Letter to the Editor about paper amt-2019-54.docx Interactive comment on "The use of O₂ 1.27 μ m absorption band revisited for GHG monitoring from space and application to MicroCarb" by Jean-Loup Bertaux et al.

Revised version, September 22, 2019.

Dear Editor,

Fisrt, we must convey our gratitude to the work performed by the Editor and referees, who all have scrutinized in detail our paper, in spite of its length. They pointed out, not only English language errors, but also a number of small errors that are now corrected. A fair number of short sentences have been added for clarification, at the request of referees. As a result, our revised paper is really improved w.r.t. the first submitted version.

Several figures have been redrawn at the request of referees, and one has been deleted. However, at the request of Referee #2, we had to produce new figures to explain the details of our data processing of SCIAMACHY Level 1c data. These new figures are displayed in one Appendix B. We think that these figures are not necessary for our paper; we are ready to follow the advice of the Editor if he thinks that this Appendix B may be removed form the final version. This appendix is also included in our response to RC3 from Referee #2.

We have not accepted the suggestions of Referee #1 to mostly remove Section 2.3, which is the heart of paper, for reasons detailed in our answer to this Referee#1. We copy one of them below:

1. The theoretical development (to obtain a theoretical spectrum of the O_2^* airglow emission) that we present here was done in 2017, and completely independently from the work of Sun et al. (2018). If we were following the suggestion to just quote the equations of Sun et al. (2018) and not present our own analysis, it would give to the reader the false impression that we have followed blindly the developments of Sun et al. 2018, which is not true. The fact that both groups have developed the same kind of theory (form the same theoretical approach based on what can be found in Simeckova et al. (2006)) re-inforce the credibility of this approach, which is very important for "hundreds of millions dollars space projects".

We think that following the suggestion of Referee#1 would give unduly a unique credit to a US team in this field, while we feel that AMT is basically a European inspired publication.

Length of the paper: We recognize that this paper is long, but we still believe that its overall length is appropriate. At an early stage one reviewer suggested to split the paper in several papers but we have been quite reluctant to continue along this line (split or shorten substantially) for the following reasons.

All parts of the paper are relevant to the same subject: is it possible to use the O_2 1.27 µm absorption band for CO_2 mixing ratio retrieval, in spite of the strong airglow contamination?

The team that was assembled for this scientific research had to cover several scientific aspects: our understanding of this airglow, building a model for the intensity, and a model for the spectral shape, validation with comparisons with

SCIAMACHY/ENVISAT data, separation of airglow from absorption. One reader is not obliged to read carefully all sections, he can pick up what he is most interested in. We estimate that if we would split our paper into two papers, the overall total length of the two papers would be longer than the present version, because of unavoidable repetitions (each paper must be self-consistent, including references). It would require also twice more reviewers and Editor work.

AMT stands for Atmospheric Measurements Techniques and therefore our paper is perfectly in scope with the profile of the publication.

Our paper is long because it is deliberately rather detailed, because we wish to ease the possibility that anybody else to be able to reproduce our results. The spirit of AMT, with public discussions before final publications, is in line with the "open source" philosophy. Cancelling parts of the paper would jeopardize this philosophy.

Remember that the results of about 30% of all scientific papers cannot be reproduced by other scientists, and this comes to 50% of papers in biology, a very embarrassing situation.

One great advantage of AMT publication is that it does not require paper printing, therefore cancelling a source of CO_2 production. Only an interested reader would potentially print it. Therefore, with AMT we may reconcile CO_2 economy and detailed description for better reproducibility of results.

In its present form, our paper is somewhat "self-consistent" on its subject. It will serve as a reference, not only for the MicroCarb project, but also on other future GHG monitoring space projects that may consider the use of the $1.27 \,\mu m$ band.

Finally, we note that the length of the paper did not discourage a fairly large number of scientists to download the paper when discussed in AMTD: The paper has been viewed HTML 262 times and the pdf downloaded 100 times (21 September 2019), about half from the US. If the final version were cut significantly, it would introduce an advantage to those who uploaded the early version versus those seeing only the final version. It would also jeopardize the efforts of the referees that have scrutinized and corrected the whole text.

The MicroCarb project is in full development now, and we hope for many new results to come before and after launch. We would be glad to continue to publish in AMT and ACP, if the present experience with AMT comes to a satisfactory conclusion.

