

## **Report on the manuscript:**

“Comment on “Radiative forcings for 28 potential Archean greenhouse gases” by Byrne and Goldblatt (2014)”

By: R. V. Kochanov, I. E. Gordon, L. S. Rothman, S. W. Sharpe, T. J. Johnson,  
and R. L. Sams (**KGRSJS**)

The authors of this manuscript, hereafter referred as KGRSJS, are the main contributors of two important and well known databases:

- The HITRAN database (Kochanov, Rothman, Gordon):  
<https://www.cfa.harvard.edu/hitran/> [Rothman et al. 2013].

HITRAN (High-resolution transmission molecular absorption database) is a compilation of spectroscopic parameters that a variety of computer codes use to predict and simulate the transmission and emission of light in the atmosphere. We will deal with the 2012 version (HITRAN-2012) of the HITRAN database [Rothman et al. 2013]. **In the rest of the text, we will consider only the line by line section of the HITRAN-2012 database (identified as “HITRAN-2012”) which is relevant for the BG and KGRSJS papers.** This line by line section includes individual spectral lines parameters (position, intensity and shape) for 47 different molecules, incorporating 120 isotopologues. The HITRAN-2012 parameters (line position, line intensity and line shape) were generated during suitable theoretical analyses of accurate laboratory measured data. The uncertainties in HITRAN-2012, which results both from the theoretical model and from the quality of the experimental data are well documented in Ref [Rothman et al. 2013]. Let us mention that the HITRAN-2012 linelist is prepared to be a “high resolution database”, while the PNNL cross-sections are at low resolution (at  $\sim 0.1 \text{ cm}^{-1}$ )

- The PNNL database (Sharpe, Johnson, and Sams)  
<https://secure2.pnl.gov/nsd/nsd.nsf/Welcome> [Sharpe et al. 2004]

The Pacific Northwest National Laboratory (PNNL) database (Sharpe et al. 2004) groups together cross sections measured in well-defined laboratory conditions at moderate resolution ( $0.1 \text{ cm}^{-1}$ ) for a large set of molecules. During the laboratory measurements the species under investigation are pressure-broadened to 760 Torr (1.013 hPa) using  $\text{N}_2$  gas. These PNNL cross sections data include contributions from hot bands or from less abundant isotopomers which may not be considered in HITRAN. For each species under consideration, an attached documentation describes the conditions of recording of the spectra. It is important to mention that the PNNL cross sections are “composite” experimental data. This means that, each time

this is possible, the PNNL data are “corrected” from the infrared signature due to impurities present in the experimental cell during the spectra recording.

Finally, the PNNL staff knows how it is difficult to get reliable cross sections, especially for unstable molecules ( $\text{H}_2\text{O}_2$  or HONO are very good examples), or for “sticky molecules” (like formaldehyde). Therefore, the accuracy associated to the PNNL cross sections may be restricted for unstable molecules.

**I suggest adding one or two sentences mentioned these points in the KGRSJS paper.**

Some molecules are considered both in the PNNL database and in the HITRAN linelist. When comparing computed cross sections with HITRAN-2012 to PNNL, one should consider the uncertainties associated to each set of parameters.

### **Main goal of the KGRSJS paper: comments on the “Radiative forcings for 28 potential Archean greenhouse gases” by Byrne and Goldblatt (2014)”**

In their recent paper [Byrne and Goldblatt (2014)], hereafter referred as BG, Byrne and Goldblatt used the HITRAN-2012 database to evaluate the radiative forcing of 28 gases present in the Earth atmosphere during the late Archean period.

As part of their study, BG calculated absorption cross sections for gases in Archean conditions using the LBLABC code written by David Crisp (Meadows and Crisp, 1996). As input to this code, BG used the line by line section of the HITRAN-2012. These computations concern several trace gases of importance in the Earth atmosphere during the late Archean period.

In a preliminary step of their study (pages 1781 to p1784 of BG’s paper), BG performed a validation of their method of cross section computation through a comparison with the PNNL data. This was done for all molecules considered both in HITRAN-2012 and in PNNL.

It is clear that this validation process is an important step for the credibility of BG’s study. Indeed, before extrapolating to the geophysical conditions of the Earth atmosphere during the late Archean period (which differ significantly from those existing presently), it is important to be confident on the quality of the calculations performed by BG.

Surprisingly enough, BG claimed that for eight out of the 28 gases, severe mismatches exist between their calculated cross sections (using the HITRAN line by line database) and the experimental entities available for these species in the PNNL database.

These gases are: nitrogen dioxide ( $\text{NO}_2$ ), nitric acid ( $\text{HNO}_3$ ), formaldehyde ( $\text{H}_2\text{CO}$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), formic acid ( $\text{HCOOH}$ ), ethylene ( $\text{C}_2\text{H}_4$ ), methanol ( $\text{CH}_3\text{OH}$ ), and methyl bromide ( $\text{CH}_3\text{Br}$ ).

