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## RESEARCH ARTICLE

## The effect of collisions with nitrogen on absorption by oxygen in the A-band using cavity ring-down spectroscopy.

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This paper reports on the effect of collisions between nitrogen and oxygen on absorption in the A-band near 760 nm under atmospheric conditions relevant for satellite retrieval studies. We use pulsed laser cavity ring-down spectroscopy with a narrow bandwidth laser and use pressure scans to increase the accuracy of the measured oxygen extinction coefficients. We use the so-called Adjustable Branch Coupling model to describe line mixing in the magnetic allowed A-Band dipole absorption and we retrieve the collision induced absorption spectrum due to N<sub>2</sub>-O<sub>2</sub> collisions.

**Keywords:** Oxygen; A-band; Collision Induced Absorption; Cavity Ring Down spectroscopy; Line Mixing;

## 1. Introduction

Satellite measurements are used extensively for climate studies. In particular, a large interest exists in accurate measurements of CO<sub>2</sub> emissions and sinks at the surface of the earth[1]. In view of the present column densities, such measurements must have an accuracy of better than 1%. To achieve this level of accuracy, the consequences of clouds reducing the visibility of the surface, and of aerosols creating extra path lengths must be quantified. Both of these effects can be accounted for by making use of spectral windows. The oxygen A-band is such a window. In this spectral region, absorption is due to O<sub>2</sub> molecules only. Furthermore the distribution of oxygen throughout the atmosphere is very well known, allowing for determinations of cloud top heights and aerosol scattering as well as air mass retrieval, by comparing the retrieved surface pressure with the actual pressure. The desired accuracy for CO<sub>2</sub> retrieval requires oxygen measurements with an even better accuracy. For the A-band highly accurate line shapes are needed beyond the simple Voigt line shapes. Effects that affect the line shapes are Dicke narrowing [2] and speed dependent effects of collision broadening[3, 4]. These effects change line shape near the line centres. The valleys in between the lines are affected mostly by line mixing (LM)[5] and collision induced absorption (CIA)[6]. In 2005, an analysis of high resolution solar spectra revealed that errors in photon paths up to

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5% were found analysing the A-Band in combination with Voigt lines and it was concluded that the description of the absorption far from the line centres needed improvement [7]. Tran and Hartmann showed that a large part of the discrepancy could be explained by the absence of line mixing and collision induced absorption [8].

Voigt line shapes result from the convolution between a Gaussian line shape, accounting for molecular motion (Doppler broadening), and a Lorentz line accounting for molecular collisions (pressure broadening). Molecular dependent coefficients for pressure broadening are found in the HITRAN database [9]. LM describes the consequences of inelastic collisions on a spectrum. Intensity shifts from the wings of the band to the centre of the band and the line shape becomes non-Lorentzian. On average, the intensity is redistributed and the integrated band strength is thus not affected. On the other hand, CIA describes the absorption by transient or metastable collision complexes. The long range quadrupole-quadrupole interaction during the collisions between oxygen and oxygen and nitrogen and oxygen lead to extra transition probabilities. The magnitude of the CIA between oxygen and nitrogen ( $O_2N_2$  CIA) seems better understood than the CIA due to oxygen oxygen collisions ( $O_2O_2$  CIA) for which no satisfactory model exists [10, 11]. As the interaction times during collisions are of the order of picoseconds or less, the CIA spectrum is expected to be broad and without rotational structure. We note, that the CIA strength scales strictly quadratically with collision rate. Its relative impact to the total extinction increases at higher densities, an aspect of which we make use in our analysis.

In recent times the A Band has been studied in considerable detail, mostly with Fourier Transform Spectroscopy (FTS) techniques. The CIA of oxygen with various partners (oxygen, nitrogen, carbon dioxide) has been quantified at high pressures [8, 12–15]. Tran and Hartmann found that a LM model is essential to retrieve a consistent CIA spectrum. At atmospheric pressures, a highly accurate line shape analysis was performed also indicating the need for LM apart from subtle effects as Dicke narrowing and speed dependent effects [16]. Earlier studies that significantly improved the HITRAN database also used FTS [17, 18]. In FTS studies at low pressures (up to several bars), CIA is difficult to retrieve because of base line uncertainties [19]. In a previous article from our group [20], referred to as FS, we confirmed the need for LM and determined the  $O_2O_2$  CIA at atmospheric relevant densities using cavity ring down spectroscopy (CRDS). Accurate data were taken with a  $0.07\text{ cm}^{-1}$  bandwidth laser in between the lines of P-branch, the region of the missing Q-branch and frequencies above the band head in the R-branch. The LM model we used was developed by Tonkov and co-workers from the co-authors of the Saint Petersburg group. Its parameters are taken directly from the HITRAN database [9]. In FS the experimental and theoretical methods are described in detail. In the present article, we expand the work performed in FS by looking at the CIA resulting from  $O_2-N_2$  collisions in the oxygen A-band studied in three different mixtures.

