points.

1. The choice of a 2% CO₂ concentration in the H₂O ice film for our laboratory experiments was guided by our aim to mimic the conditions observed on Charon's surface. Our spectral modeling of Charon's data in the region between 2.66 and 2.80 μm suggests an areal mixture of approximately 80% crystalline H₂O ice, 18% amorphous H₂O ice, and 2% crystalline CO₂. These modeling results have been included in the main text (Lines 310--315) and the reader is referred to the Spectral Modeling section in the Methods and Supplementary Figure 5 for details. This composition closely aligns with the conditions we aimed to replicate in our laboratory setting. The first paragraph of the Hydrogen Peroxide section has been revised to clarify the connection between laboratory data and observations and it now reads: “Considering the identification of CO₂ on Charon’s surface as well as on Europa, the results of our irradiation experiments with H₂O-CO₂ ice mixtures —**containing a 2% CO₂ concentration comparable to that on Charon**— are especially relevant for this analysis (see the Methods section for a detailed description of these experiments).” Finally, the first paragraph of the Laboratory Experiments section in Methods has been modified to highlight the connection between laboratory data and observations: “We deposited H₂O ice films (~1.5 μm thick) containing trace amounts of CO₂ (~2%, **which is similar to the CO₂ abundance estimated on Charon based on spectral modeling of the 2.7-μm v1 + v3 CO₂**

combination band; see text for details) relative to H₂O ice) onto a gold-coated quartz crystal microbalance (QCM).”

2. We present spectra at two levels of fluence to highlight the emergence of a shoulder feature at approximately 3.53 μm, which is likely indicative of CH₃OH. This feature is barely noticeable at intermediate fluence but becomes clearly visible in the high fluence spectra, affecting the full width at half maximum (FWHM) of the 3.5 μm absorption. The intermediate fluence corresponds to roughly 1400 Earth-years, while the higher fluence represents about 140,000 Earth-years of radiation exposure on Charon, assuming an energy flux of approximately 10⁹ eV cm⁻² s⁻¹ from solar wind at 33 au.

The text around Ln 578 has been modified: “**In the JWST spectrum of Europa, subtle structures appear on the long wavelength shoulder of the peroxide absorption, similar to those in irradiated H₂O ice films containing 2% CO₂ which we attribute to carbon-bearing organics. If these structures are confirmed by data processing with the latest JWST pipeline, they could be attributed to carbon-bearing organics.** These intriguing features are less obvious in Charon’s spectrum, (likely due to the lower signal-to-noise ratio). **We present spectra at two fluence levels to highlight the emergence of this shoulder feature around 3.53 μm. The intermediate fluence corresponds to approximately 1400 Earth-years, while the higher fluence represents about 140,000 Earth-years of radiation exposure on Charon, given 1-keV solar wind impinging at a 10¹⁰ m⁻² s⁻¹ flux [37].**”

[37] Bagenal, F. et al. in Solar Wind Interaction with the Pluto System (eds Stern, S. A., Moore, J. M., Grundy, W. M., Young, L. A. & Binzel, R. P.) The Pluto System After New Horizons 379–392 (2021).

The text around Ln 882 has been modified and it now reads “**Contrary to radiolysis of pure H₂O ice, radiolysis of H₂O:CO₂ ice mixtures not only produces H₂O₂ but also yields as well as formaldehyde, carbonic acid, and methanol [58–60]. At higher absorbed doses irradiation fluence (∼2400 eV mol⁻¹ ∼ 10¹⁸ e⁻ cm⁻², equivalent to ∼10⁵ years of solar wind exposure at Charon [61]), a shoulder, indicative of methanol, becomes evident appears at 3.53 μm in the laboratory spectrum, piercing through the nominal asymmetric peroxide absorption.**”

[61] Bennett, C. J., Pirim, C. & Orlando, T. M. Space-Weathering of Solar System Bodies: A Laboratory Perspective. Chemical Reviews 113, 9086–9150 (2013).

3. Lines 619-624. The implantation of C⁺ ions into water ice with subsequent formation of CO₂ from the Solar wind is invoked as a possible contribution to the observed CO₂. Given the low flux of C⁺ in the Solar wind, and the low yield of CO₂ in this reaction, is this really a significant source of CO₂ on Charon? Some back of the envelope calculations could be made to see if this is worth mentioning as a possible contributor.

We concur with the reviewer's suggestion that evaluating the various mechanisms contributing to the total CO₂ abundance, including C⁺ ion radiolysis and other processes discussed in the paper, is crucial to determine their significance. However, while we have revised the text to include the abundance of CO₂ responsible for the 2.7-micron absorption, we have not yet determined the CO₂ abundance at shallower depths. This determination requires a more robust spectral model than the one presented in the paper, as the stratification modeling is still qualitative. Consequently, we believe that assessing the strength of various CO₂-generating mechanisms is appropriate only after the necessary step of constraining Charon's CO₂ abundance has been completed.

4. Line 642: “The radiolytic yield for each interface is modest, around 0.05-0.1 CO₂ molecules for every incoming proton, and the utmost quantity produced doesn’t surpass approximately a few 10¹⁵ CO₂ molecules cm² per interface (due to CO₂ shielding the carbon from water and the destruction of CO₂ by incident ions).” This sentence requires a reference.

Thanks for pointing this out. We have added reference [48]

[48] Raut, U., Fulvio, D., Loeffler, M. J. & Baragiola, R. A. Radiation Synthesis of Carbon Dioxide in Ice-coated Carbon: Implications for Interstellar Grains and Icy Moons. *Astrophys. J.* 752, 159 (2012).

5. Line 719: The presence of amorphous water ice is explained through radiation-induced amorphization. Are there other processes that could lead to amorphous surface ice as well? For instance, re-deposition of water (generated from an impact, say) at Charon surface temperatures would likely also lead to amorphous ice.

Thanks for pointing this out. We acknowledge that both charged particle and UV photon irradiation of crystalline ice, as well as flash sublimation from impact heating followed by condensation on a cold surface, can damage the crystal structure, resulting in an amorphous configuration.

To address the reviewer’s point, we have revised the text in the third-to-last paragraph of the discussion section as follows: “The radiolytic synthesis of peroxide is also consistent with the presence of amorphous water ice on Charon’s surface. Impinging radiation, **as well as flash sublimation from impact heating followed by condensation on a cold surface**, can break down the crystalline structure [57]. The amorphized ice retains its ~~radiation-induced~~ disordered structure more effectively at Charon’s colder temperatures.”

6. Lines 829-849: Step two of the data reduction procedure describes the removal of flux from Pluto from the Charon spectra. Can you give a quantitative estimate of the contribution of flux from Pluto prior to removal? A figure showing the contamination spectrum, the initial Charon spectrum, and the result of the subtraction would be useful.

A figure illustrating Charon's flux before and after correction, along with Pluto's flux contamination, has been added. This figure replaces the previous Supplementary Figure 3. The contamination

from Pluto's flux is quantified in the figure's caption. Additionally, a reference to this figure has been added in the description of Step 2 of the data reduction process.

7. Line 905-926; Were the laboratory spectra taken in a reflection-absorption configuration? Can you comment on how this configuration compares to the diffuse reflectance spectra of Charon?

The reviewer raises a good point.

The text in the Laboratory Experiments section of the Methods has been revised from `` An infrared spectrum of the ice mixture, denoted by R...'' to `` A **specular reflectance** infrared spectrum of the ice mixture, denoted by R ..''

Additionally, we have added the following text at the end of the first paragraph:

`` **We note that the spectra of laboratory ice films, obtained in specular reflectance, differ from the directional hemispherical reflectance spectra of Charon's granular icy regolith. This discrepancy is primarily due to the absence of anisotropic scatterers and surface roughness in our laboratory ice films. Despite these differences, comparing the absorption band profiles—such as peak centers, asymmetry, and widths—between our laboratory data and astronomical observations proves to be a powerful method for deciphering the state or phases of surface constituents like CO₂ and H₂O₂ on Charon, as demonstrated in our study.**''

8. Line 1086. The ammonia concentration is given as approximately 1%. This seems like a useful result that should be incorporated into the main text, rather than buried in the Methods section.

We have already referred to this result in the " Compositional Inventory **Beyond Carbon Dioxide and Hydrogen Peroxide**" section (lines 613-630), in the "Discussion" section (lines 739, 939, and 956). Given that the main focus of the paper is the discovery of CO₂ and H₂O₂ on the surface of Charon, we do not believe it is necessary to further emphasize this result.

9. Figure 1: The caption refers to the 2.2 um feature as due to "NH₃-bearing species," while the figure labels the feature as "NH₃:H₂O." This is inconsistent and a bit confusing.