The authors of KGRSJS paper disagree with several conclusions of BG paper. In order to access this opinion, KGRSJS performed a new computation of the cross sections using the

HAPI (HITRAN Interface Programming Interface) code which was recently developed by Kochanov et al (2015).

However BG and KGRSJS are using a different code (LBLABC and HAPI, respectively) for the computation of cross sections from the HITRAN-012 line by line dataset. **In order to provide an impartial answer, I decided to use my “homemade” code to perform the same computations.**

However a direct comparison of HITRAN and PNNL spectroscopic data for a given molecule at a given temperature can be done easily. Considering a spectral range (from  $\sigma_{\text{Dep}}$  to  $\sigma_{\text{End}}$ , for example) covered by HITRAN and PNNL, one has to compare the sum of the

individual lines intensities in HITRAN-2012 linelist  $\left( \sum_{\sigma_{\text{Dep}}}^{\sigma_{\text{End}}} \text{Line Intensity}_{\text{HITRAN}} \right)$  to the

integrated PNNL cross sections absorbance  $\left( \int_{\sigma=\sigma_{\text{Dep}}}^{\sigma_{\text{End}}} \text{Absorbance}_{\text{PNNL}} \times d(\sigma) \right)$  in the same spectral

range. In case the  $T_{\text{PNNL}}$  temperature associated to the PNNL cross sections differ from the reference temperature ( $T_{\text{Ref}}=296\text{K}$ ) of the line by line data in HITRAN-201, it is easy to convert the line by line intensity from  $T_{\text{Ref}}$  to  $T_{\text{PNNL}}$  using a standard procedure. The HITRAN website (<https://www.cfa.harvard.edu/hitran/>) and the reference papers (Rothman et al. 2013, Rothman et al. 2005) provide all the needed informations for this temperature conversion of the intensities in HITRAN-2012: the lower state energies  $E''$  tabulated in the line by line list and the partition function at different temperature on the website.

**This “direct comparison” is a simple arithmetic procedure that I use myself each time I obtain “strange” differences between HITRAN and PNNL during my own calculations. No need for sophisticated codes like LBLABC and HAPI for such validation!**

The limits of this “direct calculation” as of the HAPI code (or of my “homemade” code) are the same: indeed one has to keep in mind that lines belonging to hot bands or to less abundant isotopic species may be absent in HITRAN.

### Overview:

This report will be organized into two parts:

- (1) Agreements or disagreements with the criticisms to the BG’s paper presented by KGRSJS

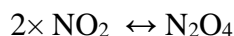
- (2) Some remarks or propositions to improve the text.
- (3) Main conclusions

**1. Agreement or disagreement with the criticisms to the BG's paper presented by KGRSJS**

**Page 3, lines 5:** Yes, I agree that the spectroscopic parameters are examined in detail through complex validation process before being included in the HITRAN database.

**NO<sub>2</sub>: in KGRSJS paper: see page 2, lines 18-20; Page 8, paragraph 3.1; and figure 1:**

Nitrogen dioxide (NO<sub>2</sub>) exist in equilibrium with its dimer form (N<sub>2</sub>O<sub>4</sub>).



NO<sub>2</sub>: The PNNL database is well documented and the difference between the "PNNL-NO<sub>2</sub>" (see the bottom trace of Fig. 1 of KGRSJS) and "PNNL-NO<sub>2</sub>-N<sub>2</sub>O<sub>4</sub>" (upper trace of Fig. 1 KGRSJS) cross sections is well described.

The attached documentation to PNNL-NO<sub>2</sub>-N<sub>2</sub>O<sub>4</sub> says:

*"Dimer (N<sub>2</sub>O<sub>4</sub>) features are at arbitrary concentration. By comparing NO<sub>2</sub> spectra at different temperatures it is possible to recognize the dimer (N<sub>2</sub>O<sub>4</sub>) features as these will increase at lower temperature and decrease at higher temperature"*

Investigating the literature [Hurtmans et al, 1993; Hepp et al. 2000], it is easy to see that the broad signatures in the (NO<sub>2</sub>+N<sub>2</sub>O<sub>4</sub>-PNNL) cross sections (see the top trace of Figure 1) are due to the  $\nu_{12}$  and  $\nu_6 + \nu_{10}$  bands (748 and 755 cm<sup>-1</sup>),  $\nu_{11}$  and associated <sub>dark</sub> band (1261 cm<sup>-1</sup> and 1264 cm<sup>-1</sup>, respectively) and  $\nu_9$  band (1757 cm<sup>-1</sup>) of N<sub>2</sub>O<sub>4</sub>.

