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Atmospheric
Chemistry
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Discussions

Interactive comment on “The quantitative infrared and NIR spectrum of CH_2I_2 vapor: vibrational assignments and potential for atmospheric monitoring” *by* T. J. Johnson et al.

T. J. Johnson et al.

Received and published: 28 March 2006

General Response to both Comments by Anonymous Referee #1 and Referee #2. (Detailed Comment for Referee #1 Below);

General Comments:

The referees have correctly gleaned that we are vibrational spectroscopists by training and atmospheric chemists only by absolute necessity. We agree with most comments and will try to better mask our heritage. We freely admit that there is a significant component of spectroscopy, and the paper could easily be published in either JPC or PCCP, for example. However, we thought the results of sufficient interest to the atmospheric community to publish it in an atmospheric journal such as ACP.

Both referees mentioned the fact that GC-MS offers better sensitivity than potential spectroscopic methods. We will modify the manuscript to mention this important point. However, it should be mentioned that while the blessing of GC-MS is that monitors at only one point in space is also the curse of GC-MS, namely that it only monitors at one point in space. An advantage of the spectroscopic methods is to remove spatial inhomogeneity artifacts by averaging over larger areas. The real point of this paper, besides the vibrational analysis, is to SUGGEST to atmospheric spectroscopists, e.g. researchers that do use DOAS on satellites or IR laser systems in the field, that this molecule has signatures of interest in appropriate “atmospheric windows”. This is not a field measurement paper, but a signatures paper that suggests where to look (spectroscopically) and that the band strengths are (almost) strong enough to suggest field measurements for the current state-of-the-art instruments, and perhaps readily measured with more common instruments a decade from now. Although detection limits are always of interest, we focus our work on cross sections which can suggest limits.

Both referees raised valid concerns about the uncertainties of the values. The error analysis shows that the maximal expected systematic errors are 3% for the PNNL static system measurements and 7% for flow system measurements, which would include CH2I2. The actual measured values are less than this, and these results have been vetted against NIST for a host of different molecules as described in the two Sharpe references (2003 and 2004), which contain all the details of the data analysis. We will modify the text to explicitly include this citation as containing information regarding uncertainties.

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REPLIES TO ADDRESS COMMENTS FROM REFEREE #1

Anonymous Referee #1 Received and published: 13 March 2006

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. S236 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 publicly 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.

> Unfortunately, this is not possible as the sponsor of the PNNL database will not allow it. There is a link to the PNNL website in the paper, where the data can be perused and downloaded. In addition to CH2I2, 400 other molecules are available at this site.

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)

> The abstract will be modified to include: "Potential bands for atmospheric monitoring and theoretical detection limits are discussed." We point out that detection limits for optical methods depend on both the instrument sensitivity and the band (line) strengths, which in turn are both a function of the wavelength region. Instrument sensitivities continuously change (for the better). The present work reports only the band strengths for use by the instrument developers. Although it would be desirable to say 'the current detection limits is xxx ppt' a (hypothetical) sensitivity analysis for the various bands and various types would be too long for the abstract. It would further depend on many other estimated parameters and is therefore relegated to the discussion.

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.

> This is a good suggestion. Text will be modified and Reaction (1) will show the photolysis of CH2I2 rather than CH3I. Ensuing chemistry remains the same.

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 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.

> Although the current organization may require some focus, the goal is to separately look at those wavelength regions that suggest the potential for atmospheric monitoring on a case by case basis (that is to say, Figures 3 though Figure 5) and discuss them

as such, results and discussion interwoven. The different bands suggest different technologies, and the present paper proffers those to the optical atmospheric community for consideration.

Figure 3: The nu 6 Q-branch at 3073 cm-1 shows promise for extractive monitoring by Pb-salt or QC diode laser systems (e.g. Fried et al. or Harris et al.) and the band strengths suggest estimated CH2I2 mixing ratios are pretty much near (or close to) the detection limit of current technology's best systems. The "best bet" for extractive low pressure laser studies would be the resolved lines of nu 8 and nu 9 bands, but more (high resolution) studies are first need. Work is in progress

Figure 4: The nu1 + nu6 band shows rotationally resolved Q-branch structure at 4426 cm-1. This band would be of little use for field measurements due to N2O interferences, but could be used e.g. in laboratory smog chambers (synthetic air, no N2O) with an FTIR or laser spectrometers. As the figure shows, one has the added benefit of being able to simultaneously measure the adjacent HI lines in e.g. a kinetic study.