We have revised the figure caption to address the reviewer's comment.

10. Figure 2: In the lower left panel, the Europa spectrum is not shown, while it is shown in the lower right panel. I suggest you include it, since there is a noticeable CO₂ peak in the Europa spectrum, and the comparison is informative. Additionally, in the lower two panels, the order of comparison spectra is different. The figure would be easier to read if the order were consistent between the two panels.

Figure 2 has been updated to address the reviewer's comment.

Reviewer #2 (Remarks to the Author):

Dear Editor,

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We appreciate the reviewer's insightful feedback. Our responses are highlighted in blue, and the text modifications made in the revised manuscript are also highlighted in blue and boldface for clarity.

Specific points

Line 64/65 – add keywords

The "Keywords" section was included in the LaTeX file template used for submission. However, we did not find any specific instructions regarding keywords in the submission guide for Nature Communications. Therefore, we left it blank for the time being.

Line 151 – “The Charon spectra” – does this mean the albedo or the absorption features/depths?

The text has been modified to improve clarity. `` The Charon spectra, **specifically the I/F level and the depth of the absorption bands, show minimal variation with longitude.** ~~do not vary significantly with longitude, with an~~ The average standard deviation between the four spectra and across the entire wavelength range ~~of~~ **is 0.4%.**``

Figure 1 – top. The “Obs #” is a bit squished in a few cases. Perhaps only list the “Obs #” at the top and remove the three “Obs #” below, keeping the actual numbers by the spectra (106, 103, 005, 004).

Figure 1 has been updated to address the reviewer's comment.

Figure 2 – bottom left, is the data from Europa missing here? Is there data from Europa? Please clarify.

Figure 2 has been updated to address the reviewer's comment and now includes the Europa spectrum in the bottom left panel. This spectrum is the same as the one shown in Figure 2a but with the continuum removed.

Line 212 – “Irradiation ...” – this refers to a previous work? Please clarify.

Thank you for pointing this out. We have inserted Ref [16], Raut et al. (2013), at the end of the relevant sentence found in the paragraph near line 248 of the revised manuscript.

Line 204 – Paragraph beginning here - the wording is a bit awkward. Initially it is stated that the band profile matches crystalline CO₂. Then it lists all the other possibilities that do not work and then it is restated that it matches crystalline CO₂ again. Perhaps make this a bit more streamlined or direct, saying the figure shows a number of different environments and then saying which is best.

Following the reviewer's suggestion, the text has been revised to enhance clarity. The text now reads:

``Carbon dioxide (CO₂) ice on the surface of Charon is identified by its characteristic absorption features, specifically the $\nu_1+\nu_3$ combination band near 2.70 μm and the C=O asymmetric stretching fundamental ν_3 at 4.27 μm (Figure 2a and b).

We modeled the continuum region near 2.7 μm (red line, Figure 2a) without including a contribution from CO₂, de-weighting the data in the 2.69–2.71 μm range where the absorption band occurs (refer to the Spectral Modeling section in Methods for details). A Lorentzian fit to the continuum-removed combination band displays a sharp, narrow absorption at 2.6966 ± 0.0001 μm with a full width at half maximum (FWHM) of 0.00198 ± 0.0004 μm **and a band depth, relative to the continuum, of $32\pm 4\%$ (Figure 2c, red solid line).** ~~, consistent with laboratory spectra of pure (poly)crystalline CO₂ [15–18, Figure 2c].~~ The uncertainties in the FWHM, ~~and~~ band center, **and band depth** parameters were determined using Markov Chain Monte Carlo (MCMC) analysis

(Supplementary Figure 2). **For comparison, the JWST spectrum of Europa [14] displays a band with similar characteristics to that of Charon, but with a band depth on the order of 12% (Figure 2c, cyan points and red dashed line). Spectra of solid CO₂, from various matrix environments as reported by multiple laboratories, were compared with the CO₂ absorption feature at 2.7 μm observed on Charon, as illustrated in Figure 2c.**

Spectra of pure amorphous CO₂ do not align with Charon's 2.7- μm absorption feature. The $\nu_1+\nu_3$ band of solid amorphous CO₂ peaks close to 2.70 μm. However, its band center is shifted towards longer wavelengths compared to crystalline CO₂ [18]. Additionally, the band profile for the amorphous phase is broader, with a FWHM approximately three times larger than that of its crystalline counterpart [see olive dash-dot line in Figure 2c, 17–19].

Solid CO₂, when mixed with other constituents, does not yield a close match to Charon's 2.7 μm feature. For instance, irradiation of pure CO₂ ice with 100 keV H⁺ results in CO₂ depletion and the accumulation of CO, O₂, and minor species such as O₃ and CO₃ [16]. The changing matrix environment results in broadening of the 2.7-μm feature, as shown by the pink dashed line in Figure 2c [16]. ~~The $\nu_1+\nu_3$ band of solid amorphous CO₂ peaks close to 2.70 μm. However, its band center is shifted towards longer wavelengths compared to crystalline CO₂ [18]. Additionally, the band profile for the amorphous phase is broader, with a FWHM approximately three times larger than that of its crystalline counterpart.~~ Similar considerations apply to CO₂ diluted in H₂O, both in its pure form (olive dashed line in Figure 2c) and post irradiation (dark green solid line in Figure 2c). ~~We performed laboratory spectroscopy experiments on H₂O-CO₂ ice mixtures to enhance our understanding of Charon's JWST data. For more detailed information, refer to the Methods section.~~ The observed shift toward longer wavelengths and the broadening of the $\nu_1+\nu_3$ band upon diluting CO₂ in H₂O, **as seen in our laboratory data**, are consistent with other laboratory studies [20]. **For a detailed description of our laboratory experiments on H₂O-CO₂ ice mixtures the reader is referred to the Methods section.** CO₂ mixed with H₂O and methanol (CH₃OH) ices in nearly equal proportions, at temperatures relevant to the surface of Charon [approximately 50K, 21], is inconsistent with the observations. This discrepancy can be seen in the purple dash-dot line of Figure 2c.

Given these lines of evidence, **amorphous CO₂, irradiated CO₂, amorphous CO₂, CO₂ diluted in H₂O, and the triple three-component mixture of CO₂, CH₃OH and H₂O ice do not match the band position and profile of the $\nu_1+\nu_3$ band observed in Charon's JWST spectrum. Instead, pure (poly)crystalline CO₂ emerges as the primary contributor, as shown by the blue and cyan solid lines in Figure 2c [15-18] (see also Supplementary Figure 3a).** A subtle variation in the $\nu_1+\nu_3$ band position has been observed in laboratory measurements of pure crystalline CO₂ [15, 16, 18], which might be influenced by the CO₂ temperature and/or the sample's degree of crystallinity. ~~We modeled the continuum region near 2.7 μm (red line, Figure 2a) without including a contribution from CO₂, de-weighting the data in the 2.69–2.71 μm range where the absorption band occurs. The continuum is well represented by an intimate mixture of both crystalline (90%) and amorphous (10%) H₂O ice (refer to the Methods section for details on the spectral modeling). Charon's 2.7 μm CO₂ band depth is 32±4% relative to the continuum (Supplementary Figure 2)."~~

Line 241 – “triple” perhaps “three-component” is better?

Agreed. Changed to three-component. See above.

Line 267 – please clarify the difference between “solid-state” and “crystalline” CO₂ mentioned earlier, as this seems contradictory. For CO₂ to be crystalline, it would have to be in the solid state and in precipitates, right?

The reviewer's observation is well-received; for CO₂ to exhibit crystalline properties, it must be in a solid state. To enhance clarity, the term 'crystalline' has been added to the text. Please refer to the revised text in the answer to the comment raised for lines 275-280.

Line 278 – Please clarify what is meant by “short wavelength absorption bands”.

To address the inquiry regarding ‘short wavelength absorption bands,’ we have identified them as ($2\nu_1+\nu_3$, $\nu_1+2\nu_2+\nu_3$, $4\nu_2+\nu_3$) in the manuscript for improved clarity. Please refer to the revised text in the answer to the comment raised for lines 275-280.

Line 279 – Please clarify what is meant by “the layer”. Is this different than the depth below the surface or the penetration depths mentioned a few lines up?

'The layer' refers to the specific depth below the surface at which CO₂ can be detected. We have revised the text to enhance clarity on this point. Please refer to the revised text in the answer to the comment raised for lines 275-280.

Line 275- 280 – it seems the authors are saying two things regarding the CO₂, that it is less abundant than on other satellites but also that it is not below the surface layer. This could be true but this sounds contradictory. First, it is stated that low wavelengths are not observed, so it is not abundant. Next, it is stated low wavelengths are not observed because of the remote sensing depth. Please clarify.