## 2. Theory

The true line shape of allowed transitions is not simple to describe. A Voigt line shape assumes the Doppler effect and the collisional broadening to be independent. Many models have been developed to introduce detailed effects of collisions and the dependence of the speed of the molecules on absorption and thus the line shape. Models of the Dicke effect and of speed dependent effects change the line shapes near the line centre. LM is an effect that has a relatively large effect in between

the lines and above the band head of the R branch. We concentrate on the valleys in between the lines and hence we can restrict our model to LM as modification of Voigt type line shapes. The LM model we used is called the adjustable branch coupling (ABC) model [21, 22]. In this model, the collisions are described as hard collisions. The ABC-model has only one free parameter, the so called interbranch coupling parameter ( $r$ ), all other parameters come from HITRAN. In one extreme **no distinction is made between lines in the different branches ( $r = 1$ )**. In the other extreme, line mixing is only allowed within the P-branch and within the R-branch but not in between the branches ( $r = 0$ ). As expected, this parameter **mostly** affects the predicted absorption in the missing Q-branch. For an extended description of the model, we refer to FS and the references therein.

The effect of foreign gas such as  $N_2$  is assumed to be additive. The collision contribution is weighed by the volume fractions, ( $V_k$ ). The total broadening for a given line ( $\gamma_j$ ) is thus given by

$$\gamma_j = V_{O_2}\gamma_{j,O_2} + (1 - V_{O_2})\gamma_{j,N_2}, \quad (1)$$

where  $V_k$  is the volume fraction of gas  $k$  and  $\gamma_{j,k}$  is the broadening of a particular line  $j$  due to gas  $k$ . In the HITRAN database [9, 23] **the broadening due to  $O_2$  (self broadening) and air are included. From the air broadening, it is possible to retrieve the broadening due to  $N_2$ , when one considers air to consist of 21%  $O_2$  and 79%  $N_2$ .**

Fano was the first to derive an expression for the effect of LM on Lorentz lines [24]. He derived the following expression for the spectral distribution:

$$\Phi(\omega) = \frac{1}{\pi} \Re \left\{ \sum_{qj,q'j'} \rho_j x_{qj} x_{q'j'} \left[ \frac{1}{i(\omega - L_0) + \Gamma(\omega)} \right]_{qj,q'j'} \right\}. \quad (2)$$

In this equation,  $\rho_j$  are the (temperature dependent) initial state populations,  $x_{qj}$  are the reduced dipole moments. The products  $\rho_j |x_{qj}|^2$  provide the line strengths as found in HITRAN [9, 23],  $\omega$  is the frequency considered. The labels  $q$  and  $q'$  are used to distinguish transitions within the two individual branches, the remaining label  $j$  simply enumerates all optical transitions.  $L_0$  is also known as the Liouville operator, which is a diagonal matrix containing all transition frequencies. The matrix  $\Gamma$  contains all collisional **effects** and is called the relaxation matrix. The diagonal of the relaxation matrix contains pressure shifts and broadenings and the off-axis elements contain line mixing effects. Hence, a diagonal relaxation matrix describes a spectrum being a simple sum of Lorentzian lines.

The hard collision model implies a direct relation between the collision rate and the LM effect. The elements of the matrix  $\Gamma$  are given by [21]:

$$\begin{aligned} \Gamma_{qj,q'j'} &= (1 - r)\delta_{qq'}\bar{\tau}^{-1} (\delta_{jj'} - A_q^{-1}\rho'_j x_{qj} x_{q'j'}) \\ &+ r\bar{\tau}^{-1} (\delta_{qq'}\delta_{jj'} - A^{-1}\rho'_j x_{qj} x_{q'j'}) + i\delta_{jj'}\Delta\bar{\nu}_j, \end{aligned} \quad (3)$$

In this equation  $\bar{\tau}^{-1}$  is the averaged collision frequency, which is obtained from the pressure broadening parameters from HITRAN, **and  $\Delta\bar{\nu}_j$  is the pressure shift of**

Table 1. The mixing ratio's of the gas mixtures used for determination of the CIA in O<sub>2</sub>N<sub>2</sub> mixtures.

	vol.% O <sub>2</sub>	vol.% N <sub>2</sub>
mixture 1	54±1	46 ±1
mixture 2	20.97±0.03	79.03±0.03
mixture 3	29.989±0.002	70.011 ±0.002

line  $j$ . We use these pressure shifts as found in HITRAN database.  $A$  is the total integrated intensity of the band and  $A_q$  is the integrated intensity of branch  $q$ . All components of the relaxation matrix can be complex, accounting for both line shifts and changes in line shape. We ignore the imaginary part of the diagonal elements, which reflect the pressure induced line shifts, in the calculation of the off-diagonal components. The only free parameter is  $r$ , which makes it possible to affect the amount of coupling between the two branches. After using the ABC-model to introduce line mixing, the Doppler effect is accounted for in a convolution procedure. For the data treatment, the absorption coefficient is calculated for 100 densities in each pressure scan. These model absorption coefficients are subtracted from the measured extinction coefficients to determine the CIA contribution.

### 3. Experiment

In order to determine the extinction for O<sub>2</sub> mixed with N<sub>2</sub>, three mixtures were used, two of which were quantified by the Netherlands Institute for Standards (NMI). The mixing ratio's are shown in table 1.

The total extinction due to these mixtures were measured at selected wavelengths using cavity ring down spectroscopy (CRDS). Light from a pulsed nanosecond laser is injected in a cavity with highly reflective mirrors ( $R \sim 0.99995$ ) The decay of this light through one of the mirrors is measured using a photomultiplier tube (PMT) selected for its linear response. The decay constant is determined by the reflectivity of the mirrors and the absolute extinction due to the gas mixture in the cavity. By making use of pressure ramps and starting at near zero pressure the mirror reflectivity is explicitly measured at each frequency. The experimental set-up is identical to that used in FS. After having evacuated our pressure cell, we slowly filled it with the gas mixture, while continuously measuring the ring-down time, laser frequency, and gas pressure, all simultaneously. In order to reduce errors in the O<sub>2</sub>N<sub>2</sub> CIA due to possible errors in the O<sub>2</sub>O<sub>2</sub> CIA, measurements on gas mixtures were alternated with measurements on pure O<sub>2</sub>. We found that this procedure gave the same results when using the averaged CIA spectrum of O<sub>2</sub>O<sub>2</sub> deduced in FS.

