You present here a paper on the viability of photosynthesis in reduced atmospheres, with methane as the prime carbon-bearing compound.

Overall, I am convinced of the scientific soundness of your study and find that I can agree with your chemical model and findings. You find that planets with a surface pressure of less than 30 bars of hydrogen could have enough harnessable solar energy reaching the surface to sustain photochemistry. I am not an expert on exoatmospheres, but H. Lammer et al. point out in a recent paper that planets inside the habitable zone that are big enough to retain their primal hydrogen atmospheres are very likely to accumulate very thick atmospheres. (H. Lammer et al. MNRAS 439, 3225–3238 (2014). This does not rule out the type of planet you postulate in this paper, but it makes their occurrence somewhat less likely. A discussion of whether such planets are likely or not should not be omitted from the manuscript.

Response: We address this indirectly in the paper, noting that a planet with a thick H₂-dominated atmosphere in the conventional habitable zone (i.e., the zone in which an Earth analogue would have liquid water on its surface) would in fact be uninhabitably hot. Such a planet would be habitable well
outside the “habitable zone”. We have added a short commentary on this, and thank the referee for bringing Lammer et al. to our attention.

Apart from this general concern about the significance of photosynthesis on exoplanets (which I might misjudge to be too low), there are two major points that need to be addressed before the manuscript is fit for publication.

- Length: I feel that the manuscript is overall too lengthy and has a number of repetitions that are plain redundant. You go to great lengths explaining your methodology in Section 2. After this very thorough explanation, Figure 1 does nothing to further enhance understanding, but rather confuses with tiny graphs and very hard to decipher scales. I suggest losing it altogether, because the explanation preceding it is way clearer than the graphs.

Response: We have removed Figure 1.

In Section 3 you repeat quite a bit of the methodology already explained in Section 2. I would like to see this 15-page long section tightened up considerably. I feel that Figure 4 is not really necessary and Figure 6 shows nothing that the text preceding it doesn’t already make clear. These suggestions are meant as examples and are not exhaustive. I believe that with less fluff, this work is much better to take in and appreciate.

Response: Referee 3 also said the paper was too long, and we hope we have addressed both referees’ concerns by very substantially shortening the discussion of the total energy requirement for building biomass from CH4 compared to CO2.

- Precision: In a number of places your otherwise very clear and good-to-follow reasoning remains rather vague. For example, I could not find out from the manuscript what the atmospheric composition for your analysis in Section 3.4 is. It says “hydrogen-dominated”, does that mean you assume 100% hydrogen for your calculations? Or do you account for the ~2% of CH4 that Uranus’ and Neptune’s atmosphere contain? I think that would be important seeing that CH4 is a very efficient greenhouse gas, and could be said to be quite central for photosynthesis as you suggest. More detail in this section would make your reasoning easier to follow.

Response: The model atmospheres considered in the paper have been described more exactly in the revised version. Collision-induced dipole absorption by H2 dominates the greenhouse effects in these atmospheres, a point we have made more explicit.

There are also a number of smaller points/remarks that need to be sorted out before publication:

- Throughout the manuscript whenever you reference another section of the paper it says “Section 0”—In my review version of the paper all Greek letters (Delta/lambda, nu...) are missing.

Response: As noted, this was an error in translating from our original .DOCX file to the file sent out to referees.

- Page 2, line 60 “than” --> “that”
- Page 5, line 159 “an” --> “and”
- Page 6, line 203 “This is simple” --> “This is a simple”
Page 6, line 216 “empirically estimated” In my understanding there is no such thing as an empirical estimate. A quantity is either measured, then it is empiric, or it is estimated, but not measured and thus not empiric. Maybe something along the lines of “informed estimate” might be better.

Response: We have changed this to simply “estimated”. We have also addressed all the smaller points below, we hope to the referee’s satisfaction.

- Page 7, Line 242 “assumptions the” --> “assumptions about the”
- Page 10, Line 332 “illustrated the” --> “illustrated by the”
- Page 11, Line 535 “under general” --> “under the general”
- Page 14, Line 443 “methane more” --> “methane is more”
- Page Figure 5, in the figure legend replace “oC” with “°C” or change to Kelvin.
- Page 16, Line 497 “phosphorous source” --> “phosphorous as source”
- Page 19, Line 584 “photons of capable” --> “photons capable”
- Page 25, Line 795 “energetic” --> “energetics”?

