

Comment on  
“Radiative forcings  
for 28 potential  
Archean greenhouse  
gases”

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

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## Abstract

In the recent article by Byrne and Goldblatt, “Radiative forcing for 28 potential Archean greenhouse gases,” *Clim. Past.* 10, 1779–1801 (2014), the authors employ the HITRAN2012 spectroscopic database to evaluate the radiative forcing of 28 Archean gases. As part of the evaluation of the status of the spectroscopy of these gases in the selected spectral region (50–1800 cm<sup>-1</sup>), the cross sections generated from the HITRAN line-by-line parameters were compared with those of the PNNL database of experimental cross sections recorded at moderate resolution. The authors claimed that for NO<sub>2</sub>, HNO<sub>3</sub>, H<sub>2</sub>CO, H<sub>2</sub>O<sub>2</sub>, HCOOH, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>OH and CH<sub>3</sub>Br there exist large or sometimes severe disagreements between the databases. In this work we show that for only three of these eight gases does a modest discrepancy exist between the two databases and we explain the origin of the differences. For the other five gases, the disagreements are not nearly at the scale suggested by the authors, while we explain some of the differences that do exist. In summary, the agreement between the HITRAN and PNNL databases is very good, although not perfect. Typically differences do not exceed 10 %, provided that HITRAN data exist for the bands/wavelengths of interest. It appears that a molecule-dependent combination of errors have affected the conclusions of the authors. In at least one case it appears that they did not take the correct file from PNNL (N<sub>2</sub>O<sub>4</sub> + NO<sub>2</sub> dimer was used in place of the monomer). Finally, cross sections of HO<sub>2</sub> from HITRAN (which do not have a PNNL counterpart) were not calculated correctly.

## 1 Introduction

In their recent article, Byrne and Goldblatt (Byrne and Goldblatt, 2014a), hereafter denoted as BG) studied the radiative forcings for 28 Archean gases. To calculate these forcings, they used the line-by-line section of the HITRAN2012 spectroscopic database (Rothman et al., 2013).

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The HITRAN database is considered the international standard for the spectroscopic parameters of the gases that are major terrestrial atmospheric absorbers of light at different wavelengths. The database consists of experimental, theoretical, and semi-empirical parameters from laboratories all over the globe. Before the data appear in HITRAN they undergo a very thorough validation process (e.g., see Fig. 1 of the HITRAN2012 paper) including comparisons with independent lab spectra. The database is used by tens of thousands of researchers and industrial engineers for a great variety of applications. The database is being constantly updated by improving the accuracy of the existing line parameters as well as by adding new bands, new molecules, and new isotopologues.

The PNNL set is a strictly experimental database recorded at moderate resolution ( $0.1\text{ cm}^{-1}$ ) with all species pressure-broadened to 760 Torr during measurement using pure  $\text{N}_2$  gas. By definition, it includes all experimental effects in its results such as hot bands, combination bands, pressure broadening, and the effects of (potential) trace contaminants (Sharpe et al., 2004; Johnson et al., 2010).

In BG, as part of the evaluation of the spectroscopy of the selected 28 Archean gases in the spectral region of interest, the cross sections generated from the HITRAN line-by-line parameters were compared with the ones provided in the PNNL database of experimental cross sections (Sharpe et al., 2004). The LBLABC code (Meadows and Crisp, 1996) was used by BG for generating cross sections from HITRAN data. The comparison is visualized in Fig. 1 of the BG paper and includes a corresponding discussion. The authors claimed that for eight out of the 28 gases there are large or sometimes extreme disagreements between the two databases. 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 ( $\text{CH}_3\text{Br}$ ). For instance, for the latter gas the authors claim that HITRAN overestimates absorption coefficients by two orders of magnitude! The authors take into account these discrepancies when evaluating possible errors in their calculation of the radiative forcings when using HITRAN (see their Fig. 11 and discussion around it).

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These conclusions have a serious impact on the trust of potential users of both the HITRAN and PNNL databases. For instance,  $\text{NO}_2$  is a very important atmospheric gas and it is imperative that the HITRAN database contains a reliable line list for this gas. In this work we have repeated the authors' calculations using the HITRAN Application Programming Interface (HAPI) (Kochanov, 2015). HAPI is a tool that we are developing and that will be distributed with the HITRAN editions in the future. It allows downloading, filtering, and sophisticated absorption calculations using the HITRAN data. Our calculations show that for only three of these gases ( $\text{HNO}_3$ ,  $\text{H}_2\text{CO}$  and  $\text{HCOOH}$ ) do disagreements observed by the authors exist, and we explain their origin. For the other five gases, the disagreements are not nearly at the scale suggested by the authors, while we explain some of the subtler differences that do exist. It appears that a combination of errors might have affected the authors' conclusions. With certainty we can tell that at least in one case BG did not take the correct file from the PNNL database ( $\text{NO}_2 + \text{N}_2\text{O}_4$  was used in place of  $\text{NO}_2$ ).

In this article, the details of the calculations using HAPI are briefly described at the beginning. We then show the results that unambiguously demonstrate that the disagreements between HITRAN and PNNL, although they do exist, are not at the disastrous scale suggested by BG. The differences that are observed are then discussed and we conclude that they are mostly associated with either a few missing bands in HITRAN or with impurities in the PNNL spectra. We separate the findings into four categories: (1) when BG compare incorrect entities, i.e. when they compare  $\text{N}_2\text{O}_4$  from PNNL with  $\text{NO}_2$  from HITRAN, (2) when our comparison plots (for  $\text{H}_2\text{O}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{Br}$ ) look nothing like the ones shown in Fig. 1 of the BG paper, with the agreement of HITRAN and PNNL being substantially better than in BG plots, (3) when our plots (for  $\text{HNO}_3$ ,  $\text{H}_2\text{CO}$  and  $\text{HCOOH}$ ) look basically the same as those from the BG paper, (4) when there was no PNNL measurement available but the calculations carried out by BG using HITRAN data are incorrect (case of  $\text{HO}_2$ ).