### 4. Results

CRDS determines total extinction coefficients as function of density. The extinction coefficients contain contributions from Rayleigh scattering, from the allowed magnetic dipole absorption of O<sub>2</sub>, from the O<sub>2</sub>O<sub>2</sub> CIA and from the O<sub>2</sub>N<sub>2</sub> CIA. Rayleigh scattering is proportional with density. The CIA contributions are strictly quadratic in density, and the line mixing causes the minima between the lines to behave approximately quadratic in density. In FS we found that the LM model predicts a quadratic dependence in between the lines in the case of pure oxygen. Our LM model predicts that oxygen-nitrogen mixtures do not behave purely quadratic.

Table 2. The refractive index ( $n$ ) and King correction factor ( $F$ ) for both  $O_2$  and  $N_2$  at 288.15 K and 1 atm. From these the Rayleigh scattering ( $\sigma$ ) cross section can be derived using  $\sigma = \frac{24\pi^3 \nu^4}{N^2} \left( \frac{n^2-1}{n^2+2} \right)^2 F$ , where  $N$  is the density at 288.15 K and 1 atm. The resulting Rayleigh scattering cross section is independent of temperature and density. To derive the Rayleigh scattering for a gas mixture, the scattering for the individual gases is weighted by their relative volume densities and then added together.

Gas	Refractive Index [26] $((n-1) \times 10^8)$	King Correction Factor [26] ( $F$ )
$O_2$	$21351.1 + \frac{21.8567 \times 10^{12}}{4.09 \times 10^9 - \left(\frac{\nu}{\text{cm}^{-1}}\right)^2}$	$1.096 + 1.385 \times 10^{-11} \left(\frac{\nu}{\text{cm}^{-1}}\right)^2 + 1.448 \times 10^{-23} \left(\frac{\nu}{\text{cm}^{-1}}\right)^4$
$N_2$	$6855.2 + \frac{324.3157 \times 10^{12}}{1.44 \times 10^9 - \left(\frac{\nu}{\text{cm}^{-1}}\right)^2}$	$1.034 + 3.17 \times 10^{-12} \left(\frac{\nu}{\text{cm}^{-1}}\right)^2$

,The experiments with mixtures are performed to higher densities than our experiments in pure oxygen. Due to the presence of oxygen isotopologues and the use of higher pressures, small deviations from pure quadratic behaviour (order of 0.5-1.5%) were found. Subtraction of the calculated LM values correct for this effect. In FS we have used literature values to subtract the Rayleigh scattering contribution from the total extinction. In this article we retrieve the Rayleigh component from the data. The advantage is twofold. Firstly, the numerical values can be compared with Rayleigh scattering data and secondly, it provides an indication if the data is treated correctly. In experiments with pure dried nitrogen, the accuracy of the retrieved Rayleigh scattering data was found to be of the order of 1 % [25]. Table 2 summarizes the Rayleigh cross section at the temperature of our experiments (293 K) which were derived from the seminal paper by Bates including the King factor correcting for the anisotropy of the molecules involved [26].

Determination of the  $O_2N_2$  CIA and Rayleigh scattering is performed as follows. Firstly, we subtract the allowed magnetic dipole absorption resulting from our ABC model. We are now left with the sum of Rayleigh scattering (linear in density) and the total CIA contribution (quadratic in density) consisting of both the  $O_2O_2$  CIA and  $O_2N_2$  CIA contribution. In the next step, we performed a weighted second-order polynomial fit on these results. In this fit, the zeroth-order results from the mirror offset, the first from the Rayleigh scattering and the second from the (total) CIA. The final step is to subtract the  $O_2O_2$  CIA contribution, taken from FS, weighted with the appropriate quadratic density. Our consistency check is the magnitude of the derived linear Rayleigh component. The quadratic coefficient is corrected for the the factor  $D_{O_2}D_{N_2}$  resulting in the CIA coefficient at a single wavelength. This procedure is repeated at many wavelengths in between the P-lines, in the region of the missing Q-branch and above the R-branch. No measurements were performed in the between the lines of the R-branch. Due to the close proximity of the individual lines in the R-branch ( $\pm 2 \text{ cm}^{-1}$  between lines), the resulting ring down signals are no longer mono-exponential and, as such, cannot be correctly analysed by our method.

In Fig. 1 the  $O_2N_2$  CIA for the three mixtures is shown. Both the magnitude and the shape of the curves are the same for all three mixtures, which reveals that the data treatment is consistent. The absolute absorption coefficients are only of the order of  $10^{-8} \text{ cm}^{-1} \text{ amg}^{-2}$ .<sup>1</sup> We note that the  $O_2N_2$  CIA is only a small fraction of the total observed absorption, which explains partially the statistical spread in the data. The negative values above the bandhead and in the Q-branch do reflect a systematic error, as the  $O_2N_2$  CIA values should be positive. We have looked at various possible sources for this effect. For the Q-branch, setting the

<sup>1</sup>The dimensionless unit amagat (amg) is defined as the ratio of the measured density to the density of the standard atmosphere.