A shortened and more concise paper that discusses the relevance and significance of the question at hand, would enable this very sound and exhaustive study of possible photosynthetic chemistry on exoplanets to be appreciated more fully. I thus recommend a thorough revision of the written paper (not the underlying study) before publication.

Response: We hope that the substantially revised paper addresses this referee’s comments.

Round 1: Reviewer 2 Report and Author Response

This is a long, detailed, and highly speculative paper about the possibility of life on H2-rich super-Earths. The basic thesis of this paper is that carbon in such planet’s atmosphere will exist primarily as CH4; hence, it will need to be oxidized to form organic matter (CH2O). By contrast, on Earth today, CO2 is the dominant carbon-bearing gas, and it must be reduced to form CH2O. If water is the material used to do this, we get oxygenic photosynthesis on Earth and “hydrogenic” photosynthesis on H2-rich super-Earths.

I have two major reactions to this paper:

1. First, I am confused by the starting point for this discussion, which is that carbon on a super-Earth will exist as CH4. This statement is made on line 243: “On a planet with a hydrogen dominated atmosphere, atmospheric photochemistry rapidly converts atmospheric carbon to methane.” Then, on line 245: “Carbon will be present as methane even if it is outgassed from the planet as CO2.” The cited papers for these statements are references [50, Hu et al., 2012] and [51, Hu et al., 2013]—both papers from this same group. There is, however, a well-known story in the terrestrial atmospheric evolution literature concerning how difficult it is to form methane through low-temperature atmospheric chemistry. See, e.g., Wen, Pinto, and Yung, JGR (1989). So, I was curious as to how Hu et al. made their methane. It turns out that they don’t! According to the upper right-hand panel of Figure 4 in [50], the dominant form of carbon in this H2-rich atmosphere is CO2, not CH4. Indeed, the authors of [50] say this about CO2: “Interestingly, CO2 is fairly long-lived and well mixed in the H2 atmosphere, meaning that
the reduction of CO₂ in the H₂-dominated atmosphere is not efficient (Figure 4).” Ref. [51], as far as I could tell, says absolutely nothing about this issue, so I am not sure why it was cited here.

Now, to be sure, the predicted concentrations of CH₄ and CO₂ in [50] depend on their assumed outgassing rates. It may be that CO₂ is more abundant than CH₄ because its outgassing rate is larger (I didn’t check this). But, in any case, this model provides little support for the statement that CO₂ will be rapidly reduced to CH₄ in such an atmosphere. It seems to me that one would need to have estimates for how fast these gases, and CO, are being outgassed, and then one would need to run a photochemical model like that of Hu et al. in order to say which carbon species would be more abundant in such an atmosphere. This, in turn, requires assumptions about the interior of the planet. In particular, how reduced is its mantle? This adds one more layer of speculation to the story.

I wonder if the authors are being confused by the giant planets in our solar system, all of which have H₂-rich atmospheres and CH₄ as the dominant carbon species. But these atmospheres are also semi-infinite, that is, they extend down to extremely high pressures and temperatures where thermodynamic equilibrium applies. The CH₄ formed down there then wafts up to the upper atmosphere, where it is gradually broken down by photolysis. This is a very different situation from a hypothetical super-Earth with a solid, or liquid, surface and an Earth-like surface temperature.

Response: We apologize to the referee for the lack of clarity in the paper in this regard. We have expanded the section on the atmospheric composition of rocky planet atmospheres with high H₂ content. In summary, photochemical and thermodynamic models show that both methane and carbon dioxide are long-lived in an atmosphere with high H₂, methane because methyl radicals generated by photolysis primarily react with hydrogen to re-form methane (a chemistry that is not common in the atmosphere of Titan, an otherwise obvious comparator), and carbon dioxide is only very slowly attacked by photochemical mechanisms. Thus the CH₄/CO/CO₂ ratio is primarily determined by a) outgassing ratios and b) the effects of life. It is not implausible that a low outgassing rate with a modest methane composition will result in an accumulation of methane. It is more plausible that a world with life will rapidly draw down CO₂ and react it with atmospheric H₂ to form CH₄, as CO₂ is drawn down by life on Earth.