## 2 Computational method

Absorption coefficients were calculated using line-by-line data from the HITRAN-2012 database. For the calculation of absorption coefficients, we have used the new software HAPI (HITRAN Application Programming Interface), which was recently created at the Harvard-Smithsonian Center for Astrophysics. For the basic algorithm of cross-section calculation, one can follow the appendix of the HITRAN1996 paper (Rothman et al., 1998). The capabilities of HAPI are briefly outlined later in this section.

Cross sections were calculated for thermodynamic conditions that were used when obtaining experimental data available in the PNNL database (Sharpe et al., 2004; Johnson et al., 2010). For constructing cross sections for each molecule, we have used isotopologues available in HITRAN-2012 in proportion to their abundance in the terrestrial atmosphere (as defined in HITRAN and also available in HAPI).

There are two important issues that one has to remember when comparing PNNL cross sections with those generated from the HITRAN database, although none of these issues are important when plotting the cross-section on the logarithmic scale as was done in the BG paper: (1) in the experiments that produced PNNL database files that are considered here, nitrogen was used as a buffer gas whereas the HITRAN database provides broadening and shifting parameters for air, i.e. a mixture of nitrogen and oxygen. In general the broadening parameters for air and  $N_2$  are different by factors that depend on the molecular species and even rovibrational transitions within these species. Nevertheless, for the purpose of this work it is quite sufficient to just use air-broadened values and that is what was used here. (2) At this time most of the HITRAN files do not include line-mixing which may account for some few percent differences in the cross sections, especially around the band heads.

Since we compare our calculations with the PNNL measurements at 5 and 25 °C and a pressure of 1 atm, we consider the Doppler broadening to be small compared to collisional broadening. For that reason, we applied a simple Lorentzian profile for all molecules. To improve the agreement with experiment, we apply the instrumental

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To better simulate gas mixtures, the user can apply custom broadening mechanisms considering the self-broadening, air-broadening (standard HITRAN-supported) and more complex foreign broadening schemes (applicability of such schemes depend on the presence of “non-standard” broadening parameters for a particular spectral line).

Apart from that, custom line profiles, partition sums, and instrumental functions can be used without a need to rewrite the HAPI code itself. This makes HAPI a powerful tool to calculate cross sections from the line-by-line data, provided by the HITRAN database (or potentially any similar line list of spectroscopic parameters). A Python program that interacts with HAPI in order to calculate cross sections generated here is provided in the supplementary material.

### 3 PNNL observations vs. calculations based on the HITRAN database

In this section we give the cross sections calculated here using HITRAN2012 line-by-line data compared with the experimental cross sections of PNNL. We made comparisons at the temperature of 5 °C whenever it was possible. For the cases in which the data of PNNL do not include 5 °C, we used the 25 °C datasets and compared to our calculations at 25 °C. All experimental spectra considered here were measured at  $760 \pm 5$  Torr pressure. In our calculations, the pressure was set to 760 Torr (i.e., 1 atm). Table 1 gives a summary of the experimental conditions that were employed by PNNL for the individual molecules which are in the focus of our comment paper. This table contains information on thermodynamic conditions, stability of samples, and both the potential and observed (subtracted) impurities. Indeed, some experiments are really non-trivial when it comes to stability of the samples, for instance the H<sub>2</sub>O<sub>2</sub> experiment was especially challenging and it is described in Johnson et al. (2009).

One should also keep in mind that the PNNL data do not exist below 600 cm<sup>-1</sup> as this is out of the region of the detectors employed in these experiments.

The calculated difference between the PNNL and HITRAN databases based on our present calculations (for the specified molecules, described in Sects. 3.1 and 3.2, over





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Devi et al. (1986), Klee et al. (1999), and Perrin et al. (1995, 1996). The data for  $\text{CH}_3\text{OH}$  originates from Xu et al. (2004). As seen in Table 2, for  $\text{C}_2\text{H}_4$ , on the contrary, BG underestimates the absorption when it employs HITRAN data. Our calculation shows that the agreement between PNNL and HITRAN is quite good. The differences between the data underneath strong peaks largely reflect uncertainties given for the corresponding intensity data in HITRAN, keeping in mind all other effects that were described earlier for the case of  $\text{NO}_2$ . The blow up of the differences around  $1440\text{ cm}^{-1}$  shows large residuals which we attribute to possibly missing hot bands in HITRAN and lack of line-mixing parameterization. In the selected spectral regions the ethylene data in HITRAN is based on the works of Blass et al. (2001), Brannon and Varanasi (1992), Cauuet et al. (1990), Legrand et al. (1995), Rotger et al. (2008), and Rusinek et al. (1998). Finally, for  $\text{CH}_3\text{Br}$ , BG overestimates absorption calculated using HITRAN. This mistake is visually enhanced in their Fig. 1 due to the apparent fact that what they present as PNNL cross sections does not actually correspond to the PNNL values and are weaker.  $\text{CH}_3\text{Br}$  data in HITRAN originate from Jacquemart et al. (2007) and Kwabia Tchana et al. (2004). It is worth mentioning that HITRAN indeed is missing a relatively strong  $\nu_3$  band at  $611\text{ cm}^{-1}$  as well as some hot bands in the region between the  $\nu_2$  ( $1335\text{ cm}^{-1}$ ) and  $\nu_5$  ( $1445\text{ cm}^{-1}$ ) bands as can be seen from the zoomed insert in the corresponding panel of Fig. 2.