On behalf of the authors

Jean-Loup Bertaux

2.3.3 Computing the distribution of O2* molecules among the various energy levels

In their 2006 paper, Simeckova et al. (2006) describe « the calculation of the statistical weights and the Einstein A -coefficients for the 39 molecules and their associated isotopologues/isotopomers currently present in the lineby-line portion of the HITRAN database ». This is all that is needed to calculate second members of equation (6) for all allowed transitions L_i , giving the rate of emission of the corresponding spectral line VER(L_i).

In an approximation of a two level system (upper m and lower n levels are denoted as 2 and 1 respectively) at <u>LTE (Local Thermodynamic Equilibrium)</u>, we have the well-known equations linking the Einstein A-coefficients and B-coefficients

$$g_1 B_{12} = g_2 B_{21}$$
(7)
$$A_{21} = 8\pi h \nu^3 B_{21}$$
(8)

where A_{21} (spontaneous emission) is in s⁻¹, and B_{12} (absorption) and B_{21} (stimulated emission) are in cm³ (J s²)⁻¹, and g_1 and g_2 are the statistical weights of the levels 1 and 2, respectively.

We start from equation (17) of Simeckova et al. (2006) with molecules in the lower level 1 and the upper level 2 (much less numerous at atmospheric temperatures), to describe their relative distribution according to their energy level E_{1i} or E_{2i} and temperature T, the index i indicating a particular rovibrational level defined by J' and <u>V'</u>. If N is the total number of molecules per unit volume at the temperature T, the population N_{2i} of one of the energy level E_{2i} of the upper level 2 is equal to:

$$N_{2i} = \frac{g_{2i}N}{q_{tot}(T)} e^{-c_2 E_{2i}/T}$$
(9)

and a similar equation for N_{di} and the energies E_{di} of the lower level (equation (17) of Simeckova et al. 2006). Here, $Q_{tot}(T)$ is the total internal partition sum of the absorbing gas at the temperature T, $g_{2i}=2J'+1$, and E_{2i} is the energy of the upper state in units of wavenumber (cm⁻¹). c_2 is the second radiation constant, c_2 -*hc*/k_B, where c is the speed of light, *h* is the Planck constant, and $k_B = 1.38065 \times 10^{-23}$ joule K⁻¹ is the Boltzmann constant. The total number of molecules per unit volume N= $\Sigma N_{11} + \Sigma N_{2i}$, and $Q_{tot}(T)$ is the sum of $Q_{tok}^{(0)}(T)$ and $Q_{tok}^{(0)}(T)$, respectively the internal partition sum of the lower level and the upper level. The index *i* refers to all possible values of J', starting at J'=2 (J'=0 and J'=1 do not exist). We have by definition:

$$Q_{tot}^{up}(T) = \sum_{i} g_{2i} \ e^{-c_2 E_{2i}/T}$$
(10)

We may find the value of $Q_{tot}(T)$ in Table 1 of the paper of Simeckova et al. (2006). For instance, $Q_{tot}(T=296 \text{ K})=215.77$ for the main oxygen isotopologue ${}^{16}O{}^{16}O$. The temperature 296 K is a reference temperature for the HITRAN database. For our purpose, we have to find $Q_{tob}{}^{up}(T)$ for the upper level of the transition, from a summation described in equation (10). The summation must be not over all the transitions, but over all energy levels, because from a given energy level having a certain population N_{2i} , there are several transitions going down to the lower level with different A_{21} . Once we have $Q_{tot}(T)$, the total internal partition sum, then we may

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compute all values of N_{2i} , for the required temperature, from the distribution of the excited molecules between the various energy levels from equation (9).