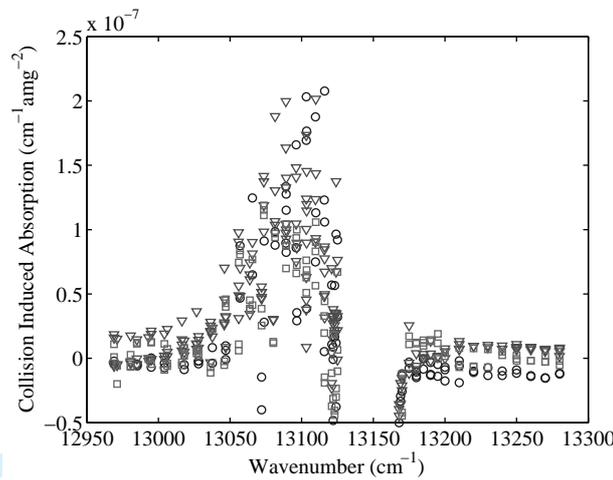


Figure 1. The  $O_2N_2$  CIA for the three mixtures (see table 1). Circles: mixture one. Triangles: mixture two. Squares: mixture three.

Rayleigh scattering to the theoretical value (table 2) increases the overlap between the measurements as well as negating the negative values. This procedure has no effect on the other measurements. For the measurements just beyond the R-branch bandhead, replacing our earlier  $O_2O_2$  CIA values by those published by Tran et al. does not mitigate this problem. **In principal, we have only one free parameter, the interbranch coupling parameter,  $r$ . This parameter also affects the  $O_2O_2$  CIA and variation showed that the most consistent data were obtained keeping the value fixed to that found in our work on pure oxygen ( $r=0.8$ ).**

We have simulated the effect of a systematic error in the pressure reading. The observed pressure determines how much of the observed absorption is ascribed to the magnetic dipole transition and the  $O_2O_2$  CIA. An overestimation of the pressure results in  $O_2N_2$  CIA values that are too small. In the final error analysis, we have allowed for an uncertainty in the pressure of  $\pm 1\%$ . It is likely that a refinement of the LM model or modifications of the line parameters may remove the unphysical negative values. We note that all mixtures consistently give near zero  $O_2N_2$  CIA values below  $13000\text{ cm}^{-1}$  and above  $13200\text{ cm}^{-1}$ , in contrast to the  $O_2O_2$  CIA spectrum as will be shown below.

Figure 2 shows the average Rayleigh Scattering (RS) retrieved from the observations and compared to the computed values. The error bars reflect the statistical spread. These data may well be the first retrieval of absolute RS values below a magnetic allowed transition. The retrieved RS spectra have a small systematic component which follows the shape of the P-branch. The RS values of mixture two are smaller than expected. Although the RS contribution is retrieved from the linear dependence in density and the CIA contribution is quadratic in density, it is noteworthy that the apparent RS values increase close to the bandhead where the apparent CIA values become negative.

In Fig. 3 we show the averaged  $O_2N_2$  CIA resulting from the three different gas mixtures. For an estimate of the error bars, we allowed for the possible  $\pm 1\%$  error in the pressure readings. The error indicated is taken to be the largest of the possible error from the pressure readings or the observed statistical error. In order to estimate the integrated CIA band coefficient **as well as provide a full  $O_2N_2$  CIA spectrum**, we fitted our observed CIA spectrum with a fit based on the A-band spectrum using Gaussian lines broadened to a width of  $7\text{ cm}^{-1}$  ( $20\text{ cm}^{-1}$  FWHM), a procedure suggested by Tabisz et al.[12] for generating CIA spectra. The resulting fit is displayed in Fig. 3 and reproduces the observed contour of

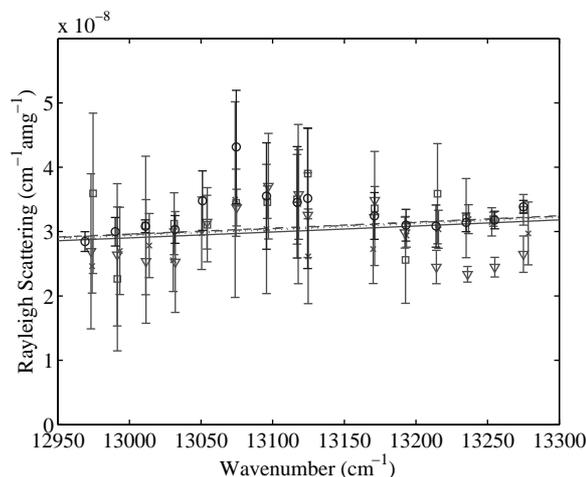


Figure 2. The observed averaged RS (cross) and theoretical value (solid line) for pure O2, mixture one (circles) and (dotted line), mixture two (triangle) and (dashed line) and mixture three (square) and (dot-dashed line) .