### 3.3 $\text{HNO}_3$ , $\text{H}_2\text{CO}$ , and $\text{HCOOH}$

Figure 3 shows the  $\text{HNO}_3$ ,  $\text{H}_2\text{CO}$ , and  $\text{HCOOH}$  cross sections calculated from the HITRAN data and their comparison with corresponding experimental cross sections from the PNNL database. We find the same differences between the databases as did the BG paper. In fact, the lack of some of the important  $\text{HNO}_3$  bands is repeatedly noticed in the remote-sensing community (see for instance discussion in the HITRAN2008 paper, Rothman et al., 2009). Unfortunately, although we introduce major improvements into every new edition of HITRAN (for instance in HITRAN2012  $\text{H}^{15}\text{NO}_3$  isotopologue data was added based on Perrin and Mbiaké (2006) and validated in Brizzi et al., 2009)

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the lack of high-resolution reliable data in many regions prevents the modeling of the missing bands. A similar situation, but slightly less dramatic for remote-sensing applications, exists for  $\text{H}_2\text{CO}$ . Most notably HITRAN is missing the  $\nu_3$  band at  $1500\text{ cm}^{-1}$ . There is a plan to add this band based on the work of (Perrin et al., 2003) into the next edition of HITRAN. Finally, major differences between the PNNL and HITRAN databases for formic acid are attributed to the impurities (especially dimer) in the experimental spectrum (see Table 1). HITRAN is missing strong  $\nu_7$  and  $\nu_9$  bands located at  $\sim 630\text{ cm}^{-1}$ . There is a lack of intensity information to generate a comprehensive line list in this region although the information on the energy levels involved in the transitions is fairly complete for calculation of the line positions (Perrin et al., 2002) (Baskakov et al., 2006). It is interesting that differences that do exist in the strong bands that are present in both databases seem to manifest themselves in between the strong lines (see Fig. 4). It could be that (1) there is a broad continuum-like feature due to an impurity that underlies the PNNL spectrum in that region, and/or (2) for experimental spectra it is sometimes very difficult to assign a zero baseline to subtract, especially in cases where it must be assigned under a broad, complex spectral band or bands.

### 3.4 $\text{HO}_2$

Figure 5 shows the cross sections for  $\text{HO}_2$  calculated based on the HITRAN data. Comparing Fig. 5 with Fig. 1 from the BG paper it is clear that the corresponding cross sections are not calculated correctly there (they are underestimated).

Similarly, we conclude that although the plot for HF in Fig. 1 of the BG paper correctly represents the data in the databases, the discussion around it is quite incorrect. They state: “the HITRAN and PNNL data do not overlap. The HITRAN data is available below  $500\text{ cm}^{-1}$  and PNNL data is available above  $\sim 900\text{ cm}^{-1}$ ”. Their statement is very misleading. The HITRAN2012 database is very complete for the HF molecule. The HF line list is described in the HITRAN2012 paper and given in more detail in Li et al. (2013). One problem is that PNNL obviously had some noise issue or an impurity in the  $800\text{--}2000\text{ cm}^{-1}$  region. That is why it may seem that there is an HF absorption

in that region if looking at the PNNL spectra in Fig. 1 of the BG paper. For HF the PNNL focus was only on the spectral region of the  $\nu_1$  fundamental at wavenumbers  $\geq 4000 \text{ cm}^{-1}$ .

In summary, our calculated absorption coefficients agree well with experimental data for the considered temperatures and pressure. Contrary to the conclusions of the BG paper, we find that the disagreements are mostly unnoticeable on the logarithmic scale in the places of strongest absorption. In the zoomed regions we show comparison on a linear scale with residuals. We considered mostly these regions, in which the HITRAN-2012 database is known to have enough data to reproduce the real absorption correctly. Most of these residuals are less than 20 to 30%. For some Q-branches, however, they can reach 70%. This effect can be due to the strong line mixing that may occur in these branches. For most of the strongest absorption bands, the agreement corresponds well with the error codes supplied with the HITRAN database. Naturally the agreement is worse for the bands with weaker absorption due to absence of lines in the database or to impurities in experimental data.

It's worth mentioning that the residuals between PNNL's data and our calculations are mostly above zero. For instance, for formaldehyde the agreement is fine for the line peaks (5–10% for the error code 5 and 10–20% for the error code 4), whereas the line wings give more systematic error (see Fig. 4).

## 4 Conclusions

In this comment we have shown that the differences between the PNNL and HITRAN databases are not nearly as severe as was purported in the BG paper, in most cases differ by only 20% or much less, not by an order of magnitude or more as claimed. In particular, in the cases of  $\text{H}_2\text{O}_2$ ,  $\text{HO}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CH}_3\text{OH}$ , and  $\text{CH}_3\text{Br}$  it is clear that BG did not calculate cross sections correctly from the HITRAN line-by-line data. In the case of  $\text{CH}_3\text{Br}$  it also seems that the PNNL cross sections shown by BG in their Fig. 1 are much weaker than those in the real PNNL database. We cannot tell on the logarithmic

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scale of that figure if that may be the case for other molecules. However, in the case of  $\text{NO}_2$ , BG clearly appears to have used the  $\text{N}_2\text{O}_4 + \text{NO}_2$  cross sections from PNNL when comparing to HITRAN  $\text{NO}_2$  data.