The text has been revised to improve clarity. The text on line 317 of the revised manuscript now reads:

“We also do not find evidence for the absorption bands of solid-state **crystalline** CO₂ [15] at 1.97 μm ($2\nu_1+\nu_3$), 2.01 μm ($\nu_1+2\nu_2+\nu_3$) and 2.07 μm ($4\nu_2+\nu_3$), consistent with the New Horizons data (Figure 1g and Supplementary Figure 1). ~~This implies that CO₂ is less abundant on Charon compared to the Uranian moons [e.g., 22] and Triton [e.g., 23].~~ It is worth noting that, based on absorption coefficient considerations [18], the $\nu_1+\nu_3$ and ν_3 CO₂ absorption bands probe penetration depths of 1 μm and 0.1 μm , respectively. **These depths refer to how far into a material the light can penetrate before being absorbed, directly relating to the depth below the surface that is being probed.** In contrast, the short wavelength absorption bands (i.e., $2\nu_1+\nu_3$, $\nu_1+2\nu_2+\nu_3$, $4\nu_2+\nu_3$ [15]) **investigate probe the occurrence of CO₂ at approximate depths of ~50 μm for $\nu_1+2\nu_2+\nu_3$, ~100 μm for $2\nu_1+\nu_3$, and ~300 μm for $4\nu_2+\nu_3$.** ~~to depths of the layer between 50 and 300 μm .~~ Therefore, the lack of detection of CO₂ absorption features at short wavelengths **near ~2 μm**

implies that this compound is sparse at penetration depths greater than several tens of microns, **contrary to the case of the Uranian moons [e.g., 22] and Triton [e.g., 23].**”

Figure 2 – it would be easier to read if the spectra in 2c and 2d were stacked the same. It looks like they are in a different order. Please modify.

Figure 2 has been modified to address the reviewer’s comment.

Line 322 – if CO₂ were embedded in H₂O-ice, the band should be asymmetric, and this is not the case. Please clarify.

Figure 2, panel d, displays two spectral representations of CO₂ diluted in H₂O: one in its pure state (represented by the olive dashed line) and the other post-irradiation (indicated by the dark green solid line). The pre-irradiation spectrum reveals an asymmetric ν_3 band profile, which aligns with the reviewer's expectations for an embedded CO₂ scenario. This asymmetry, however, is not preserved post-irradiation; the spectrum of the ice mixture after irradiation to a dose of approximately 10^{18} electrons cm^{-2} presents a pronounced peak at 4.27 μm characterized by a symmetric profile.

Line 352 – Please clarify what is meant by “complexed CO₂”.

The text has been revised to improve clarity. The text on line 415 of the revised manuscript now reads:

“While we do not provide a definitive assignment to this feature, we remain open to the possibility of ~~complexed~~ **CO₂ embedded in a complex water/organic-rich molecular environment (referred to as complexed CO₂), akin to that of Europa [14],** as an explanation for the 4.23- μm absorption band observed in the spectrum of Charon.”

Line 355 – Starting here, I would clarify that the possibility being considered is that there are not actually two peaks but there is a Fresnel peak in the middle.

The text has been revised to improve clarity. The text on line 423 of the revised manuscript now reads:

“~~An alternative explanation is that the reflectance peak in Charon's spectrum at 4.265- μm could be attributed to a CO₂ ice Fresnel reflection peak.~~ **interpretation suggests that the observed spectral feature might not result from two separate absorption bands, but possibly from the presence of a Fresnel peak of CO₂ ice at 4.265 μm , contributing to the appearance of a double-peaked structure”**

Line 377 – 389 – This explanation is reasonable and think it should be highlighted a bit more in that one could say there really is not a good lab fit to the lower wavelength peak, even though a number of environments have been considered. I would also clarify the layers the authors are considering. The way the text is written gives the impression that there is a crystalline layer of H₂O

devoid of CO₂ and a thin layer of amorphous H₂O+CO₂ that has been formed by amorphization. However, in the methods section CO₂ is in the crystalline H₂O layer. Please clarify.

The text has been revised to follow the advice of the reviewer. The text on line 466 of the revised manuscript now reads:

“Although we do not rule out the idea of complexed CO₂ or CO₂ diluted in H₂O ice and exposed to radiation, possibly in conjunction with another compound causing the short-wavelength lobe of the dual-peaked feature, our preferred interpretation for the double-peaked ν_3 band is that it originates from **crystalline CO₂ and amorphous H₂O ice resting atop a layer of crystalline H₂O ice and tholin**~~crystalline CO₂ resting atop a layer of crystalline water ice~~. This may be in conjunction with CO₂ that has undergone irradiation. This explanation is particularly convincing as it accounts for the characteristics of both the $\nu_1+\nu_3$ and ν_3 bands and aligns with the geological data on Charon as reported by the New Horizons mission. **Furthermore, laboratory data do not adequately match the short-wavelength lobe of the double-peaked feature, despite considering various environmental conditions.**”

Figure 3b –The Charon spectrum looks worse than Figure 2b. Is that the same data? Please clarify.

The Charon data presented in Figures 2a, 2b, 3a, and 3b is indeed the same. In Figures 2a and 2b, the spectrum is displayed without error bars to provide a clear view of the spectral features. In contrast, Figures 2c and 2d show the continuum-removed data along with their corresponding error bars for a more detailed analysis. Similarly, Figures 3a and 3b present the data with error bars included. To enhance clarity, we have modified the presentation in these figures by displaying the error bars in grey and the data points as black dots. This approach ensures that the reader can access different visual representations of the same dataset across the figures.

Line 466 – Is there a hypothesis for the longer wavelength feature – carbonic acid, methanol?

The sentence immediately before (around line 544) reads “The width of the 3.5- μ m absorption band can be slightly influenced by the choice of continuum, such as the polynomial order or the selection of the masking zone. Additionally, the shape of the 3.5- μ m band undergoes a notable alteration with varying irradiation fluence on the H₂O:CO₂ (1:0.02) mixture. As irradiation fluence increases, ~~the~~ structures on the long wavelength shoulder of the peroxide absorption become increasingly pronounced (see comparison between magenta dashed and dotted lines in Figure 4b). These structures are likely attributable to by-products like CH₃OH [36].”

However, we have reiterated this concept in the sentence pointed out by the reviewer and the text now reads: “**Specifically,** ~~the~~ profile of the 3.5- μ m absorption resulting from the irradiation of CO₂ diluted in H₂O can be decomposed into two distinct components: the first component, centered around \sim 3.5 μ m, is associated with H₂O₂; the second, ~~which is sharper,~~ **is and** centered at approximately 3.53 μ m,~~and~~ is linked to other species **like CH₃OH [36].**”

Line 474 – if this spectrum is in good agreement with lab experiments with CO₂ and H₂O, then is there a shoulder in the Charon spectrum? Please clarify.

The paragraph following line 474 (now line 568) addresses this aspect and has been updated to read:

“In the JWST spectrum of Europa, subtle structures appear on the long wavelength shoulder of the peroxide absorption, similar to those in irradiated H₂O ice films containing 2% CO₂ which we attribute to carbon-bearing organics. If these structures are confirmed by data processing with the latest JWST pipeline, they could be attributed to carbon-bearing organics. These intriguing features are less obvious in Charon’s spectrum, (likely due to the lower signal-to-noise ratio). We present spectra at two fluence levels to highlight the emergence of this shoulder feature around 3.53 μm. The intermediate fluence corresponds to approximately 1400 Earth-years, while the higher fluence represents about 140,000 Earth-years years of radiation exposure on Charon, given 1-keV solar wind impinging at a 1010 m⁻² s⁻¹ flux [37].”

We consider this explanation adequate to suggest that there is likely a long wavelength shoulder present, but its definitive identification is challenging due to the constraints imposed by the limited signal-to-noise ratio.

Line 481 – 485 – Is the structure apparent in both the NIMS feature as well as the JWST? Please clarify.

We have updated the text to provide further clarification on this matter. For details, please refer to the revised text provided in the point above.

Line 480ish – the Europa data from JWST has structure that looks similar to an irradiated pure H₂O ice sample that has been cooled (see Figure 8 in Loeffler 2006). I am not saying that is what the structure is but interestingly it is in about the same spot.

We appreciate the reviewer's observation, which is indeed intriguing. However, as noted by Loeffler et al. (2006), the shoulder at short frequencies becomes apparent only under specific conditions: when the irradiated film is annealed to 120 K and then cooled back to 20 K. The diurnal temperature range on Europa is between 80 K and 130 K, and although temperatures at higher latitudes may drop to as low as 50 K, they do not reach 20 K.