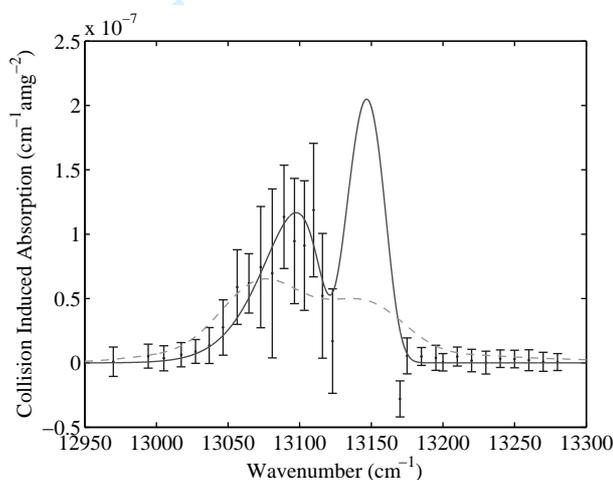


Figure 3. The averaged O<sub>2</sub>N<sub>2</sub> CIA spectrum at 293 K. Furthermore, a fit to the data (solid line) and the spectrum obtained by Tran et al.[14] (dashed line) is shown.

the P-branch remarkably well. The total integrated absorption including the part under the R-branch yields  $(1.24 \pm 0.3) \times 10^{-5} \text{ amg}^{-2}$ , which agrees reasonable well with the value obtained with the value of  $(0.96 \pm 0.1) \times 10^{-5} \text{ amg}^{-2}$  reported by Tran et al.[14]. The difference can be understood by comparing our results with the CIA spectrum retrieved by Tran et al. with a  $0.5 \text{ cm}^{-1}$  resolution FT instrument at several pressures between 50 and 150 amg (see Fig. 3). Their O<sub>2</sub>N<sub>2</sub> CIA spectrum predicts smaller values below the R-branch ( $(0.42 \pm 0.1) \times 10^{-5} \text{ amg}^{-2}$ ) than below the P-branch ( $(0.54 \pm 0.1) \times 10^{-5} \text{ amg}^{-2}$ ). Integrating our spectrum from  $129750 \text{ cm}^{-1}$  to  $13123 \text{ cm}^{-1}$  yields  $(0.63 \pm 0.3) \times 10^{-5} \text{ amg}^{-2}$ , reducing the difference between the two experiments. Our spectrum is more structured and predicts a minimum near the Q-branch. The LM-models used by Tran et al. and here are very similar. A small difference is that in Tran et al. a smoothing has been applied to the O<sub>2</sub>O<sub>2</sub> CIA spectrum which may also affect their O<sub>2</sub>N<sub>2</sub> CIA spectrum slightly. In view of the very different experimental methods and the very different pressure ranges of both studies, the agreement in the spectrum and the integrated value is surprisingly good. We stress that to our knowledge our method is the first to determine the CIA below an allowed band using experiments at single frequencies.

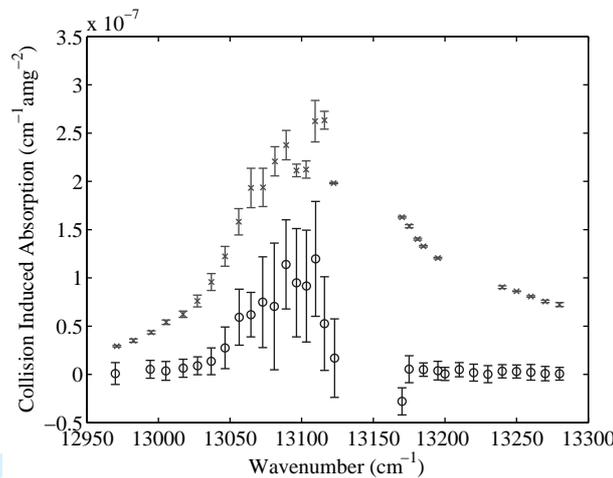


Figure 4. The averaged  $\text{O}_2\text{N}_2$  CIA (circle) and  $\text{O}_2\text{O}_2$  CIA (cross) spectra at 293 K. The  $\text{O}_2\text{O}_2$  CIA spectrum is taken from FS[20].

When comparing the spectrum of  $\text{O}_2\text{N}_2$  CIA with the  $\text{O}_2\text{O}_2$  CIA (see Fig. 4), large differences can be seen. The largest difference is found above the bandhead. The  $\text{O}_2\text{O}_2$  CIA is slowly decreasing, while the  $\text{O}_2\text{N}_2$  CIA almost directly goes to zero. The wings are often explained invoking exchange between photon energy and the kinetic energies of the collision partners. Whether excitation energy and kinetic energy can be exchanged, depends on the change in the intermolecular potential during the excitation process and the impact parameter of the collisions involved. As had been concluded already in earlier theoretical treatments of Tipping and co-workers, the mechanism that generate the  $\text{O}_2\text{N}_2$  CIA spectrum is insufficient to describe the  $\text{O}_2\text{O}_2$  CIA completely. We note here that whereas the average photon energy  $\langle \bar{\nu} \rangle$  of the  $\text{O}_2\text{O}_2$  CIA spectrum is larger than the average photon energy of the allowed magnetic dipole transition, our results indicate that for the  $\text{O}_2\text{N}_2$  CIA spectrum the average photon energy is equal to the average of the allowed dipole transition. Here, the average photon energy is defined as

$$\langle \bar{\nu} \rangle = \frac{\int_0^\infty \alpha(\bar{\nu}) \bar{\nu} d\bar{\nu}}{\int_0^\infty \alpha(\bar{\nu}) d\bar{\nu}}, \quad (4)$$

where  $\alpha(\bar{\nu})$  is the absorption at wavenumber  $\bar{\nu}$ . In comparison, the CIA spectrum reported by Tran et al. implies that the average photon energy is smaller than that of the allowed magnetic dipole spectrum, as the CIA coefficients below the R-branch are smaller than below the P-branch. On average, in the CIA process involving two oxygen molecules part of the photon energy is converted in either internal rotational energy of the other partner or in extra kinetic energy of the two collision partners, whereas this is not the case for  $\text{O}_2\text{N}_2$  CIA.