In their other paper (Byrne and Goldblatt, 2014b) it is mentioned that they take cross sections from the Virtual Planetary Laboratory (VPL) and give the following link <http://depts.washington.edu/naivpl/content/molecular-database>. We could not find any actual data at that address, only graphical overviews of the data from PNNL. With that we note that under the  $\text{NO}_2$  link at that site one can find the figure showing the  $\text{NO}_2 + \text{N}_2\text{O}_4$  absorption. In fact, thanks to our interactions with thousands of researchers across the globe we can state that the most common error associated with using HITRAN or PNNL data is the use of data that were obtained not from the databases themselves, but from secondary sources and were very likely altered at some point. Unfortunately, the conclusion of this comment is that Fig. 1, Fig. 11 and discussions around them in the BG paper are simply incorrect. Consequently, the radiative forcings calculated there for the aforementioned molecules are in error. At the same time, certain discrepancies do in fact exist for  $\text{HNO}_3$ ,  $\text{H}_2\text{CO}$  and  $\text{HCOOH}$  and are mostly due to the missing bands in HITRAN and to a lesser extent impurities in the PNNL experimental spectra (for instance, dimer presence in the  $\text{HCOOH}$  spectra). In the supplementary material we provide a Python script that can be run with HAPI. The current version of HAPI is available at ([www.hitran.org](http://www.hitran.org)) along with its manual.

As managers of both databases we are happy to jointly announce that large portions of the PNNL database will be added to the cross-sectional part of the HITRAN database; we hope that this will minimize future errors associated with the use of both databases simultaneously.

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## References

Baskakov, O. I., Markov, I. A., Alekseev, E. A., Motiyenko, R. A., Lohilahti, J., Horneman, V. M., Winnewisser, B. P., Medvedev, I. R., and De Lucia, F. C.: Simultaneous analysis of rovibrational and rotational data for the  $4^1$ ,  $5^1$ ,  $6^1$ ,  $7^2$ ,  $8^1$ ,  $7^1 9^1$  and  $9^2$  states of HCOOH, *J. Mol. Struct.*, 795, 54–77, doi:10.1016/j.molstruc.2006.02.052, 2006.

Blass, W. E., Jennings, L., Ewing, A. C., Daunt, S. J., Weber, M. C., Senesac, L., Hager, S., Hillman, J. J., Reuter, D. C., and Sirota, J. M.: Absolute intensities in the  $\nu_7$  band of ethylene: tunable laser measurements used to calibrate FTS broadband spectra, *J. Quant. Spectrosc. Radiat. Trans.*, 68, 467–472, doi:10.1016/S0022-4073(00)00050-9, 2001.

Brannon, J. F. and Varanasi, P.: Tunable diode laser measurements on the  $951.7393\text{ cm}^{-1}$  line of  $^{12}\text{C}_2\text{H}_4$  at planetary atmospheric temperatures, *J. Quant. Spectrosc. Radiat. Trans.*, 47, 237–242, doi:10.1016/0022-4073(92)90141-P, 1992.

Brizzi, G., Arnone, E., Carlotti, M., Dinelli, B. M., Flaud, J. M., Papandrea, E., Perrin, A., and Ridolfi, M.: Retrieval of atmospheric  $\text{H}^{15}\text{NO}_3/\text{H}^{14}\text{NO}_3$  isotope ratio profile from MIPAS/ENVISAT limb-scanning measurements, *J. Geophys. Res. Atmos.*, 114, 1–12, doi:10.1029/2008JD011504, 2009.

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.

Byrne, B. and Goldblatt, C.: Radiative forcing at high concentrations of well-mixed greenhouse gases, *Geophys. Res. Lett.*, 41, 152–160, doi:10.1002/2013GL058456, 2014b.

Cauuet, I., Walrand, J., Blanquet, G., Valentin, A., Henry, L., Lambeau, C., de Vleeschouwer, M., and Fayt, A.: Extension to third-order Coriolis terms of the analysis of  $\nu_{10}$ ,  $\nu_7$ , and  $\nu_4$  levels of ethylene on the basis of Fourier transform and diode laser spectra, *J. Mol. Spectrosc.*, 139, 191–214, doi:10.1016/0022-2852(90)90251-K, 1990.

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Jacquemart, D., Kwabia Tchana, F., Lacome, N., and Kleiner, I.: A complete set of line parameters for in the  $10\ \mu\text{m}$  spectral region, *J. Quant. Spectrosc. Radiat. Trans.*, 105, 264–302, doi:10.1016/j.jqsrt.2006.10.006, 2007.

Johnson, T. J., Sams, R. L., Burton, S. D., and Blake, T. A.: Absolute integrated intensities of vapor-phase hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in the mid-infrared at atmospheric pressure, *Anal. Bioanal. Chem.*, 395, 377–386, doi:10.1007/s00216-009-2805-x, 2009.

Johnson, T. J., Profeta, L. T. M., Sams, R. L., Griffith, D. W. T., and Yokelson, R. L.: An infrared spectral database for detection of gases emitted by biomass burning, *Vib. Spectrosc.*, 53, 97–102, doi:10.1016/j.vibspec.2010.02.010, 2010.