We have tried to summarize this in as brief a form as possible, so as to not add to the length of the paper.

(2) Second, I am concerned that the hypothesis presented in the paper is not testable. The authors conclude that the major biogenic byproduct of hydrogenic photosynthesis should be H₂. They then acknowledge that this would not be detectable in an atmosphere that is already filled with H₂. They suggest (Line 501) that hydrogen sulfide and ammonia might also be produced and that ammonia could conceivably be detected. The idea of ammonia as a biosignature was proposed previously by these same authors in other papers published within the last two years. But, would ammonia actually be considered a reliable biosignature? Ammonia might be produced within hydrothermal vents (Kasting et al., Icarus, 1993) or by surface reactions catalyzed by TiO₂ (Kasting, JGR, 1982). If we detected ammonia in the atmosphere of an H₂-rich super-Earth, we might indeed have a conversation about whether it was produced by life, but to argue that this is convincing evidence for hydrogenic photosynthesis seems like a bit of a stretch.
Response: This is an important point, and is a major (although disappointing) conclusion of the paper. The referee is correct that geochemical processes can produce ammonia, although usually in very small amounts. We have made this conclusion clearer—that, unlike photosynthesis in an oxidized environment (which is likely to produce a distinct biosignature), photosynthesis in a hydrogen-rich environment is likely to produce weak or ambiguous signatures. This is important for the search for life on such worlds, as it means that the old adage ‘Absence of evidence is not evidence of absence’ applies particularly strongly to the search for life on rocky exoplanets with H2-rich atmospheres.

There are some other minor problems with the paper. Section 0 is referred to multiple times, and all of the “nu’s” are missing from the symbol “hv”. I had no particular reaction to the other elements of the paper: they seemed speculative but reasonably well done. But I would like to see how the authors respond to points 1 and 2.

Response: We hope our responses are satisfactory. We have addressed the issue of section numbering and greek letters.

Round 1: Reviewer 3 Report and Author Response

This paper describes possible photosynthetic reactions in a hydrogen-rich atmosphere and concludes that the major byproduct of such reactions would be H2 gas. The paper spends considerable time describing calculation of the Gibbs energies of these reactions compared to similar oxygenic photosynthesis, but the value of these calculations is questionable. The authors then discuss some possible alternative reactions, determine the necessary photon energies and fluxes to drive these reactions and describe the stellar and atmospheric parameters that would permit sufficient photon flux to the surface. In general, I find the topic interesting, but much of the thermodynamic work seems unnecessary, and there are a few other issues the authors should address. The paper also feels disorganized and would benefit from eliminating repetitive material.

Response: We are particularly grateful to Referee 3 for very detailed, helpful and constructive comments. We discuss the specific points below.

Major Comments

My primary science complaint is with the thermodynamic analysis of the Gibbs energies. The calculation of Gibbs energies of ~3000 representative molecules is done to estimate the amount of energy that hydrogenic photosynthesis needs to capture to be viable, yet it is unclear how (or if) this data set is used in Section 3.3, which discusses the photon energies. Either the methods need to be more explicitly described, or most of Section 3.2 should be eliminated or drastically shortened.

Furthermore, the comparison of Gibbs energies of formation in oxidizing versus reducing conditions is trivial. (Figure 2, lines 410–417, also lines 441–448). Simply comparing the Gibbs energies of formation of CO2 (gas ~394 kJ/mole, aq ~385 kJ/mole) and CH4 (gas ~50 kJ/mole, aq ~35 kJ/mole) shows that any reaction involving CO2 as the C-bearing reactant will necessarily have a more positive Gibbs energy of reaction than a similar reaction with CH4 as the reactant. The trends with Rr are related to the amount of H2O necessary to balance the products. Much of this discussion and
several figures could be eliminated with a simple thermodynamic analysis of Reactions (8) and (9). Figure 3 is an interesting comparison that concisely shows both the difference in energies between oxygenic/hydrogenic photosynthesis and the necessary energy to generate the chemical space, but again, this should somehow be tied in to the discussion of photon energies in Section 3.3.