Line 487 – can the authors give an approximate abundance?

Thank you for your question about the relative abundance of H₂O₂ on Charon compared to Europa. While we understand the desire for a quantitative comparison, accurately determining the abundance of H₂O₂ requires complex spectral modeling. This modeling must take into account various factors, including grain size variations, which can significantly influence abundance estimates. Furthermore, the potential stratification on Charon and uncertainties in the optical constants of amorphous H₂O ice around 3.5 microns add to the complexity. Consequently, a direct comparison between the H₂O₂ abundances on Charon and Europa is challenging without extensive modeling that addresses these considerations, and this is beyond the scope of our current study.

Line 491 – H₂O₂ and ammonia are both detected on the surface, yet H₂O₂ and NH₃ have been shown to react thermally (Loeffler Hudson 2015), perhaps comment on the possibility of spatial variations that could be observed in future studies. Also, thermal reactions between these species may explain the lower abundances of H₂O₂ detected even though the temp is lower than on Europa; this should be considered in the text.

The reviewer raises an excellent point. We have added the following in the second-to-last paragraph of the Discussion section: **"Additionally, solid NH₃, present on Charon's surface, can also react with and destroy H₂O₂ at temperatures exceeding 50 K [65], which may partially explain the lower H₂O₂ levels on Charon compared to Europa."**

[65] Loeffler, M. J. & Hudson, R. L. Descent without Modification? The Thermal Chemistry of H₂O₂ on Europa and Other Icy Worlds. *Astrobiology* 15, 453–461 (2015).

Line 536 – 7 – Please clarify how it is concluded that amorphous H₂O is in a thin surface layer. I believe I understand that it is in comparison to the near-IR data but I don't think this is clear as is written. I do see text following this that explains the reasoning but perhaps this can be tweaked a bit to make it more clear.

The text has been revised to improve clarity. The text on line 631 of the revised manuscript now reads:

"Our ~~The~~ analysis of Charon's 3- μ m spectral region, as detailed in the Spectral Modeling section of the Methods, reveals the presence of amorphous H₂O ice, **which accounts for approximately 20%** ~~accounting for about 10%~~ of the surface. **This finding contrasts with previous studies that have primarily detected crystalline H₂O ice, constituting at least 90% of the surface composition, in the shorter wavelength range below 2.5 μ m [e.g., 5]. These studies suggested a minimal presence of amorphous H₂O ice, a conclusion also supported by New Horizons data analyses, which did not favor including amorphous H₂O ice in spectral models for wavelengths of 1.2-2.5 μ m [8]. The disparity in H₂O ice absorption coefficients at different wavelengths provides further insight,** ~~which focused on the shorter wavelength range below 2.5 μ m, identified a dominant presence of at least 90% crystalline H₂O ice on Charon's surface [e.g., 5]. Such a high percentage suggested only a limited presence of amorphous H₂O ice, particularly in light of the existence of dark materials. Furthermore, analysis of New Horizons data did not support the inclusion of amorphous H₂O ice in the models [8]. Regions with a higher likelihood of containing amorphous ice frequently appear darker in panchromatic images, potentially suggesting an older age [6]. The necessity of incorporating amorphous H₂O ice for accurately modeling the 3- μ m region aligns with the observation of a much stronger absorption in this wavelength range and suggests that the amorphous H₂O ice predominantly exists in a very thin surface layer. At 40K, the H₂O ice absorption bands at 1.5 and 2.0 μ m present peak absorption coefficients of approximately 50 and 100 cm⁻¹, respectively [38]. These values correspond to photon penetration depths in ice of around 200 and 100 μ m, respectively. The 3.0- μ m H₂O ice absorption band displays peak absorption coefficients nearing 14450 cm⁻¹ [34], corresponding to photon penetration~~

depths in ice of approximately 0.7 μm . As a result, spectroscopic measurements beyond 2.5- μm probe a surface layer less than a micron in depth. **The necessity to include amorphous H₂O ice for accurately modeling the 3- μm region, coupled with the absence of amorphous ice signatures in spectroscopic measurements below 2.5 μm , leads us to conclude that amorphous H₂O ice is present primarily in a very thin surface layer.**

Line 535 – 549 – Is a grain size being assumed here? Please clarify.

For comprehensive details on our spectral modeling approach, including grain size determination, we refer the reader to the Spectral Modeling section in the Methods. This section outlines the model's free parameters, which include the effective grain diameter (D_i) and the contribution of each surface terrain to the mixture, expressed as either fractional area (F_i) or fractional volume (V_i), depending on the specific mixture being analyzed. The optimization of these parameters is performed using the Levenberg-Marquardt χ^2 minimization algorithm, ensuring a close fit between the model and the spectral observations [74].

Line 578 – pure CO₂ is segregated – is this contradictory with the modeling which shows crystalline H₂O and amorphous CO₂ mixed with amorphous water

We are grateful for the chance to clarify this aspect and have adjusted our manuscript to prevent any potential misunderstanding. To clarify, our model explicitly accounts for crystalline CO₂, not amorphous CO₂. The distinct 2.7 μm Lorentzian absorption feature suggests that a portion of the surface CO₂ has segregated and crystallized, likely due to thermal processes. This specific observation is in agreement with our spectral model, which is tailored to qualitatively reproduce the observed spectral features at longer wavelengths and to reflect Charon's geological makeup, including its mixtures of ices and tholin-like compounds.

Further clarifications include:

1. The model consists of two principal surface units: the first, `runit1`, is an intimate mixture comprising crystalline water ice, amorphous water ice, crystalline CO₂ ice, and tholin-like materials; the second, `runit2`, is characterized by a stratified medium where amorphous water ice and crystalline CO₂ overlie a bed of crystalline water ice and tholin-like materials. We have revised our text to underscore that CO₂ is modeled solely in its crystalline form.
 - Line 432. The text has been revised and it now reads `` This is particularly relevant when visualizing a two-layered structure where amorphous H₂O ice and **crystalline** CO₂ particles overlay a bed of crystalline H₂O ice and tholin-like materials (Figure 3).’’
 - Line 452. The text has been revised and it now reads “This model displays two Fresnel peaks, one due to H₂O ice at 3.1 μm and one at 4.265 μm due to **crystalline** CO₂.’’
 - Line 440. We have updated the text as follows: “**The model shown as red solid line in Figure 3 consists of an areal mixture of two distinct surface units: the first comprises an intimate mixture of crystalline H₂O ice, amorphous H₂O ice, crystalline CO₂ ice, and tholin-like materials (`runit1`); the second unit is characterized**

by a two-layer medium dominated by amorphous H₂O ice and crystalline CO₂ on top of crystalline H₂O ice and tholins (runit2). ``

2. The aforementioned segregation pertains to surface CO₂ crystallization events, which are a result of localized thermal effects, and this detail complements the presence of crystalline CO₂ within the model's framework.
3. At no point do we suggest the incorporation of amorphous CO₂ in our model.
4. Our modeling strategy employs the effective medium theory with the Bruggeman mixing formula to estimate the optical constants of the layered structures. In accordance with our model, the upper layer consists of a mix of amorphous H₂O ice and crystalline CO₂ ice, while the lower layer combines crystalline H₂O ice with tholin-like compounds. We clearly state in the Spectral Modeling section in Methods “This method assumes that the medium’s end-members are distinct from one another at the molecular level and retains the spectral characteristics of each individual end-member.”

Thus, the segregation and crystallization phenomena of CO₂ align with the model we propose.

Line 599 and below – “ly-alpha” should be “lyman-alpha”, right?

Corrected. Both "Ly-alpha" and "Lyman-alpha" are acceptable as long as "L" is capitalized. We use the full spelling in the first mention. The text (line 752) has been updated to: "Processing of Charon’s hydrocarbons by interplanetary medium (IPM) and **solar Lyman α (Ly-α) UV photons**, ..."

Line 629 – the statement that many lab experiments match the Lorentzian peak seems to contradict what is said earlier about the CO₂ band simply being altered from Fresnel reflection. Please clarify.