Klee, S., Winnewisser, M., Perrin, A., and Flaud, J.: Absolute line intensities for the  $\nu_6$  band of  $\text{H}_2\text{O}_2$ , *J. Mol. Spectrosc.*, 195, 154–161, doi:10.1006/jmsp.1999.7807, 1999.

Kochanov, R., Hill, C., Gordon, I., Wcislo, P., Rothman, L., and Wilzewski, J.: HITRAN Application Programming Interface (HAPI) – Beta version, Zenodo, available at: <http://dx.doi.org/10.5281/zenodo.17719>, 2015.

Kwabia Tchana, F., Kleiner, I., Orphal, J., Lacome, N., and Bouba, O.: New analysis of the Coriolis-interacting  $\nu_2$  and  $\nu_5$  bands of  $\text{CH}_3^{79}\text{Br}$  and  $\text{CH}_3^{81}\text{Br}$ , *J. Mol. Spectrosc.*, 228, 441–452, doi:10.1016/j.jms.2004.05.011, 2004.

Laraia, A. L., Gamache, R. R., Lamouroux, J., Gordon, I. E., and Rothman, L. S.: Total internal partition sums to support planetary remote sensing, *Icarus*, 215, 391–400, doi:10.1016/j.icarus.2011.06.004, 2011.

Legrand, J., Azizi, M., Herlemont, F., and Fayt, A.: Saturation spectroscopy of  $\text{C}_2\text{H}_4$  using a  $\text{CO}_2$  laser sideband spectrometer, *J. Mol. Spectrosc.*, 171, 13–21, doi:10.1006/jmsp.1995.1099, 1995.

Li, G., Gordon, I. E., Hajigeorgiou, P. G., Coxon, J. A., and Rothman, L. S.: Reference spectroscopic data for hydrogen halides, Part II: The line lists, *J. Quant. Spectrosc. Radiat. Trans.*, 130, 284–295, doi:10.1016/j.jqsrt.2013.07.019, 2013.

Meadows, V. S. and Crisp, D.: Ground-based near-infrared observations of the Venus nightside: the thermal structure and water abundance near the surface, *J. Geophys. Res.*, 101, 4595, doi:10.1029/95JE03567, 1996.

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Ngo, N. H., Lisak, D., Tran, H., and Hartmann, J. M.: An isolated line-shape model to go beyond the Voigt profile in spectroscopic databases and radiative transfer codes, *J. Quant. Spectrosc. Radiat. Trans.*, 129, 89–100, doi:10.1016/j.jqsrt.2013.05.034, 2013.

Perrin, A. and Mbiaké, R.: The  $\nu_5$  and  $2\nu_9$  bands of the  $^{15}\text{N}$  isotopic species of nitric acid ( $\text{H}^{15}\text{NO}_3$ ): line positions and intensities, *J. Mol. Spectrosc.*, 237, 27–35, doi:10.1016/j.jms.2006.02.005, 2006.

Perrin, A., Valentin, A., Flaud, J. M., Camy-Peyret, C., Schriver, L., Schriver, A., and Arcas, P.: The  $7.9\ \mu\text{m}$  band of hydrogen peroxide: line positions and intensities, *J. Mol. Spectrosc.*, 171, 358–373, doi:10.1006/jmsp.1995.1125, 1995.

Perrin, A., Flaud, J.-M., Camy-Peyret, C., Schermaul, R., Winnewisser, M., Mandin, J.-Y., Dana, V., Badaoui, M., and Koput, J.: Line intensities in the far-infrared spectrum of  $\text{H}_2\text{O}_2$ , *J. Mol. Spectrosc.*, 176, 287–296, doi:10.1006/jmsp.1996.0089, 1996.

Perrin, A., Flaud, J.-M., Bakri, B., Demaison, J., Baskakov, O., Sirota, S., Herman, M., and Auwera, J. V.: New high-resolution analysis of the  $\nu_7$  and  $\nu_9$  fundamental bands of trans-formic acid by Fourier transform infrared and millimeter-wave spectroscopy, *J. Mol. Spectrosc.*, 216, 203–213, doi:10.1006/jmsp.2002.8659, 2002.

Perrin, A., Keller, F., and Flaud, J.-M.: New analysis of the  $\nu_2$ ,  $\nu_3$ ,  $\nu_4$ , and  $\nu_6$  bands of formaldehyde  $\text{H}_2^{12}\text{C}^{16}\text{O}$  line positions and intensities in the  $5\text{--}10\ \mu\text{m}$  spectral region, *J. Mol. Spectrosc.*, 221, 192–198, doi:10.1016/S0022-2852(03)00207-8, 2003.

Rotger, M., Boudon, V., and Vander Auwera, J.: Line positions and intensities in the  $\nu_{12}$  band of ethylene near  $1450\ \text{cm}^{-1}$ : an experimental and theoretical study, *J. Quant. Spectrosc. Radiat. Trans.*, 109, 952–962, doi:10.1016/j.jqsrt.2007.12.005, 2008.

Rothman, L. S., Rinsland C. P., Goldman A., Massie S. T., Edwards, D. P., Perrin, A., Dana, V., Gamache, R. R., and Jucks, K. W.: The HITRAN molecular spectroscopic database and HAWKS (HITRAN atmospheric workstation): 1996 edn., *J. Quant. Spectrosc. Radiat. Trans.*, 60, 665–710, 1998.