Response: We understand the referee’s comments, and they are fair. There is however a subtlety in this argument which makes our calculations useful, although perhaps not useful enough to justify their very extensive exposition here. Synthesis of organics from methane is in general more thermodynamically favorable than synthesis from carbon dioxide, and synthesizing a specific molecule from CO$_2$ always takes more energy than from CH$_4$. However, when comparing the synthesis of biomass from CH$_4$ and from CO$_2$, we are not comparing the synthesis of like with like, as the two biochemistries could be very different. The point we were trying to make was that synthesizing a specific fraction of all chemical space from methane was consistently always more energetically favorable than synthesis from carbon dioxide. However we agree that our discussion of the method of proving this was over-extended for the point made.

Consequently, we have reduced the exposition of the Gibbs Free Energy calculation, as follows.

(a) Removing the explanations of why the calculations were done from the methods section (2.2). This is now only discussed in Section 3.2. (We believe that it is important to retain the method section on calculating Gibbs free energy in Section 2.2, so others can replicate and improve on this work in the future).

(b) Removing the discussion of ln(Q) from the methods section—discussion of reagent concentrations is now explicit in the Results section.

(c) Starting Section 3.2 with an explicit discussion of the relative ease of making molecules from CH$_4$ vs. CO$_2$, and illustrated that with a new, and we hope clearer, figure calculated from solution $\Delta G$ values of actual molecules rather than computer ones.

(d) Subsequently making the discussion of why we did the calculations more concise, and emphasizing that we are trying to estimate the free energy of synthesis of two different biochemistries, not the synthesis of the same biochemistry from two different starting materials. Specifically, we have removed discussion of the calculation methods from Section 3.2, and Figures 2, 4 and 5 (original paper numbering).

(e) We have added a new sub-section to contain an abbreviated discussion of electron acceptors other than hydrogen. While this is also a thermodynamic argument, it is distinct from the argument about total energy requirement.

(f) We have also added an explicit explanation of why photon energy and overall thermodynamics are distinct issues.

Regarding conclusions of the paper, there are two things that I think should be addressed:

The authors discuss the possibility of CO$_2$ being present in the atmosphere as a product of degassing, but high temperature volcanic gases from a planet with a reduced interior will likely consist of H$_2$ + CO gas (see e.g., [45]). How stable would CO gas be in this atmosphere, and could it serve as the biological source for carbon?
Response: We have addressed the atmospheric composition questions in more detail in our response to Referee 2.

For ammonia to be detectable as a biosignature, its rate of biological production must exceed its rate of photochemical destruction. Can you provide an estimate for its photochemical lifetime in this kind of atmosphere?

Response: We have made reference to previous studies on ammonia accumulation in an H\textsubscript{2}-rich atmosphere.

Regarding the clarity of the paper, I find some of the text, particularly Sections 2–3.3, to be repetitive and poorly organized. The authors’ arguments would be easier to follow if the repetition were eliminated (e.g., one concise explanation of oxygenic photosynthesis would support your argument better than several repeated, but slightly different descriptions (e.g., Section 1.1, Section 3.1, Section 3.3). These could be combined into a single explanation at the start of the paper, say Section 1.1. One or two equations to describe oxygen photosynthesis, rather than ~5 slightly different formulations, etc.)

Response: We agree, and regret this duplication. As the referee suggests, we have gathered all the discussions of oxygenic photosynthesis together in Section 1.1.

Minor Comments:

- Line 62: where in the paper do you return to heterotrophy? I believe it is in Lines 761–787, but it might be helpful if you made this more explicit for the astronomers who may be reading.

Response: The referee is correct—the short reference in Section 1.1 to heterotrophy was (indirectly) taken up in Section 4.2. We have removed the forward reference in Section 1.1 as it is a minor point and therefore distracting to be brought up at this stage.

- Section 2.2: Please clarify: are all reactants/products assumed to be in aqueous solution? Also clarify states in all written equations and in Table 1.

Response: MOPAC calculations are for energy in a vacuum, and as noted we have not corrected these for solvation energy. Section 2.2 has been substantially changed, and we hope the new version is clearer on this and other points.

- How are you determining concentration of reagents to calculate Q?

Response: This was a selection based on what was considered reasonable. We have been more explicit on this, and also that the selections do not actually affect the qualitative conclusions of the calculations.