Figure 5: These two bands with strong structure near 5950 cm-1 may be of interest to e.g. the "DOAS on a satellite" researchers (e.g. Platt et al, Burrows et al.) as the long optical paths increase the burden for greater optical depth, and the wavelengths are just accessible on the red end of many current spectrometers.

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?

$>$ If desired, the above (answer to 4) could be put into the summary. GCMS (currently) has unequivocally better sensitivity, but is not capable of long path monitoring, let alone global mapping. The goal of the present paper is not to actually monitor CH2I2, but to provide to atmospheric sensor groups (e.g. OP-FTIR folks, DOAS researchers, IR laser diode researchers) who do atmospheric monitoring the quantitative data that suggests

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“where to look” and what to expect. While HITRAN is an invaluable reference, it only contains ˜36 molecules, while the present quantitative set contains ˜400.

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 knowledge of the accuracy of the spectral reference. See later specific note with reference to Page 1279, line 25.

> Very good suggestion. The error analysis shows that the maximal expected systematic errors are 3% for the static system measurements and 7% for flow system measurements. The actual measured random values are much less than this, and these results have been vetted against NIST for host of different molecules as described in the two Sharpe et al. references. A sentence calling out these values and statistical methods with citation will be included in the text.

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.

> changed.

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.

> Original version was italicized, as Latin phrases normally are in English. ACP editors do not follow this format and removed the italics.

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.

> Not known. 30 to 50 year old dispersive instruments, mostly used for liquids.

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

> Changed. Carl L. Yaws, Chemical Properties Handbook, McGraw-Hill, New York, (1999). ISBN 0-07-073401-1.

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

> Minimal is correct. The data always extend from at least 600 up to 6500 cm-1. If bands are seen at wavenumbers lower than 600 or higher than 6500 with reasonable S/N they are also included.

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

> We will check with editor to follow ACP protocol.

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.

> A sentence will be included to the effect, “Temperature is measured by placing a NIST-traceable temperature probe directly into the gas in the White cell. Stated accuracy is ś 0.2 K.”

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.

> This is documented in the two papers by Sharpe et al. and the paper by Chu et al. We continuously monitor for H2O, CO2 and common contaminants, and for uncommon contaminants compare the IR data to any and all known references, commonly the Aldrich vapor phase library. As the system is continuously checked for leaks, and typically can maintain a vacuum of 0.001 Torr for 1 hour, we are confident in this regard. Also, we will be happy to include Dr. Allen et al.'s first reference that documents their approach (the second paper has perhaps the wrong page numbers? and simply cites the statistical approach in the first). We note that Allen et al's PAN paper was chemically far more challenging as PAN is not as stable as CH2I2. However, we direct the referee again to the papers by Chu et al and Sharpe et al. as a careful reading will show that in fact these methods are in the first instance the SAME as those of Allen et al, namely a linear least squares fit of A = f (P) where P is the analyte partial pressure. The Chu/Sharpe methods goes further, however, in that 1) in addition the raw absorbance data linear fit at each wavelength bin, the raw data also have a %T weighting factor to account for detector/Beer's law nonlinearities, 2) in the Chu/Sharpe method the residual fit vector is carefully analyzed, as any chemical impurity, including uncommon ones, will manifest itself in the residual vector, and 3) the PNNL method typically measures ˜15 separate burdens ranging over two orders of magnitude, as opposed to the six burdens discussed by Allen et al. These three points are valid for each of the 400 molecules in the PNNL database. In addition, for CH2I2 and a handful of other species, high resolution (0.0015 cm-1) studies have assigned all observed bands to the analyte.

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

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bosely.

> Change made, though we generally try to avoid verbosity.

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?

> It was decided against actually including the peak positions of Ford or Voelz et al. Due to the (30 to 50 year) older dispersive and uncalibrated equipment used in those studies, peak positions were far less accurate (perhaps only 5 or 10 cm-1?).

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 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?