Rothman, L. S., Gordon, I. E., Babikov, Y., Barbe, A., Chris Benner, D., Bernath, P. F., Birk, M., Bizzocchi, L., Boudon, V., Brown, L. R., Campargue, A., Chance, K., Cohen, E. A., Coudert, L. H., Devi, V. M., Drouin, B. J., Fayt, A., Flaud, J.-M., Gamache, R. R., Harrison, J. J., Hartmann, J.-M., Hill, C., Hodges, J. T., Jacquemart, D., Jolly, A., Lamouroux, J., Le Roy, R. J., Li, G., Long, D. A., Lyulin, O. M., Mackie, C. J., Massie, S. T., Mikhailenko, S., Müller, H. S. P., Naumenko, O. V., Nikitin, A. V., Orphal, J., Perevalov, V., Perrin, A., Polovtseva, E. R., Richard, C., Smith, M. A. H., Starikova, E., Sung, K., Tashkun, S., Tennyson, J.,

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Toon, G. C., Tyuterev, V. G., and Wagner, G.: The HITRAN2012 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Trans.*, 130, 4–50, doi:10.1016/j.jqsrt.2013.07.002, 2013.

5 Rothman, L. S., Gordon, I. E., Barbe, A., Benner, D. C., Bernath, P. F., Birk, M., Boudon, V., Brown, L. R., Campargue, A., Champion, J.-P., Chance, K., Coudert, L. H., Dana, V., Devi, V. M., Fally, S., Flaud, J.-M., Gamache, R. R., Goldman, A., Jacquemart, D., Kleiner, I., Lacombe, N., Lafferty, W. J., Mandin, J.-Y., Massie, S. T., Mikhailenko, S. N., Miller, C. E., Moazzen-Ahmadi, N., Naumenko, O. V., Nikitin, A. V., Orphal, J., Perevalov, V. I., Perrin, A., Predoi-Cross, A., Rinsland, C. P., Rotger, M., Šimečková, M., Smith, M. A. H., Sung, K., Tashkun, S. A., Tennyson, J., Toth, R. A., Vandaele, A. C., and Vander Auwera, J.: The HITRAN 2008 molecular spectroscopic database, *J. Quant. Spectrosc. Radiat. Trans.*, 110, 533–572, doi:10.1016/j.jqsrt.2009.02.013, 2009.

15 Rusinek, E., Fichoux, H., Khelkhal, M., Herlemont, F., Legrand, J., and Fayt, A.: Subdoppler study of the  $\nu_7$  band of  $C_2H_4$  with a  $CO_2$  laser sideband spectrometer, *J. Mol. Spectrosc.*, 189, 64–73, doi:10.1006/jmosp.1998.7539, 1998.

Sharpe, S. W., Johnson, T. J., Sams, R. L., Chu, P. M., Rhoderick, G. C., and Johnson, P. A.: Gas-phase databases for quantitative infrared spectroscopy, *Appl. Spectrosc.*, 58, 1452–1461, doi:10.1366/0003702042641281, 2004.

20 Tennyson, J., Bernath, P. F., Campargue, A., Csaszar, A. G., Daumont, L., Gamache, R. R., Hodges, J. T., Lisak, D., Naumenko, O. V., Rothman, L. S., Tran, H., Zobov, N. F., Buldyreva, J., Boone, C. D., De Vizia, M., Gianfrani, L., Hartmann, J.-M., McPheat, R., Weidmann, D., Murray J., Ngo, N. H., and Polyansky, O. L.: Recommended isolated-line profile for representing high-resolution spectroscopic transitions, *Pure Appl. Chem.*, 86, 1931–1943, doi:10.1515/pac-2014-0208, 2014.

25 Xu, L. H., Lees, R. M., Wang, P., Brown, L. R., Kleiner, I., and Johns, J. W. C.: New assignments, line intensities, and HITRAN database for  $CH_3OH$  at  $10\ \mu m$ , *J. Mol. Spectrosc.*, 228, 453–470, doi:10.1016/j.jms.2004.05.017, 2004.



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**Table 1.** Characteristics of PNNL data on considered molecules.

Molecule	Temperature, °C	PNNL class	PNNL comments on possible impurities (including those subtracted)
NO <sub>2</sub>	25 ± 2	I	N <sub>2</sub> O <sub>4</sub> , NOCl [0.48 %], NO [0.33 %], HNO <sub>3</sub> [0.15 %] and H <sub>2</sub> O [0.13 %]
CH <sub>3</sub> Br	5.03 ± 0.02	I	Dimethyl Ether (CH <sub>3</sub> OCH <sub>3</sub> ) [0.10 %]
C <sub>2</sub> H <sub>4</sub>	5.03 ± 0.02	I	–
H <sub>2</sub> CO	5.00 ± 0.02	III <sup>1</sup>	Air, CO <sub>2</sub> , polymers, water vapor
HCOOH	25 ± 2	II	Water contamination [4.70 %] (corrected by rescaling and spectral subtraction). Dimer features present at 3400–2500, 1736, 1365, 1221 and 926 cm <sup>-1</sup> .
H <sub>2</sub> O <sub>2</sub>	25 ± 2	I	50 % hydrogen peroxide was distilled in house to 82.78 % by weight which is 70.698 % by volume. H <sub>2</sub> O was subtracted.
CH <sub>3</sub> OH	4.98 ± 0.02	I	Air, Water. Multiple freeze–thaw cycles at –60 °C to remove air. Sample placed over CaSO <sub>4</sub> for removal of water
HNO <sub>3</sub>	5.05 ± 0.02	III <sup>2</sup>	Individual absorbance spectra corrected and accounted for H <sub>2</sub> O, CO <sub>2</sub> , NO, NO <sub>2</sub> , N <sub>2</sub> O and HCl contamination.