We appreciate the reviewer's attention to this detail. We have concluded the Section “Carbon Dioxide Detection” by stating “Although we do not rule out the idea of complexed CO₂ or CO₂ diluted in H₂O ice and exposed to radiation, possibly in conjunction with another compound causing the short-wavelength lobe of the dual-peaked feature, our preferred interpretation for the double-peaked ν_3 band **is that it originates from crystalline CO₂ and amorphous H₂O ice resting atop a layer of crystalline H₂O ice and tholins**~~crystalline CO₂ resting atop a layer of crystalline water ice~~. This may be in conjunction with CO₂ that has undergone irradiation. This explanation is particularly convincing as it accounts for the characteristics of both the $\nu_1+\nu_3$ and ν_3 bands and aligns with the geological data on Charon as reported by the New Horizons mission. **Furthermore, laboratory data do not adequately match the short-wavelength lobe of the double-peaked feature, despite considering various environmental conditions.**”

Around Line 752, we discuss the aspect related to the potential contribution of radiolysis of hydrocarbons mixed with water ice to Charon's CO₂ inventory. We mention that the band profile of

the ν_3 CO₂ absorption band generated from photolysis/radiolysis of hydrocarbon-water ice mixtures in multiple laboratory experiments reasonably matches Charon's 4.27 μm Lorentzian peak.

Therefore, there is no contradiction in our statements. The reference to laboratory experiments matching the Lorentzian peak is specific to the context of radiolysis of hydrocarbons mixed with water ice.

Line 635 – it seems this paragraph is intended to say CO₂ formed at the interface could explain the 2.7 micron feature. However, it does not actually link the previous paragraph to the next paragraph and so the authors' intentions/argument are not clear. Also, wouldn't the interfacial CO₂ have to diffuse and aggregate to make the 2.7 micron feature. Thousands of single ML layers of CO₂ that are separated probably would not have the appearance of polycrystalline CO₂. Please consider/clarify.

The opening of the "Discussion" section has been revised to clarify the goal of this discussion. The text at the beginning of the section now reads: "**We explore ~~Solid CO₂ on Charon likely originated from~~ multiple potential sources for the solid CO₂ detected on Charon, which include –endogenic, exogenic, and/or produced in-situ formation from radiation processing. Each source is considered for its ability to contribute to the spectral features observed on Charon, with careful consideration of the moon's environmental conditions. This discussion aims to decipher the complex processes that could have contributed to shaping Charon's present composition, as indicated by spectroscopic evidence.**"

Additionally, the text related to the formation of CO₂ from radiolysis at the interphase between carbon and water has been revised to directly address the reviewer's comment. The text on line 791 of the revised manuscript now reads:

"Radiolysis at the interfaces between carbon and water, involving carbonaceous residues embedded in water ice, offers an additional mechanism for producing solid CO₂ on Charon's surface [46–48]. These residues could be native to Charon or derived exogenously from Kuiper belt impactors or interplanetary dust particles [8]. The radiolytic yield for each interface is modest, around 0.05-0.1 CO₂ molecules for every incoming proton, and the utmost quantity produced doesn't surpass approximately a few 10^{15} CO₂ molecules cm^{-2} per interface (due to CO₂ shielding the carbon from water and the destruction of CO₂ by incident ions) [48]. However, the cumulative effects of multiple interfaces within Charon's meters-thick radiolytic layer (considering GCRs) makes this a viable mechanism that adds to Charon's CO₂ stockpile. **The 4.27- μm CO₂ absorption band observed on the surface of Charon could be produced by this mechanism after diffusion or desorption followed by gravitational return [48].** The interfacial oxidation reaction likely prevents complete carbonization of the dark neutral absorber or tholins thought to be present at levels of up to 50% by volume fraction [3, 8]. These dark absorbers likely contribute to the greyish coloration on Charon, especially towards lower latitudes below $\sim 70^\circ$.

In summary, ~~delivery of, and/or excavation of primordial CO₂ by impactors can explain the 2.7- μm and 4.27- μm features.~~ CO₂ produced in-situ from radiation processing could contribute to the most surficial (**$\sim 0.1 \mu\text{m}$ penetration depth**) CO₂ layer. **However, laboratory experiments simulating these formation mechanisms do not show the resulting 2.7- μm absorption band,**

challenging the possibility to assess whether these processes alone would be compatible with the overall CO₂ spectral behavior observed on Charon. Given the laboratory results for CO₂ embedded in other compounds before and after irradiation, we speculate that the 2.7- μ m feature resulting from in-situ processing might not be consistent with the observations, and thermal annealing would be required. Further discrimination between these processes This has potentially interesting implications for the fate of CO₂ Charon may have inherited from the proto-Pluto and the Charon-forming impactor during and after the formation of Charon itself. ``

Line 668 – perhaps a subsection here.

We appreciate the suggestion for a subsection at Line 668. However, we believe that the current structure of the Results section, which is divided into three parts: 1) Carbon Dioxide Detection, 2) Hydrogen Peroxide Detection, and 3) Compositional Inventory **Beyond Carbon Dioxide and Hydrogen Peroxide**, effectively organizes our findings. The Discussion section is designed to provide an overarching understanding of the mechanisms at play on Charon, in light of the compositional portrait revealed by the JWST. Therefore, we do not see a necessity for an additional demarcation at this point. Additionally, the formatting guidelines for the Discussion section do not permit the use of subheadings.

Line 695 – this is the first time electrons are mentioned in the manuscript but it is possible they also play a role. Perhaps they should be mentioned earlier?

Agreed. We revised the text around line 752 to read: “Processing of Charon’s hydrocarbons by interplanetary medium (IPM) and **solar Lyman α (Ly- α) UV photons**, solar wind (SW) **ions and electrons** and Galactic Cosmic rays (GCRs) could yield a fraction of the observed CO₂.”

Line 696 – it is unclear whether the SW ions and electrons are only impinging on the sunlit hemisphere. Please clarify.

| Yes, solar wind ions and electrons only impact the sunlit hemisphere.

The text has been revised to improve clarity. The text on line 867 of the revised manuscript now reads: “Charon’s **global** H₂O ice rich surface is ~~continually~~**continuously** processed by **GCRs**, ~~solar ultraviolet~~ and IPM Ly- α photons [54], **as well as** by solar wind ions and electrons and solar UV photons on the sunlit hemisphere [37, 55], ~~and GCRs to collectively synthesizing~~**peroxide**.”

Line 703-5 – please add a reference for the gardening

We have added references [56] and [57]:

Grün, E., Horanyi, M. & Sternovsky, Z. The lunar dust environment. Planet. Space Sci. 59, 1672–1680 (2011).

[57] Costello, E. S., Phillips, C. B., Lucey, P. G. & Ghent, R. R. Impact gardening on Europa and repercussions for possible biosignatures. *Nature Astronomy* 5, 951–956 (2021).

Line 706-708 – please add a reference

We have added [58–60]:

[58] Pirronello, V., Brown, W. L., Lanzerotti, L. J., Marcantonio, K. J. & Simmons, E. H. Formaldehyde formation in a H₂O/CO₂ ice mixture under irradiation by fast ions. *Astrophys. J.* 262, 636–640 (1982).

[59] Gerakines, P. A., Moore, M. H. & Hudson, R. L. Carbonic acid production in H₂O:CO₂ ices. UV photolysis vs. proton bombardment. *Astron. Astrophys.* 357, 793–800 (2000).

[60] Pilling, S. et al. Radiolysis of H₂O:CO₂ ices by heavy energetic cosmic ray analogs. *Astron. Astrophys.* 523, A77 (2010).

Line 714 – 5 “Charon’s...” – this sentence seems out of place here. Perhaps rework this paragraph to be more concise.

The text has been revised to improve the logical flow. The text on line 882 of the revised manuscript now reads:

“Contrary to radiolysis of pure H₂O ice, radiolysis of H₂O:CO₂ ice mixtures not only produces H₂O₂ but also yields as well as formaldehyde, carbonic acid, and methanol [58-60]. At higher absorbed doses irradiation fluence ($\sim 2400 \text{ eV mol}^{-1}$, $\sim 10^{18} \text{ e}^{-} \text{ cm}^{-2}$ equivalent to $\sim 10^5$ years of solar wind exposure at Charon [61]), a shoulder, indicative of methanol, appears becomes evident at 3.53 μm in the laboratory spectrum, piercing through the nominal asymmetric peroxide absorption. Although this feature is not apparent While this methanol-related shoulder at 3.53 μm is not observable in the Charon JWST/NIRSpec spectra, the presence of CO₂ implies that the 3.5 μm absorption feature might not be solely attributable to H₂O₂. We cannot rule out the enhancing contribution of C-bearing species to the 3.5 μm feature due to overlapping absorptions. Charon’s 3.5 μm absorption may not be exclusive to H₂O₂, given the presence of CO₂. Consequently, we cannot dismiss the potential enhancing contribution of overlapping absorptions from other radiolytic organics. Additionally, weaker methanol absorption bands, that are expected at around 2.27 μm , remain undetected as well.”

Line 734 – Please clarify different radiation environments means – this might require invoking some timescale arguments.