- Table 2: Why list the reducing electrode potential for the “electropositive elements” when you don’t refer back to this at any point? It seems to add little to the discussion. A more descriptive title than “Analysed in Table 3” should be given for panel 2.

Response: The point of Table 2 was simply to provide a list of the elements considered, and illustrate the reasons for considering them further as electron acceptors for CH\textsubscript{4}-based photosynthesis. Given that all referees considered the paper too long, and this referee thought that the majority of Table 2 did not add anything, we have removed this table from the paper.
• Lines 383–392: repetition of material discussed in Section 2.2. Most of this could be eliminated.
  Line 392: How big of a difference would including solution energies cause in your calculated free energies of formation?
• Lines 539–542: I find this sentence confusing. Are the photons only driving Reaction (11a)? This relates back to my previous comment on the Gibbs energies.
• Figure 8: clarification: Is this photosynthetically-active flux or total flux to the surface?
  General recommendations for figures: remove horizontal grid lines. They distract, especially for figures which have nearly horizontal plotted lines (e.g., Figures 4 and 6). Also place a box around the legends so they are clearly indicated.

Grammar/Typo:
• All references to “Section 0” need to be updated with proper section numbers. See e.g., Line 62.
• All symbols, such as capital delta and nu are missing (e.g., cap-Delta G, Line 178).

Response: This was an error introduced by the Publishers in converting our MSS into their format, as was deleting all the Greek letters from the MSS. This is regrettable, and all three referees noted it. We hope it did not damage comprehension too much.

Please check subscripts and superscripts. Please use consistent notation in numbering equations. All equations should be numbered.

Response: We have also addressed all the smaller points below, and are very grateful to the referee for pointing these out.

• Line 34: “source on the surface”
• Line 72: remove “the” before ‘sun-like stars’
• Line 153: “surface temperature is element.”
• Line 159: please fix typos/phrasing within the parentheses. Meaning is currently unclear.
• Line 199: “oxidation or reductio
• Line 200: add “in” before [13].
• Line 201: Rr equation should be numbered.
• Line 203: “This is a simple …”
• Line 205: “energetic measures”
• Line 215: “DH values were used,”
• Line 237: “bins of 10 kJ / mole”; “The calculation…”
• Line 247: explain [ ] notation.
• Line 250: remove “(N2)”
• Line 256: “built” should be “build”
• Line 263: equation is not numbered or balanced.
• Line 318: “of of hydrogenic photosynthesis”
• Line 332: “as illustrated by the”
• Line 423: “enthalpy” should be “Gibbs free energy” of formation.
• Figure 4b: typo in x-axis label (concentration). What are the units of concentration? Is it atmospheric mole fraction? Aqueous molar fraction?
• Figure 5: superscript degree symbols in legend.
Second Round of Evaluation

Round 2: Reviewer 1 Report and Author Response

You present here a major revision of the original paper from June 2014. My major points of critique have been addressed. Apart from tightening the paper considerably, you have also included a discussion of how likely a planet with such specific atmospheric conditions is.

Apart from a little spell checking, especially checking for mix-ups between "in" and "is" in a number of instances, I can recommend this vastly improved paper for publication. It now makes for interesting reading material with concise description of methods and results, doing justice to the very interesting topic at hand.

Response: We are grateful for this very supportive statement, and we hope that we have picked up residual typing errors.

Round 2: Reviewer 2 Report and Author Response

The new version of this paper is shorter and more to the point than the previous version, which is good. One of my previous comments still applies—these proposed biospheres based on hydrogenic photosynthesis are essentially unobservable—the authors are straightforward about admitting this. They waffle a bit by saying that ammonia might be a potential biosignature on such H$_2$-rich planets; however, seeing NH$_3$ in a planet’s atmosphere would still not test their basic hypothesis. This is a major weak point of the paper. That said, I’m happy to see the paper published essentially as is, as it lays out the possibilities for life on such planets, and this is something that various folks, including the authors, are worried about.

Response: We have tried to address this, but the basic conclusion—that the photosynthesis of life on a world with an H$_2$-rich atmosphere may be almost unobservable—is our conclusion. We are grateful that this referee is OK with that.