Our experiments unravel the various contributions to the total extinction of solar light around the oxygen A-band spectrum for an Earth-like atmosphere containing 79% nitrogen and 21% oxygen. We show the results on a log scale (Fig. 5). As a reference, Figure 5 also shows the relative contributions in the case of pure oxygen. In both cases the absolute contribution of Rayleigh scattering is approximately the same. As the contribution of the oxygen A-band is a factor five smaller in air, the relative contribution of Rayleigh scattering is significantly higher in the case of air. The CIA contribution of collisions with nitrogen is comparable to the CIA contribution due to oxygen due to the larger nitrogen content of air. The integrated impact of CIA at ambient pressures is small. CIA contributes to about 2% of the

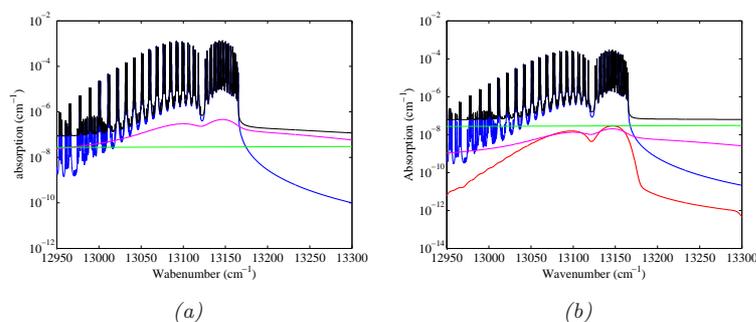


Figure 5. Left: The extinction contributions in pure  $O_2$  at 1amg and 296K. The blue line displays the absorption due to magnetic dipole absorption, the purple line collision induced absorption and the green line the Rayleigh scattering. The total extinction is given by the black line. Right: The extinction contributions in a mixture of 21%  $O_2$  and 79%  $N_2$  at 1amg and 296K. The blue line displays the absorption due to magnetic dipole absorption, the purple line the collision induced absorption due to  $O_2O_2$  complexes, the red line the collision induced absorption due to  $O_2N_2$  complexes (identical to the fit of Fig. 3) and the green line the Rayleigh scattering. The total extinction is given by the black line.

For both figures, the  $O_2O_2$  CIA spectra results from interpolation of the measurements of FS, except for the R-branch region, which is modelled in the same way as the  $O_2N_2$  CIA.

total extinction. The relative contribution is largest in the region above the R-branch bandhead and the windows between the lines. We stress that the effects are small in the case of linear absorption. The CIA becomes quantitatively more relevant in cases where the maxima of the resonances are saturated such as in the Earth atmosphere. As Rayleigh scattering is linear and CIA is quadratic in density, the relative contribution is valid for one density, being 1 amagat in this case. It is of interest to note that in the minima between the lines LM results in general in a small decrease in the predicted absorption whereas CIA increases the absorption, reducing the error in case both effects are neglected. Nevertheless, recently Tran and Hartmann showed that with their values errors in retrieving local atmospheric pressure values based on the total atmospheric column reduced from larger than 1.5 % to less than 0.5% after inclusion of LM and CIA[8].

## 5. Conclusion

For determination of  $CO_2$  emissions using remote sensing, accurate oxygen spectra are needed especially far away from the line centres. Line mixing and collision induced absorption must be taken into account. In FS we determined the  $O_2O_2$  CIA spectrum. In this work, we expanded our measurements to the effects of LM and CIA in mixtures of oxygen and nitrogen, in order to determine the  $O_2N_2$  CIA.

Using cavity ring-down spectroscopy in combination with density ramps, we determined absolute absorption coefficients for mixtures of  $O_2$  and  $N_2$  in the oxygen A-band (760 nm) at room temperature as function of the density. We employed the ABC-model to describe the absorption spectrum due to magnetic dipole absorption with line mixing and Doppler broadening. We used our knowledge of the  $O_2O_2$  CIA and deduced the  $O_2N_2$  CIA and, as a control of our analysis, the Rayleigh scattering cross section. The RS determination may well be the first below an allowed band.

The resulting  $O_2N_2$  CIA spectrum could be fitted well using Gaussian broadened lines of the magnetic dipole transitions, with resonance frequencies and intensities based on the HITRAN08 database. The FWHM width of the lines turned out to

be about  $20 \text{ cm}^{-1}$ .

Our method shows to be able to retrieve very small absorption coefficients and to unravel the different processes determining the A band spectrum at ambient conditions.

## 6. Acknowledgments

We thank Prof. Dr. Tonkov of the Saint Petersburg University for his inspiration. We thank Dr. Tran and Dr. Hartmann for providing us with numerical data of their CIA spectra of pure  $\text{O}_2$ . We acknowledge the financial support from NWO (Echo project).

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4 Dear Professor Softley ,  
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7 We would like to express our thanks to both referees for the care they have taken to read through  
8 our manuscript. In reaction to both referees, in particular to referee 2, we have made a serious series  
9 of changes to our manuscript that we discuss in some detail below. We not only have made changes  
10 to the manuscript but also have used time to perform several integrals based on the remarks of  
11 referee 2 to convince ourselves that we believe in our research strategy.  
12

13  
14 We hope that with these changes we have reacted carefully on the referee comments. Below, we  
15 will provide a general discussion for the points indicated by the referees.