NO<sub>2</sub>: KGRSJS paper; page 2, lines 18-20:

Yes, I agree with the conclusions of the KGRSJS paper that in the BG paper (see Figure 1 of the BG paper, page 1782), the "PNNL-NO<sub>2</sub>-N<sub>2</sub>O<sub>4</sub>" cross sections were used instead of "PNNL-NO<sub>2</sub>". This is a major error in BG paper.

NO<sub>2</sub>: KGRSJS paper; Page 8, paragraph 3.1; and figure 1:

I used my "homemade" code to compute cross sections from the HITRAN line by line parameters. The difference that I achieved between the "observed "(NO<sub>2</sub>-PNNL) and calculated cross sections are similar to the ones with are observed on the bottom part of Figure 1 of the KGRSJS paper.

NO<sub>2</sub>: In the KGRSJS paper (lines 13 to 15 in page 8):

*The zoomed spectral region inset shows that differences do exist, nevertheless, and they are attributed largely to experimental impurities described in Table 1, lack of line-mixing*

*parametrization and hot bands in HITRAN, as well as for mentioned differences between broadening by pure nitrogen vs. that by air.*

I agree with all these points. In addition, to my opinion, the broad structure centered in the 1263.68 cm<sup>-1</sup> in the NO<sub>2</sub>-PNNL cross section originates from the  $\nu_{11}$  band (and its associated dark band) of N<sub>2</sub>O<sub>4</sub> [Hepp et al. 2000].

**KGRSJS paper: H<sub>2</sub>O<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>OH and CH<sub>3</sub>Br : see paragraph 3.2 in Page 8 and figure 2:**

### **H<sub>2</sub>O<sub>2</sub>:**

I used my “homemade” code to compute cross sections from the HITRAN-2012. The difference that I achieved between the “observed” (H<sub>2</sub>O<sub>2</sub>-PNNL) and calculated (with HITRAN-2012) cross sections do not differ from the ones observed on the top part of Figure 2 of KGRSJS.

According to my own computations, the intensity ratio between HITRAN-2012 and PNNL in the 8  $\mu$ m region ( $\nu_6$  band) is:

$$\text{HITRAN-2012(H}_2\text{O}_2\text{) / PNNL(H}_2\text{O}_2\text{)} \approx 1.15$$

Hydrogen peroxide is a highly unstable molecule. According to the uncertainties associated with the intensities measurements, getting such a reasonable agreement between HITRAN-2012 and PNNL is really very satisfactorily.

To my opinion the difference between the PNNL (measured) and HITRAN-2012 (calculated) cross sections in the 1200-1320 cm<sup>-1</sup> spectral region (see the blue line in the upper panel of Figure 2 of KGRSJS) are due to first to the imperfections of the theoretical model used to calculate line positions and intensities for the  $\nu_6$  band of H<sub>2</sub>O<sub>2</sub> (centered at 1265 cm<sup>-1</sup>). The other reason is linked to the quasi absence of line shape parameters for this molecule in the literature.

So I agree completely with the conclusions which are stated in lines 18 to 26 of the KGRSJS paper.

### **C<sub>2</sub>H<sub>4</sub> :**

C<sub>2</sub>H<sub>4</sub>: For ethane, my calculations state that the PNNL data are about 10% and 12% stronger than HITRAN-12 in the regions corresponding to the strong  $\nu_7$  band (849 cm<sup>-1</sup>) and  $\nu_{11}$  (1450 cm<sup>-1</sup>) bands, respectively. More explicitly, I obtain ratios of

$$\text{PNNL(C}_2\text{H}_4\text{) / HITRAN(C}_2\text{H}_4\text{)} \approx 1.10 \text{ at } 849 \text{ cm}^{-1}$$

$$\text{PNNL(C}_2\text{H}_4\text{) / HITRAN(C}_2\text{H}_4\text{)} \approx 1.12 \text{ at } 1450 \text{ cm}^{-1}.$$

Let us also mention that the regions corresponding to the 1850  $\text{cm}^{-1}$  bands are still missing in HITRAN-2012: this is because  $\text{C}_2\text{H}_4$  represents quite a challenge for spectroscopists on the theoretical point of view.

For the regions covered by HITRAN the central parts of the Q branches *look narrower* in the PNNL database than *in my computation*. This is because my calculation does not account for the strong line mixing effect which is significant in the Q branches. This was also the case for the HAPI calculation of the KGRSJS paper.

So, I agree with KGRSJS for  $\text{C}_2\text{H}_4$  also.

### **$\text{CH}_3\text{Br}$ :**

For  $\text{CH}_3\text{Br}$ , my calculations are in full agreement with the conclusions of the KGRSJS paper.

The 600  $\text{cm}^{-1}$  ( $\nu_3$  band) and the 1900  $\text{cm}^{-1}$  regions are missing in HITRAN.