However, $Q_{tok} = (T)$ is very small when referred to all molecules N. For convenience, we have replaced in equation (10) the values E_{2i} by E_{2i} - E_{20} , where E_{20} is the energy of the lowest energy populated level with J'=2. With this approach we found <u>new values $Q'_{101} = Q_{102} \exp(c_2 E_{20}/T)$ for the upper level; $Q'_{10k} = (T=296 \text{ K})$ for 296 K, and $Q_{tok} = (T=200 \text{ K})$ is 100.143. In Fig. 4 are represented both the exponential term and the statistical weight, product of the exponential term and 2J'+1. Only the V'=0 are kept here, because levels V'=1 are weakly populated, though they are present in the line list that are extracted from HITRAN line-by-line data base in our selected wavelength interval of interest (transition (1,1).</u>



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Figure 4. Partition function of the O_2^* molecule as a function of rotation state J'. Blue triangles: exponential term for population, =1 for the lowest; Black circles: the population computed for all HITRAN transitions with V'=0, V''=0. There are 5, 7, or 8 values (and transitions) for each black circle in the figure, present in the HITRAN list, because of transitions selection rules and weak lines (below a certain threshold) are not in HITRAN. The V''=1, V'=1 transitions (1,1) are not shown. The first point for J'=2 is obviously 5=2J'+1, and exp(0)=1.

Fig.5 presents the various energy levels (in cm⁻¹) of the upper state, the O₂* molecule. The energy is <u>here</u> counted above the lowest energy level of the fundamental state $X^{3}\Sigma_{g}^{-}$.



Figure 5. Energy levels (in cm^{-1}) of the excited molecule O_2^* as a function of rotational and vibrational quantum numbers J' and V'.

At LTE and atmospheric temperatures, $Q_{tot}^{up} \ll Q_{tot}^{lo} \approx Q_{tot}(T)$ with a factor $\frac{Q_{tot}^{up}(T)}{Q_{tot}(T)}$ near 10⁻¹⁶, while

$\frac{Q'_{tot}^{up}(T)}{Q_{tot}(T)}$ is approximately between 0.1 and 1.

The partition functions described above, as well as the connection between the A_{21} and the strength of the transition S_{HIT} were established with considering a gas at LTE conditions. But then the value of A_{21} does not depend if there is LTE or not. In particular, when a population of excited O_2^* molecules are produced from ozone photolysis, the ratio $\Sigma N_{2t}/N$ may be much larger than with LTE conditions. Whatever rotational level in which they will be produced by photolysis, they will soon re-equilibrate among the various rotational upper levels because the lifetime is quite long versus the collision time with ambient molecules, without changing $\Sigma N_{2t}/N$.

2.3.4. Computing the total decay rate of the excited molecule O_2^{\star}

The actual distribution $Q(J',T)/Q_{totup}(T)$ of the excited molecule O_2^* is a function of the rotational state J' and of the temperature, such that the sum over all J' is equal to one:

$$\frac{\sum Q(J',T)}{Q_{tot}^{up}(T)} = 1 \tag{11}$$

Each particular rotational level may decay through several transitions, each transition with its own decay rate, or Einstein probability of spontaneous emission, called A_{21} , which is given in HITRAN tables of line-by-line lists. The total (average) decay rate from the upper level is obtained by summing all A_{21} on all transitions weighted by the relative population of each rotational level;

$$A_{21tot} = \sum A_{21}(J') \frac{Q(J',T)}{Q_{tot}^{up}(T)}$$
(12)

Since there is the emission of one photon around 1.27 μ m for each decay of one excited O₂* molecule, A_{21tot} is the weighted sum of all rates of all transitions going down, which is the total emission rate, the total number of photons emitted in the whole band per second by one single molecule of O₂*.

Then we must multiply by the number density of O_2^* to get the volume emission rate in photons per (cm³ s). We found from the HITRAN data that the total decay rate is $A_{21tot}=2.29 \ 10^{-4} \ s^{-1}$, slightly different from 2.22 $10^{-4} \ s^{-1}$ derived from the rounded value 75 mn of the lifetime quoted by Lafferty et al. (1998). We may compute the lifetime 1/ $A_{21tot}=4367 \ s^{-7}$ 3 mn. The excited molecule O_2^* will, in average, stay excited for more than one hour (in the absence of quenching, de-excitation by collisions without the emission of one photon, not addressed here).

It must be realized that it is experimentally very difficult to measure directly such a long lifetime. Instead, because the values of A_{21} are connected to the values of absorption coefficients B_{21} , it is easier to measure the absorption of O_2 molecules, and then make the appropriate calculations to derive the A_{21} values, according to

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bertaux 30 sept. 19 15:54 Supprimé: principles explained in Simeckova et al. (2006), which have been used to fill the HITRAN line-by-line lists with A₂₁ rates for each transition.

