

Interactive comment on “The quantitative infrared and NIR spectrum of CH₂I₂ vapor: vibrational assignments and potential for atmospheric monitoring” by T. J. Johnson et al.

Anonymous Referee #1

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This work represents an important new quantitative spectral reference dataset for both the atmospheric and wider scientific community. The quantitative spectroscopy aspect to the paper is thorough and generally well-presented, although currently lacking a good quantitative discussion of potential error, which is crucial if the dataset is to be used in further quantitative applications. The resulting dataset is relevant to the atmospheric community through potential CH₂I₂ remote-sensing applications and the consequent insight such measurement would give into its role in organic aerosol formation and general tropospheric chemistry.

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This work is presented in the context of atmospheric measurement and a much clearer and correct analysis of the potential for such measurement is required, given the title of the paper. It would appear to me that the retrieval of CH₂I₂ gas concentrations from spectral measurements in the atmosphere would be extremely challenging, if not impossible, with little or no benefit over existing techniques. If that is so, then this should be emphasized and discussed in this paper.

A good quantitative discussion of both new spectroscopy for CH₂I₂ as well as a treatment of the potential for atmospheric monitoring, as suggested by the title of the paper, is ambitious for a single work and the authors might consider a more thorough treatment of each in independent submissions. However, publication in ACP is recommended subject to a major revision for the reasons now discussed.

General comments:

1/ Most importantly, although the data may be publically accessible through PNNL, the dataset should be available to the reader as an electronic supplement to this paper. The dataset should be submitted to ACP as an ASCII file supplement.

2/ The abstract makes little reference to the potential for atmospheric monitoring, despite the theme of the paper. A more, possibly quantitative, conclusion (e.g. a rough detection limit using some spectral band or resolved line) for such monitoring should be given in the abstract as well as a mention of the limitation of those techniques proposed in the paper. Such a discussion has been made later in the paper, but would benefit from some improvement (see points 4 and 5)

3/ The introduction begins by discussing the role (reactions with ozone) of methyl iodide in atmospheric chemistry, but does not include the key role (reactions) of CH₂I₂. These should be given in preference to CH₃I.

4/ The results section of the paper combines both a description of the quantitative spectroscopy, and a discussion of the potential for atmospheric monitoring. These should

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be separated into independent sections, e.g. a Results and a separate Discussion section. The current awkward merging of these two areas make the discussion of the potential for atmospheric monitoring difficult to digest at present.

5/ The conclusions of the discussion of potential monitoring are unclear; is the author suggesting that monitoring of CH₂I₂ by spectral means is preferable to existing in situ chemical techniques (e.g. GCMS) or if such monitoring is even possible at all in the atmosphere?

6/ An error analysis of the quantitative parameters (integrated band intensities etc..) is fundamental if these results are to be of used in remote-sensing applications, which rely on a knowledge of the accuracy of the spectral reference. See later specific note with reference to Page 1279, line 25.

7/ On several occasions, this work makes reference to planned future work or work in progress by the authors. Such statements should not be included and should rather be replaced by mention of the importance and need for future work of the type described.

Technical and specific comments:

Page 1276, Line 6: it is not clear in the abstract whether or not bands are resolved at 760 Torr of pure CH₂I₂ or for total pressure and what the carrier gas is, i.e. include “with Nitrogen” in this sentence.

Page 1276, Line 11: I believe it is ACP convention that “Ab initio” should be italicised. Please check and repeat this for all occurrences throughout.

Page 1278, Line 5: It is stated that ro-vibrational structure was not resolved for CH₂I₂ in previous measurements. Please state what spectral resolution was insufficient in previous works.

Page 1278, Line 11: The saturation vapour pressure of CH₂I₂ is given without reference, please provide one.

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Page 1278, line 16 and 17: The word “minimal” is used twice where I suspect “nominal” is what is meant? Please correct if this is so.

Page 1278, line 29: I think that the conventional acronym for “parts-per-trillion-by-volume” is pptv (without the subscript v). Please check this and correct all other instances if necessary.

Page 1279: Line 9: A temperature of 298.1 K is stated for the cell temperature. A brief mention of how the temperature was measured and the accuracy of such measurement should be given.

Page 1279: Line 25: You mention that the purity of the sample was “monitored” by spectroscopic means. How did you do this? Were you looking for the presence of other known infrared-active contaminants e.g. Water vapour, CO₂? How did you assess the presence of other possible non-infrared active contaminants? A brief description on your experimental setup for controlling purity should be given along with a good description of other potential sources of spectroscopic error. This is absolutely necessary if the quantitative spectroscopy reported here is to be used further. Refer to Allen et al, 2005a, (ACP, 5, 47-56, 2005, SRef-ID: 1680-7324/acp/2005-5-47) and Allen et al., 2005b (ACP, 5, 3139-3151, 2005, SRef-ID: 1680-7324/acp/2005-5-3139) for a good guide to detailing such errors in spectroscopic reference datasets.

Page 1280, line 19. Change 17 to “seventeen”. Quantities should be expressed verbosely.

Page 1281, line 13: You state that there is good agreement for vibrational frequencies with previous published work. Can you give a short quantitative discussion or perhaps a table?

Page 1282, Line 28: The spectral resolution of 0.0015 cm⁻¹ you state is higher than the capability of the Bruker IFS 166v/s. Did you use another spectrometer to perform these high resolution measurements? Why aren't these high-resolution measurements

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used in the rest of your analysis? If you measured spectra at 0.0015 cm^{-1} , aren't those superior to the dataset reported here at 0.1 cm^{-1} ?

Page 1283, line 18: What is the wavenumber spacing of the rotational lines? Can you calculate this or are you observing it from the measured spectrum?

Page 1284, line 12: Some readers may be unfamiliar with LWIR as an acronym, consider expanding the acronym.

Page 1284, Line 23: You mention that the resolution of line structure at low pressures may be useful in monitoring CH₂I₂. Is there enough (or any) CH₂I₂ expected at the levels of the atmosphere where pressure is low enough to resolve these lines? This could be quickly checked and commented on.

Page, 1286, line 5: You state that a weak CH₂I₂ line at 3073 cm^{-1} could be of use in remote-sensing and that CH₄ lines could overlap. Firstly, in Figure 3, you have simulated a 1 ppmv concentration of CH₂I₂; this is a factor of over 1000 greater than those expected to be observed, making the comparison of relative line intensities in the figure misleading. Secondly, would you expect CH₄ to be constant in a marine environment, as you have stated? Aren't their marine sources of CH₄? Also, there are some H₂O lines in Fig. 3. that are seen to overlap with the CH₂I₂ line. I suspect you would need to perform a joint retrieval of all three gases across a wider spectral interval, and at a high spectral resolution, to be able to extract CH₂I₂ concentrations. I truly sympathize with the difficulty of retrieving trace gas concentrations in the atmosphere spectroscopically, but it would be well to emphasize such difficulty here without restraint.

Page 1287, line 2: What is a detection limit of 10^{-4} ? Does this have a unit or is it some ratio?

Page 1287, line 13: I am unfamiliar with “telecommunicatons diode lasers”. Do you have a reference to this instrumentation?

Page 1287, line 24: Summary: Again, the summary includes little of the potential for

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atmospheric monitoring which is the title of the paper. Please include further comment.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 1275, 2006.

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