<sup>1</sup> Extremely unstable due to rapid polymerization.

<sup>2</sup> Extremely reactive. Undergoes rapid decomposition when exposed to heat and reducing agents (e.g., metals, organics...).

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**Table 2.** Differences between HITRAN and PNNL for molecules for which conclusions were erroneous in BG.

Molecule	Integration limits cm <sup>-1</sup>	$\Delta^a$	Erroneous conclusion in BG <sup>b</sup>
CH <sub>3</sub> OH	947.7–1090.9	0.7 %	Over order of magnitude larger
H <sub>2</sub> O <sub>2</sub>	1175.7–1369.8	+5 %	More than twice larger
CH <sub>3</sub> Br	547.8–1097.2	-19 %	About 13 times larger
	1242.6–1335.1	-14 %	
C <sub>2</sub> H <sub>4</sub>	1334.8–1625.5	-16 %	About order of magnitude lower
	825.5–1160.0	-16 %	
HF <sup>c</sup>	1381.6–1515.6	-10 %	HITRAN and PNNL do not overlap
	3581.9–4336.8	+7 %	
NO <sub>2</sub>	635.5–923.5	-13 %	About order of magnitude lower
	1518.9–1728.6	-0.6 %	

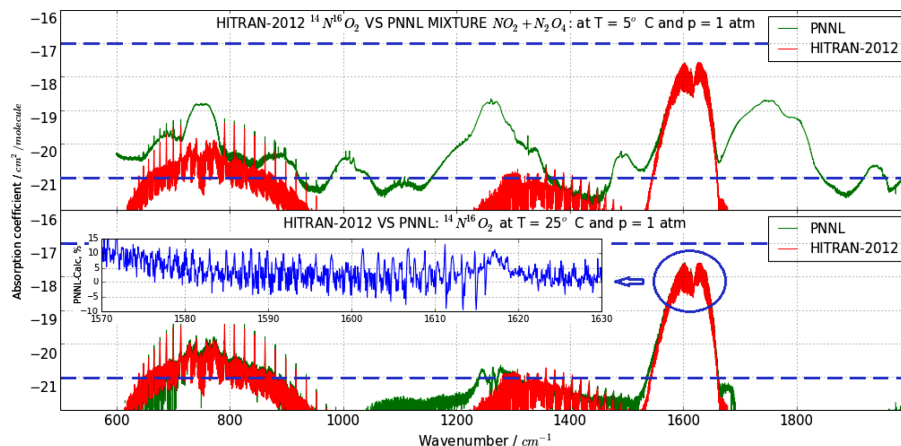
<sup>a</sup>  $\Delta = (\text{HITRAN} - \text{PNNL})/\text{HITRAN} \times 100\%$ .

<sup>b</sup> BG comments in terms of HITRAN data with respect to PNNL.

<sup>c</sup> HITRAN and PNNL overlap perfectly; it is just that absorption is very weak in the region considered by BG.

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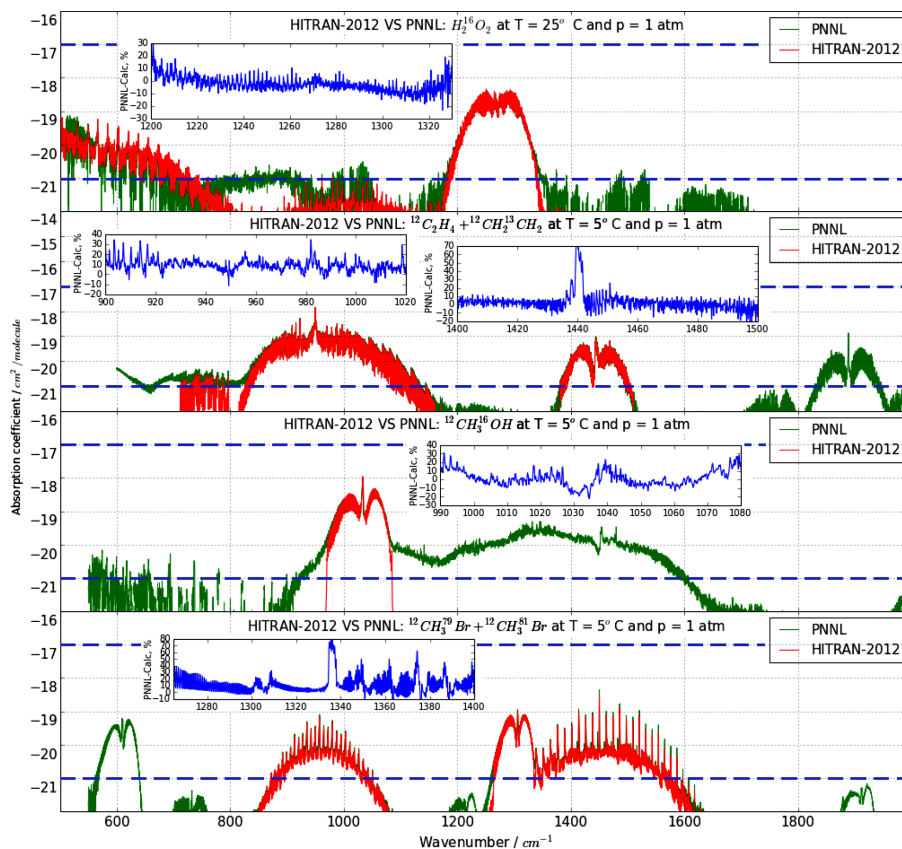
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**Figure 1.** Comparison of HITRAN with PNNL: case of  $\text{NO}_2$ . The top panel shows cross sections from PNNL for the mixture of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  (green trace) compared to HITRAN  $\text{NO}_2$  data as was done in the BG article. The bottom panel compares  $\text{NO}_2$  from PNNL to  $\text{NO}_2$  in HITRAN showing very good agreement. The area inside the thick dashed horizontal grid lines corresponds to the area shown in the panels of Fig. 1 in the BG article.