2.3.5. Computing the emission spectrum of the excited molecule O_2^*

The emission rate per O_2^* molecule $\epsilon(k)$ of a transition k is obtained by multiplying the Einstein Coefficient $A_{21}(k)$ by the relative population of the upper level:

$$\varepsilon(k) = A_{21}(k) \frac{Q(J'(k),T)}{Q_{tot}^{up}(T)}$$
(13)

When plotted as a function of wavelength of transition k it represents the emission spectrum for one molecule, per molecule and per second. It is displayed in Fig. 6 for 296 K (right scale) and compared to the absorption line intensities. SS which are found in the line-by-line HITRAN line list (left scale). The distribution of the lines in three branches is clearly observed (Q branch: J'-J''= 0; P branch: J'-J''= -1; R branch: J'-J''= +1). The transitions from V'=1 to V''=1 are very weak and near the zero line.



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Figure 6: Emission rate per excited molecule $O_2^* eps=\varepsilon(k)$ from eq(13) in photons/s per molecule O_2^* , (left scale) compared to the absorption line strengths SS at 296 K found in HITRAN data (in units of cm⁻¹(cm²/ molecule). See text for more explanations.

Therefore, a spectrum of the local emission in the band could be computed, by describing each emission transition by a gaussian with an appropriate width (associated to the temperature), adding all transitions to form a full spectrum, and multiplying by the actual density of O_2^* molecules.

However, we have implemented another method, to take advantage of LBLRTM software (Line By Line Radiative Transfer Model, Clough and Iacono, 1995) which computes for the terrestrial atmosphere absorption

spectra (either local, or integrated over one LOS, line-of-sight) from HITRAN data base. Indeed, with the adequate scaling of both right and left scale of Fig. 6, it is noted that the strength of absorption lines are just above the emission rates on the left side of the graph (short wavelength), while it is the reverse on the right side. As we shall see below, there is a theoretical reason for this progressive change of the ratio of emission to absorption strength.

2.3.6. Theoretical computation of the ratio emission/absorption

We first repeat here the equation (19) from Simeckova et al. (2006) which links A21 to the line strength SS

(below, $S_{V}(k,T)$) in which k designates one transition from energy level E_{lk} with a wave number v_{0} :

$$S_{\nu}(k,T) = \frac{g_2}{\rho_{tot}(T)} \frac{A_{21}(k)}{8\pi c \nu_0^2} \exp\left(\frac{-c_2 E_{1k}}{T}\right) (1 - \exp\left(\frac{-c_2 \nu_0}{T}\right))$$
(14)

We may extract the expression of $A_{21}(k)$ from equation (14) and put it in equation (13). Taking into account that $E_{2k}-E_{1k}=v_0$ and that the statistical weight of energy level E_{2k} is:

$$Q(J'(k),T) = (2J'+1)\exp\left(-\frac{c_2 E_{2k}}{T}\right) = g_2 \exp\left(-\frac{c_2 E_{2k}}{T}\right)$$

we could find a very simple result on the ratio of emission $\epsilon(k)$ to absorption line strength $S_{v}(k,T)$ for each line:

$$\frac{\varepsilon(k)}{S_{\nu}(k,T)} = 8\pi c \nu_0^2 \frac{Q_{tot}(T)}{Q_{tot}^{up}(T)} \frac{1}{\exp({}^{C_2\nu_0}/_T) - 1}$$
(15)

In Fig. 7 the ratio of our calculated emission to the HITRAN line strength SS for all transitions within our spectral interval is plotted <u>for two temperatures</u> (black <u>and blue</u> dots), together with the analytical formula (15) (a continuous function of wavenumber v_0) computed on a regular wavelength grid. Both share the same scale on the left: there is a perfect coincidence, which validates our derivation of equation (<u>15</u>).

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HITRAN line strength SS <u>are plotted (respectively black and blue dots)</u> <u>ref</u> all 375 transitions of HITRAN Table (between 1.2238 and 1.32068 μ m). The solid lines (respectively red and purple) are <u>computed from the analytical</u> formula (15) on a grid of wavelength/wavenumber using the same scale on the left as the ratio emission/line strength, in units of photon cm⁻² s⁻¹/cm⁻¹.