We have revised the text to address the reviewer’s comment. The text on line 921 of the revised manuscript now reads: “ We find that the abundance of H₂O₂ on Charon is approximately a factor of two lower compared to Europa. Charon’s surface temperature is cooler than Europa’s (approximately 50 K [21] versus 90–130 K [63]). While laboratory studies suggest an increased production of H₂O₂ at lower temperatures [29], the differences between Europa and Charon H₂O₂ content could be attributed to different radiation environments encountered by the two satellites and/or to

~~the varying concentrations of CO₂ on the surfaces of these bodies. Europa experiences intense bombardment from charged particles (H⁺, Sn⁺, On⁺) trapped in the Jovian magnetosphere, with energies ranging from tens of keV to MeV and fluxes between 10¹⁰ and 10⁷ particles cm⁻² s⁻¹ [64]. These levels significantly exceed the keV solar wind impinging on Charon, which has a flux of approximately 10⁶ cm⁻² s⁻¹ [37]. Additionally, solid NH₃, present on Charon's surface, can also react with and destroy H₂O₂ at temperatures exceeding 50 K [65], which may partially explain the lower H₂O₂ levels on Charon compared to Europa. Furthermore, different concentrations of CO₂ may also affect the abundance of radiolytic H₂O₂. Systematic laboratory work investigating the impact of irradiation on H₂O-CO₂ mixtures, with diverse dilution levels at various temperatures, is essential to further explore the similarities and differences between these two intriguing satellites.”~~

Line 752 – 754 – I may have missed something but this seems to be the first time endogenous source has been used to explain what is found on Charon. According to the text, there is a pure crystalline h₂O layer with a layer of amorphous H₂O/CO₂ on the surface. Please clarify as this seems contradictory. Note the first line of the discussion says CO₂ came from a number of sources.

We acknowledge the reviewer's concern about the introduction of an endogenous source for CO₂ on Charon, as mentioned for the first time in lines 752-754. To address this, we have revised the opening of the Discussion section to better explain the meaning of “Solid CO₂ on Charon likely originated from multiple sources – endogenic, exogenic, and/or produced in-situ from radiation processing.”. The text at the beginning of the Discussion section now reads: **“We explore Solid CO₂ on Charon likely originated from multiple potential sources for the solid CO₂ detected on Charon, which include –endogenic, exogenic, and/or produced in-situ formation from radiation processing. Each source is considered for its ability to contribute to the spectral features observed on Charon, with careful consideration of the moon's environmental conditions. This discussion aims to decipher the complex processes that could have contributed to shaping Charon's present composition, as indicated by spectroscopic evidence.”**

The second paragraph of the Discussion section explores the scenario where exogenous impactors deliver CO₂ to Charon's surface and/or expose subsurface endogenic CO₂ reservoirs through cratering events. This scenario can account for the observed 2.7- and 4.23-micron CO₂ absorption bands.

The third and fourth paragraphs discuss the role of in-situ formation of CO₂ from radiation processing. The summary states:

~~“In summary, delivery of, and/or excavation of primordial CO₂ by impactors can explain the 2.7- μ m and 4.27- μ m features. CO₂ produced in-situ from radiation processing could contribute to the most surficial (~0.1 μ m penetration depth) CO₂ layer. However, laboratory experiments simulating these formation mechanisms do not show the resulting 2.7- μ m absorption band, challenging the possibility to assess whether these processes alone would be compatible with the overall CO₂ spectral behavior observed on Charon. Given the laboratory results for CO₂ embedded in other compounds before and after irradiation, we speculate that the 2.7- μ m feature resulting from in-situ processing might not be consistent with the observations, and thermal annealing would be required. Further discrimination between these processes This has~~

potentially interesting implications for the fate of CO₂ Charon may have inherited from the proto-Pluto and the Charon-forming impactor during and after the formation of Charon itself.”

The last paragraph of the Discussion section has been updated to reflect the modified text.

Line 928 – I only saw 5 keV electrons in the paper, were 10 keV electrons also used? Please clarify. Thanks for pointing this out. We only used 5 keV electrons in this work.

Line 1030 – 1035 – I don’t think this is clearly stated in the manuscript. Please double check this.

We have modified the text around line 423 to address this point. The text reads:

“An alternative ~~explanation is that the reflectance peak in Charon's spectrum at 4.265 μ m~~ ~~could be attributed to a CO₂ ice Fresnel reflection peak.~~ **interpretation suggests that the observed spectral feature might not result from two separate absorption bands, but possibly from the presence of a Fresnel peak of CO₂ ice at 4.265 μ m, contributing to the appearance of a double-peaked structure.** This is particularly relevant when visualizing a two-layered structure where amorphous H₂O ice and **crystalline** CO₂ particles overlay a bed of crystalline H₂O ice and tholin-like materials (Figure 3). Impinging radiation like solar wind can amorphize a thin rim of crystalline icy grains, especially at Charon’s cold temperatures. In such a configuration, the Fresnel reflection at the interface between these two layers becomes significant and must be considered. **The model shown as red solid line in Figure 3 consists of an areal mixture of two distinct surface units: the first comprises an intimate mixture of crystalline H₂O ice, amorphous H₂O ice, crystalline CO₂ ice, and tholin-like materials (runit1); the second unit is characterized by a two-layer medium dominated by amorphous H₂O ice and crystalline CO₂ on top of crystalline H₂O ice and tholins (runit2).** Further elaboration on this scenario is provided in the **Spectral Modeling section in Methods-section**. This model displays two Fresnel peaks, one due to H₂O ice at 3.1 μ m and one at 4.265 μ m due to **crystalline** CO₂. While the match is not perfect, it is important to stress that the exact position of the CO₂ Fresnel peak strongly depends on the adopted CO₂ optical constants and their temperatures. Also, the overall model is challenged by the lack of a robust set of optical constants for tholin-like materials at long wavelengths.

Also, in this multilayer model, please clarify how thick the layers being modeled are.

We refrain from providing quantitative numbers on abundances and layer thickness in the text. As pointed out in the text, “This model serves as a qualitative attempt to emulate the observed spectral features at long wavelengths, taking into account the known geology of Charon” The model is complex and further work needs to be performed to validate the interplay between the several free parameters.

Reviewer #3 (Remarks to the Author):

The manuscript presents very interesting observational results obtained with the NIRSpec JWST instrument for Pluto's moon Charon. The observational data are thoroughly analyzed, and the conclusions are well supported by the analysis of the observations and lab experiments. The main content of the paper suits Nature Communications very well.

However, the paper is not focused on the main topic, announced in the title. It is organized rather eclectically, mixing the analysis of the main results with other topics that makes it hard to read and hard to detach the crucial information from the unnecessary details or details which are of interest only to the readers specializing in planetary spectrometry.

I suggest a significant editing of the paper to make it focused on the main results: discovery of the CO₂ and H₂O₂ spectral features and possible formation of the carbon dioxide and hydrogen peroxide in the surface layers of Charon.

Specifically, I am concerned about the following parts of the paper, which contain details not necessary for understanding the main results of the paper but divert the readers from the main topic of the paper:

- Section "Compositional Inventory" and related to it subsection of Methods "Ammoniated Species." They contain information that is not required for understanding the main results of the paper. It would be better to write a separate paper, focused on the ammonia-related bands in the Charon's spectrum.

The section formerly known as "Compositional Inventory" has been retitled "Compositional Inventory Beyond Carbon Dioxide and Hydrogen Peroxide" to better highlight its objective of discussing additional compounds discerned from JWST data analysis. This encompasses the identification of amorphous water ice and the interpretation of the 2.21-micron spectral feature, which, while typically associated with ammoniated species, has been newly attributed to a mixture with about 1% ammonia in water ice.

Although the paper's primary discoveries pertain to CO₂ and H₂O₂, these additional findings are crucial for reinforcing several aspects: 1) the concept of a stratified surface on Charon, 2) the investigation into the potential endogenic sources of Charon's CO₂ as argued with the 1% NH₃ in H₂O ice in the Discussion Section, indicating CO₂ could be endogenously exposed by impacts, and 3) the analysis of the differences in the H₂O₂ band area between Charon and Europa. As an extension to point 3), the Discussion Section now includes the consideration that "Solid NH₃, present on Charon's surface, may react with and reduce H₂O₂ at temperatures over 50 K [Loeffler and Hudson, 2015], which might partly explain the lower levels of H₂O₂ on Charon compared to Europa."

- Subsection "Spectral modeling" in "Methods." It looks as if its results either duplicate the results from the lab measurements reported in the main body of the paper or fail to reproduce the spectra

as it is in the case of H₂O₂ feature. Thus, this subsection contains information that is not very helpful, but it significantly complicates the paper.