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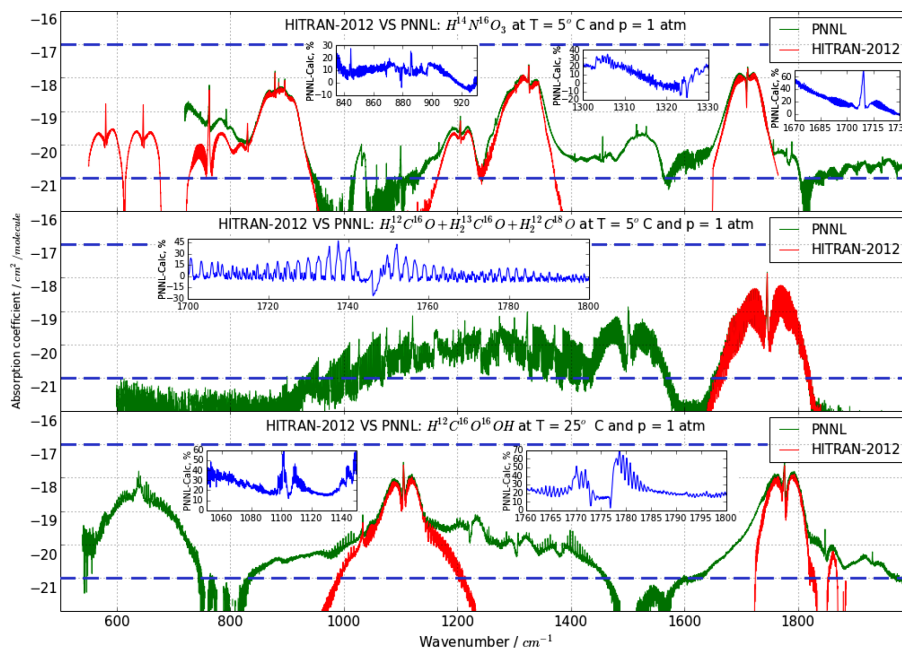
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**Figure 2.** Comparison of HITRAN with PNNL: from top to bottom  $\text{H}_2\text{O}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{Br}$ . The area inside the thick dashed horizontal grid lines corresponds to the area shown in the panels of Fig. 1 in the BG article.

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**Figure 3.** Comparison of HITRAN with PNNL: from top to bottom  $\text{HNO}_3$ ,  $\text{H}_2\text{CO}$ ,  $\text{HCOOH}$ . The area inside the thick dashed horizontal grid lines corresponds to the area shown in the panels of Fig. 1 in the BG article.

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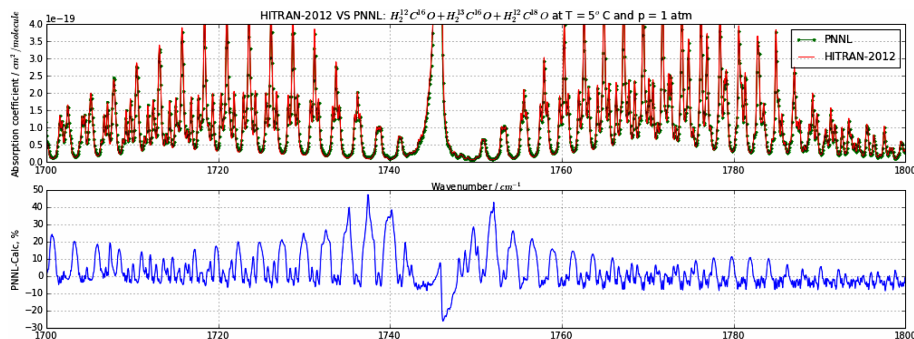
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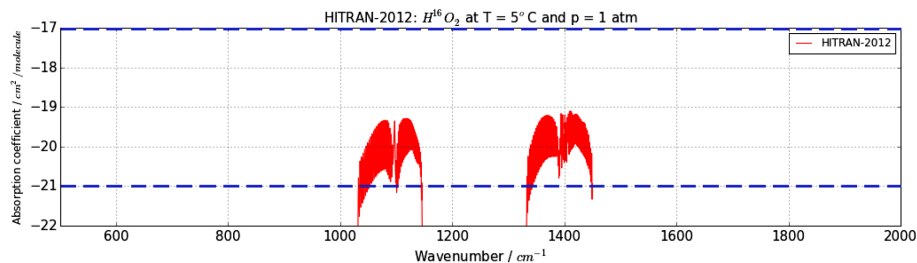
**Figure 4.** Residuals between calculated and experimental cross sections of  $\text{H}_2\text{CO}$  in the  $1700\text{--}1800\text{ cm}^{-1}$  spectral region.

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**Figure 5.** Cross sections generated from the HITRAN data for  $HO_2$ . The area inside the thick dashed horizontal grid lines corresponds to the area shown in the panels of Fig. 1 in the BG article.

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