16 Sincerely yours,  
17

18 On behalf of all authors,  
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21 Frans Spiering  
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The corrections proposed by the first referee are accepted and incorporated in the text:

*Page 2, line 19 should read.. interaction times...*

The sentence previously read: "As the interaction time during a collision are..." and now reads: "As the interaction times during a collision are...".

*Page 3 line 16. Shouldn't the term times (1-DO2) be gi,N2?*

The referee is correct and formula (1) is changed to the correct version. The equation is furthermore changed due to remarks of the second referee. These changes will be explained later.

*Page 3 line 18 should be left justified.*

This part of the text has undergone some rewriting, for which an explanation will be given at the corresponding point of referee 2.

*Page 4 line 52 should read ...do not...*

The sentence previously read: "Our LM model predicts that oxygen-nitrogen mixtures no not behave purely quadratic." and now reads: "Our LM model predicts that oxygen-nitrogen mixtures do not behave purely quadratic."

*Page 5 line 22/23 should read,,second-order polynomial...zeroth-order results...*

The sentence previously read: "weighted second order polynomial fit on these results. In this fit, the zeroth order results..." and now reads: "weighted second-order polynomial fit on these results. In this fit, the zeroth-order results...".

*Page 5 line 39 the exponent on amg should be -2 not -21*

This error results from the footnote regarding the amagat. In order to make clear that the footnote is not part of the power, the dot to end the sentence has been moved to in between the 1 and 2, i.e. <sup>2</sup>.<sup>1</sup>

*Page 6 line 44 should read... line parameters...*

The sentence previously read: "modifications of the line parameters may..." and now reads: "modifications of the line parameters may...".

Based on the comments provided by the second referee, we have made the following changes in the manuscript:

*Abstract, last line: I think "to the absorption" at the end of the sentence should be removed*

The suggestion is followed and "to the absorption" has been removed.

*Page 1, line 38: Not only the CO2 sources but also the sinks are of interest. I thus suggest "emissions and sinks". I also think adding reference(s) to the OCO or GOSAT satellite projects may be of interest to the reader.*

The suggestion is followed and "and sinks" is added. Furthermore, a reference to OCO is now included.

*Page 1, around line 41: Even in the absence of aerosols and clouds the O2 A band is of interest for the check of the total air mass since it enables a check or retrieval of the surface pressure.*

The suggestion is followed and "as well as air mass retrieval, by comparing the retrieved surface pressure with the actual pressure." is added to the line.

*Page 1, line 53: "Recently, in 2005". Recently is unnecessary here.*

Recently is removed from the line.

*Page 2, line 2: The authors should mention that it was demonstrated in Ref. 13, that the errors in te photon path obtained in ref. 6 were due to the use of Voigt shapes and the neglect of both LM and CIA.*

The referee is correct and the following sentence is added: "Tran and Hartmann showed that a large part of the discrepancy could by explained by the absence of line mixing and collision induced absorption [8]." A reference is added as well to support the statement.

*Page 2, Line 6: The reason why different molecules have different broadenings is not only due to the different masses. It also results from the rotational structure.*

The sentence is removed.

*Page 2, line 8: Note that, for a given active molecule, HITRAN only provides the self-broadening coefficient at room temperature and the value (plus the T dependence coefficient) for air*

1  
2 broadening (assumed 21% O<sub>2</sub> and 79% N<sub>2</sub>).

3 This point is discussed at the remark concerning page 3, line 20.

4 *Page 2, line 21: The sentence may be misleading. In fact the CIA increases the total*  
5 *extinction just because CIA exists, and not because it is quadratic in density (if it were linear in*  
6 *density it would increase the extinction as well).*

7  
8 The sentence is change from "...and hence with the density and increases the total extinction, an  
9 aspect of which we make use in our analysis." to "Its relative impact to the total extinction increases  
10 at higher densities, an aspect of which we make use in our analysis."

11 **Page 2, line 32:** *As written, the sentence is too restrictive and not correct. In fact, this*  
12 *sentence is only correct for FTS measurements under conditions where the CIA contribution is*  
13 *small and comparable to the base line uncertainty. This clearly depends on the density range. In*  
14 *fact, there have been numerous FTS measurements of CIA absorption (eg, the Tran et al for the O<sub>2</sub>*  
15 *A band, and other studies, for instance by Lafferty et al on the O<sub>2</sub> and N<sub>2</sub> CIA fundamental bands)*  
16 The referee is correct. As such, we added a pressure requirement which is more or less needed to  
17 detect the studied effect. The sentence read: "In FTS studies CIA..." and now reads: "In FTS studies  
18 at low pressures (up to several bars), CIA..."

19  
20  
21 *Page 2, line 39: the sentence is complicated; I suggest something like 'The LM model was*  
22 *developed by the co-authors from the St Petersburg group.*

23 The sentence is indeed complicated, so we have changed the sentence to be clearer from: "The LM  
24 model we used was developed by Tonkov and co-workers from the group of two of us (NNF and  
25 MBK)." to "The LM model was developed by the co-authors from the St Petersburg group.", in  
26 accordance with the suggestion.

27  
28 **Page 3, line 3:** *I suggest "coupling parameter r" at the end of the sentence.*

29 The suggestion is implemented. The sentence previously read: "...so called interbranch  
30 coupling parameter, all..." and now reads: "...so called interbranch coupling parameter (r), all..."