In response to the reviewer's concern, we emphasize that the "Spectral Modeling" section is integral to the paper, providing essential background and methodological detail that underpin the analyses in the main text. The modeling outcomes, particularly for the continuum around key features such as the 2.7-micron CO₂ band, are foundational for the thorough interpretation of the CO₂ band and its correlation with laboratory measurements. This section's inclusion is not intended to over-complicate the narrative but to offer a robust framework for the results discussed.

The "Spectral Modeling" section is crucial for substantiating several key findings: 1) it validates the identification of the 2.21-micron feature as a 1% NH₃ solution in water ice, a conclusion dependent on the detailed modeling of the 2.0-micron band continuum; 2) it supports the detection of amorphous water ice at wavelengths beyond 2.5 microns but not at wavelengths below 2.5 microns, which is significant for the discussion on stratification; and 3) it clarifies the modeling techniques depicted in Figure 3; 4) it addresses the content of CO₂ responsible for the 2.7-micron band, which was included in the revised manuscript in response to another reviewer's point. Regarding H₂O₂, the Method section explains why physical spectral modeling for the continuum, as applied in other wavelength ranges, was not feasible. Instead, a polynomial fit was used.

In response to the reviewer's critique, we have revised the text to highlight the connections to the spectral modeling section more clearly. This revision underscores the section's essential role in supporting the paper's analyses.

- Also, I would remove supplementary figures. I have found that in many cases the paper refers to them together with the reference to a figure in the main body of the paper or together with references to other papers. Supplementary figures 2 and 4 might be OK for an astronomical paper, but the information they provide is too special to be in a paper in Nature Communications. Thus, it looks as if the supplementary figures contain some specific details but are not crucial for the paper. At the same time, they are very busy and complicated and contain very long and hard-to-comprehend captions.

We respect the reviewer's perspective, however, we contend that Supplementary Figure 2 is essential for demonstrating the precise measurement of the CO₂ band's width and position, which are vital in confirming the association of the 2.7-micron band with pure crystalline CO₂—a significant finding for elucidating the processes involved in CO₂ formation. Regarding Figure 4, it addresses an ongoing discussion within the planetary science community regarding the optimal solar spectrum to use for reducing JWST spectra of Solar System objects. Supplementary Figure 4 provides the rationale and justification for our chosen method to compute the I/F spectra of Charon. Without this inclusion, the spectral profile and absorption bands in Charon's spectra might be misinterpreted or seem unfounded. We believe our approach aligns with the guidelines of Nature Communications. However, we respect the editor's judgment on the suitability of these figures as Supplementary material in a Nature Communications paper.

We removed Supplementary Figure 3.

Two additional figures have been included in the supplementary material to address another reviewer's request.

As I said above, those parts of the paper are not wrong, but they make the paper loose and do not let the readers grasp the main reported achievements: the discovery of CO₂ and H₂O₂ on Charon, the mechanism of their formation, and the possible structure of the upper layers of Charon's surface.

We appreciate the reviewer's insights. The paper is deliberately structured to prioritize the primary discoveries, namely the detection of CO₂ and H₂O₂ on Charon, highlighted under their own sub-headings. Yet, it is crucial to contextualize these discoveries within the broader understanding of Charon's surface composition. This context is not merely supplementary; it is integral to comprehending the significance of the discoveries and their contribution to the evolving narrative of Charon's origin and evolution history.

The paper is also overwhelmed with the details of the data analysis which are not necessary but make it difficult to read the paper. Examples of such unnecessary details are: the mentioning of the opposition effect on page 5; the discussion on the bands around 2 microns and comparison with the Uranian satellites on page 6; the discussion that refers to Supplementary Figure 3b on page 7; details in the selection of the polynomial fit on pages 9-10, including the unproved influence of CH₃OH, and many smaller pieces of unnecessary information which I have not mentioned. Specifically, I would recommend removing numerous cases where the authors discuss some details of the spectra or their interpretation ending up with a conclusion "this is not clear," "this may be a result of the uncertainties..." Such statements are often not related to the main topic of the paper but reduce confidence in the results.

We justify our choices below:

1. **Opposition effect on page 5:** The inclusion of the opposition effect is essential in elucidating the discrepancies in the I/F absolute values between observations from JWST and New Horizons. This effect has a substantial impact on the reflectance spectra's continuum level. Given that JWST is a novel instrument in planetary science, providing a clear explanation for these discrepancies is vital for ensuring the credibility of our spectral measurements and data reduction. By detailing this phenomenon, we enhance the transparency of our data analysis and support the reproducibility of our findings.
2. **Bands around 2 microns and comparison with Uranian satellites on page 6:** The comparison with Uranian satellites aims to draw parallels between similar spectral features observed in different celestial bodies within our solar system. This comparison provides a contextual framework that may help in identifying compositional similarities and differences, thereby enhancing the reader's understanding of Charon's unique spectral characteristics.
3. **Discussion referring to Supplementary Figure 3b on page 7:** In alignment with the reviewer's suggestion, we have omitted the text pertaining to Supplementary Figure 3b to

streamline the paper's focus on its central findings. Supplementary Figure 3 is no longer included in the paper.

- 4. Details in the selection of the polynomial fit on pages 9-10, including the influence of CH₃OH:** The selection of the polynomial fit is a critical part of the data analysis process, directly impacting the interpretation of the 3.5-micron spectral feature and its attribution to H₂O₂. As pointed out by the reviewer, the H₂O₂ detection is one of the main finding. Discussing the potential influence of CH₃OH, although its presence is not definitively proven, illustrates the comprehensive nature of our analysis, considering all plausible factors that might affect our results.

In each case, while we understand the reviewer's concerns about the density of detail potentially obscuring the paper's main findings, we believe that these details contribute to the robustness and credibility of our analysis.

The abstract and Conclusions should be updated correspondingly. For example, I suggest, in Conclusions, changing the emphasis by moving the H₂O₂ discussion closer to the beginning of the section and a more hypothetical result on a layer of crystalline CO₂ closer to the end. Also, I strongly recommend removing the two last sentences in this section. I think Nature Journals' mission is to report outstanding scientific results, not possible plans for future research.

The Conclusion section has been integrated into the Discussion section to adhere to the formatting guidelines of Nature Communications. Additionally, the final two sentences of the former Conclusion section have been omitted.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

The authors have adequately addressed all of my comments, and I believe the manuscript is ready for publication.

Reviewer #2 (Remarks to the Author):

Dear Editor,

Please find my review for the revised version of "Discovery of Carbon Dioxide and Hydrogen Peroxide on Charon's Stratified Surface with JWST" by Protopapa et al. below. I appreciate the authors' thoughtful responses to my comments and think the manuscript is suitable for publication after these last few issues are addressed.

To make estimates regarding the flux, the authors are using values for the solar wind. However, the range of 1 keV protons in H₂O is very small (~50 nm with a max penetration of ~100 nm), much smaller than the analysis depth of the infrared light cited for any of the discussion. I don't think this approach is accurate, as the solar wind will never reach those depths. I specifically referring to lines 590-595 and line 885-888. The authors probably have to take into account GCRs or other radiation that will penetrate deeper. I don't think this should be a big issue to fix, as other works have done this for this region of the solar system (Cooper 2003, Strazzulla 2003, Hudson 2008 and recently Loeffler 2020). Please correct these estimates or give an argument why the solar wind is actually the correct approach.

Other items related to the revisions:

Line 326 – these probe depths are for pure CO₂, right? If so, they would not be correct here. They would have to scale to the concentration, right? Pure H₂O which is essentially what this is would have a much larger probe depth. Please clarify. I would also double check this assumption is not being made for the other bands that have been discussed.

Line 305 – 318 – this is not clear, are these the best fits? The transition here is pretty rough, consider rewording this.

Other notes that the authors can decide whether they address:

Line 305 – the 2.78 micron band is not in the lab spectra but is discussed as if it is

Line 931 – 940 – the argument regarding the different radiation environments may be ok but I am thinking both surfaces should be at equilibrium, so the actual fluxes may not matter. Of course, the presence of heavy ions on Europa may also help, although the side being bombarded with sulfur does not show H₂O₂ in high (or in some cases any) amounts.

Reviewer #2 (Remarks on code availability):

I cannot see anything, it seems to be restricted

Reviewer #3 (Remarks on code availability):

The access to the code was restricted, so I could not see any details.

Reviewer #1 (Remarks to the Author):

The authors have adequately addressed all of my comments, and I believe the manuscript is ready for publication.