> The spectrometers used for those measurements were two, a Bruker IFS 120 and IFS 125, and this is already called out in the Maki et al. reference. Such high resolution measurements/data would only be of use for extractive measurements (e.g. diode laser systems) whereas the PNNL database is designed only for data for species pressure broadened to 760 Torr with N2 for open path monitoring. Since the PNNL database focuses exclusively on 760 Torr P-broadened data for tropospheric monitoring, a resolution better than ˜0.1 cm-1 would be superfluous. In fact, the IFS 66v gives far better performance (though at lower resolution) that the 120/125 due to its much higher etendue.

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?

> These were observed in the high resolution (IFS 125) measurements to be reported later.

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

$>$ Already defined, p. 1278, Line 15.

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.

$>$ We do not know at this time, but the comment actually reflects on the fact that for extractive optical systems, the gas cells are held at low pressure (˜30 Torr) to reduce effects of P broadening on the spectra.

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.

$>$ This is a valid concern for ambient monitoring, but both the figure and the legend clearly state the plotted mixing ratios. Also, the figure might suggest the higher concentrations that one might see in a chamber experiment, and it is hoped that at high resolution some of the CH2I2 Q-branch lines will “break out” and allow for low pressure monitoring in a long path gas cell. As water is the anathema of infrared spectroscopists, the real point of Figure 3 is that although there are 6 orders of magnitude more water in the atmosphere than expected CH2I2, nature is somewhat kind in this instance and the CH2I2 Q-branch falls between the two enormously strong water lines.

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

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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.

> Atmospheric retrieval is indeed difficult, but that is not the focus of the present work. The methane is generally well mixed. Although swamps and marshes are sources of CH4, the ocean is generally considered at best a weak source, and especially weak since it has a low flux, yet covers 70% of the earth's surface. The primary sources are rice paddies, cattle flatulence and biomass burning. See for example, P. Warneck, Chemistry of the Natural Atmosphere, p. 153.

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

> This is optical density (absorbance) and is dimensionless.

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

> Telecom lasers operate at 0.78, 1.3 and 1.55 um, wavelengths familiar to those in the laser spectroscopy.

Page 1287, line 24: Summary: Again, the summary includes little of the potential for atmospheric monitoring which is the title of the paper. Please include further comment.

> As described above, a secondary focus of this laboratory study is to suggest potentially useful wavelengths for monitoring. The present work purports only to suggest useful wavelengths and cross sections to that end, but its primary focus is to offer for the first time the highly quantitative spectrum of CH2I2 vapor. It is hoped other researchers in the field avail themselves of this data. We point out that other papers in ACP also report only the data (see e.g. the Allen et al. papers cited above) needed for atmospheric measurements, without establishing any detection limits or discussing

interferences.

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FROM NUMBER 2:

Following points should be considered: P1276, L2-3 The role of di-iodomethane goes beyond providing precursors of new particle formation. This opening sentence is misleading and certainly out of place in the abstract.

> Good suggestion. Changed. See above.

P1277, L5 Reference to older literature (Schmitt, Kasper) is to be encouraged, but not when the conclusions drawn are irrelevant for the atmospheric chemistry of di-iodomethane. As the authors point out later, the formation of I2 and reformation of CH2I2 are not atmospheric processes in di-iodomethane photolysis. The “atmospheric chemistry“ text fails to mention the fundamental fact that the photolysis of CH2I2 results (via reaction 2) in IO formation, and that CH2I2 is a major contributor to coastal IO formation.

> Also suggested by referee #1. Text and reaction 1 changed to show CH2I2 rather than CH3I.

P1277, L16 Hoffmann et al did not show that OIO is formed in the reactions of IO. The first detection of OIO may be attributed to Himmelmann et al (Chem. Phys. Lett, 1996). Neither Harwood et al not Gilles et al observed OIO as a product of the IO self reaction or the reaction of IO with BrO. The correct citation is to Bloss et al (J. Phys. Chem 2001) and Rowley et al (J. Phys. Chem. 2001). The authors are encouraged to re-read the publications of e.g. Vogt et al, McFiggans et al and Cox et al and write a more concise and accurate summary of the role of iodine chemistry in the marine boundary layer.

> Changed. The citations will be corrected.

Will the IR spectra reported here will be available as supplementary information to readers of the Journal?

> Yes, but indirectly. It is not directly possible as the sponsor of the PNNL database will not allow it. However, there is a link to the PNNL website in the paper, where the data can be perused and downloaded. In addition to CH2I2, 400 other molecules are available at this site.

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