For the regions covered by both databases the intensities are in the ratio:

$$\text{PNNL}(\text{CH}_3\text{Br})/\text{HITRAN}(\text{CH}_3\text{Br}) \approx 1.1$$

Furthermore one can see evidence of line mixing in the central part of the Q branches.

### **$\text{CH}_3\text{OH}$ :**

I agree with the conclusions of the KGRSJS paper. It is not a surprise that only the 9  $\mu\text{m}$  region is covered by HITRAN-2012, because methanol represents quite a challenge on the theoretical point of view.

### **$\text{HNO}_3$ , $\text{H}_2\text{CO}$ and $\text{HCCOH}$ :**

As pointed out in the KGRSJS paper, the HITRAN database is still not fully satisfactory for  $\text{HNO}_3$ ,  $\text{H}_2\text{CO}$  and  $\text{HCOOH}$ .

Indeed for these three molecules the spectroscopy is difficult on the theoretical point of view. In addition,  $\text{HNO}_3$  is highly reactive and difficult to handle in laboratory conditions. Formaldehyde is a sticky molecule and formic acid.

Yes, some bands are still missing (the  $\nu_1$  band for example at 3  $\mu\text{m}$  for nitric acid), and for other ones, the parameters are not yet at the quality that we would like to have. I agree completely with the comments given in the paragraph 3.3 in page 9-10 of the KGRSJS paper.

### **$\text{HO}_2$ radical :**

Yes my calculations lead to computed  $\text{HO}_2$  cross sections (using the HITRAN-2012 parameters) which agree perfectly with those computed in KGRSJS paper (see the text in lines 18-20 in page 1994 and Figure 5 on page 2007 of KGRSJS paper).

## The BG paper:

**On the other hand, I do not agree** with the conclusions of the **BG paper** which say (text in page 1783, and Figure 1 in page 1782)

C<sub>2</sub>H<sub>4</sub>: “*the HITRAN data are about an order of magnitude less than PNNL*”.

CH<sub>3</sub>Br: “*HITRAN cross sections are over an order of magnitude greater than the PNNL cross sections*”

H<sub>2</sub>O<sub>2</sub>: “*HITRAN cross sections (for H<sub>2</sub>O<sub>2</sub>) are about twice the value of the PNNL*”.

Also in the BG paper, the computed cross sections for HO<sub>2</sub> are completely wrong (by one order of magnitude).

## 2. Some additional remarks:

☒ Page 1987, lines 11-14: I propose to mention that the cross sections included in the PNNL database are “composite” data. They result from many experiments. Furthermore, infrared signatures due to impurities were removed numerically from the experimental cross sections. A good example is given in the text with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) which exist in a laboratory cell in equilibrium with water, oxygen as impurities. This is the same for nitrogen dioxide (NO<sub>2</sub>) which exist in equilibrium conditions with its dimer (N<sub>2</sub>O<sub>4</sub>).

☒ Page 1992, paragraph 3.1:

The identification of the main infrared bands of N<sub>2</sub>O<sub>4</sub> are given in the following references [Hurtmans et al, 1993; Hepp et al. 2000]. I propose to add these references to the text.

☒ Table 1, page 2001:

I do not understand the column “PNNL classes” (the letters I, II and III). Please add a comment to the Table caption.

☒ Page 1992, paragraph 3.1 line 15 :

Please correct:

*...parametrization and hot bands in HITRAN, as well as **mentioned** differences between*

☒ The reference “Rothman 2005” is missing.

## 3. Main conclusions:

I agree with the conclusions presented in the present manuscript

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At the end of this present review report, I would like to stress the following points:

- This paper evidences major errors in the Byrne and Goldblatt paper.
- Yes, we know that HITRAN is not perfect. The spectroscopists all around the world, together with the HITRAN committee members are working hard to improve this database.
- For the eight gases (nitrogen dioxide (NO<sub>2</sub>), nitric acid (HNO<sub>3</sub>), formaldehyde (H<sub>2</sub>CO), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), formic acid (HCOOH), ethylene (C<sub>2</sub>H<sub>4</sub>), methanol (CH<sub>3</sub>OH), and methyl bromide (CH<sub>3</sub>Br)) for which Byrne and Goldblatt claimed “major errors” I do consider that HITRAN-2012 and PNNL agree **within the uncertainties associated to each of these databases** in the spectral ranges covered by HITRAN.
- In the BG paper, the computed cross sections for HO<sub>2</sub> are completely wrong.

So, I consider that the proposed manuscript (KGRSJS) should be published as soon as possible.

### References:

[BG] Byrne, B. and Goldblatt, C.: Radiative forcings for 28 potential Archean greenhouse gases, *Clim. Past*, 10, 1779–1801, doi:10.5194/cp-10-1779-2014, 2014a.

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