We thank the reviewer for their positive feedback. We are pleased to hear that the revisions have satisfactorily addressed all comments. We appreciate the constructive input throughout the review process and are glad that the reviewer finds the manuscript ready for publication.

Reviewer #2 (Remarks to the Author):

Dear Editor,

Please find my review for the revised version of "Discovery of Carbon Dioxide and Hydrogen Peroxide on Charon's Stratified Surface with JWST" by Protopapa et al. below. I appreciate the authors' thoughtful responses to my comments and think the manuscript is suitable for publication after these last few issues are addressed.

We thank Reviewer #2 for the additional comments provided.

To make estimates regarding the flux, the authors are using values for the solar wind. However, the range of 1 keV protons in H₂O is very small (~50 nm with a max penetration of ~100 nm), much smaller than the analysis depth of the infrared light cited for any of the discussion. I don't think this approach is accurate, as the solar wind will never reach those depths. I specifically referring to lines 590-595 and line 885-888. The authors probably have to take into account GCRs or other radiation that will penetrate deeper. I don't think this should be an issue to fix, as other works have done this for this region of the solar system (Cooper 2003, Strazzulla 2003, Hudson 2008 and recently Loeffler 2020). Please correct these estimates or give an argument why the solar wind is actually the correct approach.

The reviewer is correct in stating that the solar wind is less penetrating than galactic cosmic rays (GCRs) and radiolyzes the ice to generate peroxide up to a depth of ~50 nm, much shallower than the ~50 μm depth probed by infrared sensing around 3.5 micron.

While GCRs penetrate deeper into the regolith, the time to accumulate a dose of 1 eV per water molecule at ~50 μm depth is approximately ~25 million years (Loeffler et al., 2020). By comparison, the solar wind requires only ~5 years to deliver this dose at the top 50 nm veneer.

The regolith is churned by micrometeoroid impacts, which mix the solar wind-synthesized H₂O₂ to greater depths while exposing fresh material to the solar wind.

We add the following text at Ln 563: **While Galactic Cosmic Rays (GCRs) penetrate deeper into the regolith than the solar wind, accumulating a dose of 1 eV per water molecule at approximately 50 μm depth requires about 25 million years (Loeffler et al., 2020). This depth of 50 μm aligns with the sensing capabilities of infrared observations in crystalline water ice at temperatures around 40K and wavelengths near 3.5 μm (Mastrapa et al., 2009). In**

contrast, the solar wind can deliver this dose at the top approximately 50 nm veneer in only about 5 years. Micrometeoroid impacts may further facilitate the penetration of peroxide, initially produced by the solar wind, deeper into the surface while also exposing fresh material to the solar wind (Costello et al., 2021).

Other items related to the revisions:

Line 326 – these probe depths are for pure CO₂, right? If so, they would not be correct here. They would have to scale to the concentration, right? Pure H₂O which is essentially what this is would have a much larger probe depth. Please clarify. I would also double check this assumption is not being made for the other bands that have been discussed.

We thank the reviewer for pointing this out. We have revised the text to improve clarity on this aspect. The revised text now reads:

We do not find evidence for the absorption bands of solid crystalline CO₂ [22] at 1.97 μm ($2\nu_1+\nu_3$), 2.01 μm ($\nu_1+2\nu_2+\nu_3$) and 2.07 μm ($4\nu_2+\nu_3$), consistent with the New Horizons data (Figure 1g and Supplementary Figure 1). It is worth noting that, based on absorption coefficient considerations [15], the $\nu_1+\nu_3$ and ν_3 CO₂ absorption bands probe penetration depths **on the order** of 1 μm and 0.1 μm, respectively. These depths refer to how far into a material the light can penetrate before being absorbed, directly relating to the depth below the surface that is being probed. In contrast, the short wavelength absorption bands (i.e., $2\nu_1+\nu_3$, $\nu_1+2\nu_2+\nu_3$, $4\nu_2+\nu_3$, [22]) probe the occurrence of CO₂ at approximate depths of ~50 μm for $\nu_1+2\nu_2+\nu_3$, ~100 μm for $2\nu_1+\nu_3$, and ~300 μm for $4\nu_2+\nu_3$. **The probe depths listed for the CO₂ absorption bands are based on measurements of pure CO₂. These depths will differ if CO₂ is dispersed in water ice, as we propose here on Charon based on the modeling of the 2.7 μm range (refer to the Spectral Modeling section in the Methods). In this context, the values obtained for pure CO₂ represent a lower limit. Nevertheless, when accounting for CO₂ dispersed in water ice, the short wavelength bands near 2 μm will still probe hundreds of microns, contrary to the $\nu_1 + \nu_3$ and ν_3 bands that will probe the first ~5 and ~1 μm, respectively.** Therefore, the lack of detection of CO₂ absorption features at short wavelengths near ~2 μm implies that this compound is sparse at penetration depths greater than several tens of microns, contrary to the case of the Uranian moons [e.g., 23] and Triton [e.g., 24].

Line 305 – 318 – this is not clear, are these the best fits? The transition here is pretty rough, consider rewording this.

We have revised the text to improve the transition from the previous paragraph, ensuring a smooth flow. Additionally, the text now clearly indicates that the described model is the best fit. The updated text is as follows:

~~We modeled~~ **The spectrum of Charon in the wavelength range spectral region between 2.66 and 2.80 μm, which includes both the $\nu_1+\nu_3$ and $2\nu_2+\nu_3$ CO₂ absorption bands, was modeled using the Hapke radiative transfer model [12]. Specifically, the best-fit model consists of ~~with~~**

an areal mixture of 80% crystalline H₂O ice, 18% amorphous H₂O ice, and 2% crystalline CO₂ (for details, refer to the Spectral Modeling section in the Methods and Supplementary Figure 5).

Other notes that the authors can decide whether they address:

Line 305 – the 2.78 micron band is not in the lab spectra but is discussed as if it is

In response to the point raised on line 305, the 2.78 micron band is indeed discernible in the laboratory spectra of pure crystalline CO₂.

The discussion in the paragraph prior to the one highlighted by the reviewer establishes that the presence of the 2.7 micron band in Charon's spectrum is consistent with the characteristics of pure (poly)crystalline CO₂.

Following this, we draw a comparison between laboratory data and Charon's observations at 2.78 microns. While this band is clearly present in the spectra of pure crystalline CO₂ in laboratory settings, its manifestation is less pronounced in Charon's spectral data. To reinforce this observation, we have incorporated references to the relevant laboratory spectra, particularly citing the studies by Quirico & Schmitt (1997), Raut & Baragiola (2013), and Gerakines & Hudson (2020). The manuscript has been updated to clearly indicate that our discussion pertains to pure crystalline CO₂.

The text now reads: "While the $2\nu_2+\nu_3$ combination/overtone band near 2.78 μm is evident in the laboratory spectra of **pure** crystalline CO₂ [15, 18, 22], it is challenging to identify in Charon's JWST spectra due to the low signal-to-noise ratio in this wavelength region (i.e., $I/F < 10^{-2}$)."

Line 931 – 940 – the argument regarding the different radiation environments may be ok but I am thinking both surfaces should be at equilibrium, so the actual fluxes may not matter. Of course, the presence of heavy ions on Europa may also help, although the side being bombarded with sulfur does not show H₂O₂ in high (or in some cases any) amounts.

We appreciate the reviewer's comment regarding the equilibrium states of the surfaces under different radiation environments. In light of this, we have revised our discussion to focus on the differences in the energy environments rather than the fluxes.

Reviewer #2 (Remarks on code availability):

I cannot see anything, it seems to be restricted

Apologies for the confusion. We make available the grand average spectrum of Charon used for the analysis presented in the paper. The code availability section has been modified and it now reads "All relevant code is publicly available: the JWST science data calibration pipeline is at <https://github.com/spacetelescope/jwst>; the Planetary Spectrum Generator is at

<https://psg.gsfc.nasa.gov/>. Details on the numerical simulations are discussed within the text and are available from the corresponding author upon request.”

Reviewer #3 (Remarks on code availability):

The access to the code was restricted, so I could not see any details.

Apologies for the confusion. We make available the grand average spectrum of Charon used for the analysis presented in the paper. The code availability section has been modified and it now reads “All relevant code is publicly available: the JWST science data calibration pipeline is at <https://github.com/spacetelescope/jwst>; the Planetary Spectrum Generator is at <https://psg.gsfc.nasa.gov/>. Details on the numerical simulations are discussed within the text and are available from the corresponding author upon request.”

REVIEWERS' COMMENTS

Reviewer #2 (Remarks to the Author):

Thanks for addressing my numerous comments. I will enjoy seeing the paper in print.