There are, however, still a few minor things that should be corrected:

1) LINE 33: “Light is by far the most abundant chemical energy source…”

Response: With respect, we have left this as it is. We understand the rationale for a changed wording, but formally we cannot really say “is” about a planet we do not know exists, and as we discuss in Section 3.6 a “thin” (i.e., not Jovian) atmosphere can still be optically thick, blocking out most light, and depending on the geochemistry other sources could rival light as an energy source in such an environment. So we would rather leave this as a future tense and less strong statement.

-- Light is not chemical. Omit the word “chemical” from this sentence.

Response: We have corrected this.
(2) Line 53: “...is interpreted by some as evidence that microbial Rubisco-based carbon fixation occurred at this early date”.

--You should add the words “by some”, as I have done. Schidlowski’s 1988 interpretation of the carbon isotope record from Isua is not widely accepted. Consequently, the last sentence of this paragraph should be revised to say that anoxygenic photosynthesis evolved rapidly on Earth. Whether oxygenic photosynthesis evolved rapidly is a major point of contention amongst Precambrian paleobiologists.

Response: Fair point, and we have moderated our discussion accordingly. We have also noted that evolution of Rubisco and evolution of oxygenesis are two unrelated events, so even if the isotope record is evidence of rubisco-mediated carbon fixation, that evidence does not imply oxygenesis.

(3) Section 0 still appears in several places. Apparently, this is simply a problem with the publisher’s software.

Response: Yes.

(4) Line 241: Reaction [3] is not balanced. It should read:

\[ \text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O} \]

The authors should also mention that this reaction can be performed by most or all modern methanogens.

Response: Thank you, we have balanced the equation and added an additional mention of terrestrial methanogens.

(5) Section 3.4 and Table 2: Why would elements such as P, S, Fe, Mn, and others be present in their oxidized forms on the surfaces of such H2/CH4-rich planets? The planets’ interiors must be highly reduced to make CH4 the dominant outgassed carbon species. How would these elements get oxidized in the first place to make them available later as redox partners for CH4 oxidation? Perhaps something should be said about why they are being considered.

Response: The referee is correct that these elements might be deposited on the surface or the atmosphere as reduced species. Table 2 is meant to illustrate the energy available for capture from their reduction by atmospheric hydrogen if they are present in an oxidized form. In fact, the high energy needed to reduce phosphate means that we consider it unlikely that phosphorus would be present in any form other than phosphate or (possibly) phosphite. Sulfur we explicitly say is likely to be outgassed as hydrogen sulfide (as it is on Earth). We have made this clearer and more explicit in the revised version.

Round 2: Reviewer 3 Report and Author Response

The authors’ revisions have substantially improved the quality and clarity of the paper. In particular, the new Figure 1 does a much better job of highlighting the difference in the use of CH4 vs. CO2 as reactants. The authors have adequately addressed the comments of myself and the other reviewers. My remaining comments are extremely minor, and mostly typographic.

The text still contains references to Section 0 (Lines 127, 160 and 359)

Response: We believe this is a format conversion error again: we have screened all the section references in the .DOCX. I hope I have fixed this by removing all the hyperlinks in the .DOCX document, changing section, table and figure references to plain text.
Most references to a Table or Figure in the text have the first letter in bold-type.

Response: All the references to a specific figure or table (as in Figure 1) have upper case first letters in the text as these are the names of the figure, and so we have capitalized them like other names. If MDPI house style requires lower case, we can of course change this.

- line 20: H2 subscript --> fixed
- lines 60–61: parentheses --> fixed
- line 247: “atmosphere of” --> fixed
- line 249: “atmosphere of” --> fixed
- line 312: “set of chemicals” --> fixed
- line 370: too many commas --> fixed
- line 371–372: change “energetics” to “energy” --> fixed
- Table 2: Mn - subscript on H2 --> fixed
- line 558: “Water vapour is” --> fixed
- line 446: Reaction (6) --> fixed
- line 626–627: “the same biomass” implies same in composition. Yet you distinguish earlier that these are two different biomasses. How about “same fraction of biomass”?

Response: We have reworded this to make this clearer.

- Line 679: “Reaction X”. (I’m not sure which reaction you are referring to here.)

Response: Apologies, this was an error. It is reaction.

- Line 727: extra period at end of line --> fixed

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