31  
32 **Page 3, line 4:** *For  $r=0$  it is indeed obvious, from Eq. (2) that the P and R branches are*  
33 *completely uncoupled. Nevertheless, for  $r=1$  there are some non zero relaxation matrix elements*  
34 *within the P branch and within the R branch. Unless there is a mistake in the equation, the*  
35 *statement "the branches are coupled completely" is incorrect. In fact, the reader would expect for*  
36 *completely coupled branches that only inter-branch mixings would be non zero.*

37 Obviously, the meaning of the sentence is not completely clear, so we changed it from: "In one  
38 extreme the (P- and R-) branches are coupled completely ( $r = 1$ )." to : "In one extreme no  
39 distinction is made between lines in the different branches ( $r = 1$ )."

40  
41 **Page 3, line 8:** *the value of r not only affects absorption in the trough between P and R*  
42 *branches. It affects all regions.*

43 This is correct. However, the influence of r is most obvious in the trough between the P and R  
44 branch. The sentence is changed to reflect this behavior. The original sentence read: "...parameter  
45 affects the predicted". The new sentence reads: "...parameter mostly affects the predicted..."

46  
47 **Page 3, line 16:** *The last gamma should be  $\gamma_{i,N_2}$ . Also, the use of D for mole fractions*  
48 *(ie with values between 0 and 1) may be confusing since one expects D to be used for densities.*  
49 *Furthermore, the index i is used in this equation to designate a line while j is used for the collision*  
50 *partner. These two indexes are then used in Eq. (2) to designate lines. This is confusing.*

51 The error concerning the gamma is discussed in the section regarding the first referee. Secondly, the  
52 D has been replaced by a V, which is hopefully clearer in meaning. Lastly, the indexes are changed:  
53 j is replaced by k, and i is replaced by j in order to be consistent with the other equations.

54  
55 *Page 3, line 19: I suggest "line i due to gas j"*

56 The suggestion is followed and updated with regard to the remarks for page 3, line 16. The old  
57 sentence read: "particular line due to gas j." and now reads: "...particular line j due to gas k."

58  
59 **Page 3, line 20:** *HITRAN does not directly provide the broadening by N<sub>2</sub> but the broadening*  
60 *by air. Of course, for O<sub>2</sub>, since the self broadening is also provided, one can deduce the N<sub>2</sub> value.*  
We thank the referee for pointing this out. We checked that the parameters are sufficiently equal that  
it has no effect on our analysis. Furthermore, a description is included of the procedure to deduce

1  
2 the N<sub>2</sub> value. The sentence read: "In the HITRAN database [7, 21] both broadening due to O<sub>2</sub>  
3 (self broadening) and N<sub>2</sub> are included." and now reads: "In the HITRAN database [9, 23] the  
4 broadening due to O<sub>2</sub> (self broadening) and air are included. From the air broadening, it is possible  
5 to retrieve the broadening due to N<sub>2</sub>, when one considers air to consist of 21% O<sub>2</sub> and 79% N<sub>2</sub>."

6  
7 **Page 3, line 30:** *In this equation, the indexes used for the matrices are  $q_j, q'_j$  whereas  $q_q, j_j$*   
8 *is used in Eq. (3). This should be corrected for consistency. I think the first one is more correct.*

9 We agree with the referee and updated the equation according to the suggestion.

10 **Page 3, line 39:** *"collisional effects" would be more appropriate than "collision dynamics"*  
11 *"Collisional dynamics" is replaced by "collisional effects."*

12 **Page 3, line 41:** *"coefficients" is not correct. In fact "broadening coefficient" is usually*  
13 *used to designate the density (or pressure normalized values (eg in cm<sup>-1</sup>/atm). Since the relaxation*  
14 *matrix in Eq. (2) contains the density it would be better to say "collisional shift and width". Note*  
15 *that saying somewhere that the relaxation matrix is proportional to density my be considered.*

16 We thank the referee for pointing this out and updated the sentence. It now reads: "...contains  
17 pressure shifts and broadenings and..." where it previously read: "...contains pressure shifts and  
18 collisional broadening coefficients and...".

19 **Page 3, line 45:** *adding a reference (from the St Petersburg group) where Eq. (3) was first*  
20 *introduced should be considered.*

21 A reference is now included at the end of the sentence.

22 **Page 3, line 57:** *I think it would be better to say that the entire imaginary part of the*  
23 *relaxation matrix is neglected. In fact, since it is said, just above, that the collision frequency  $\tau$  is*  
24 *taken from the broadening, it is obvious that the relaxation matrix in Eq. (3) is purely real..*

25 We changed the formula to include the pressure shifts as well, since they are also used. These  
26 complex numbers are only located on the diagonal. Additional lines are included to describe the  
27 symbol used for the pressure shift in formula (3). The additional lines are: "and  $\Delta_j$  is the  
28 pressure shift of line  $j$ . We use these pressure shifts as found in hitran database"

29 **Page 3, line 59:** *I have not found, in the paper, any place explaining how the value of  $r$  is*  
30 *determined and what value is obtained. This should be explained and the value of  $r$  should be given*  
31 *(note that comparing it to the value obtained for pure O<sub>2</sub> may be of interest). My guess is that  $r$  is*  
32 *chosen to make the CIA as smooth as possible but I am not sure.*

33 The referee is correct and we thank him for pointing this out. We replaced on page six the last  
34 sentences of the second paragraph. Previously it read: "The only free parameter in our LM-model,  
35 the interbranch coupling parameter,  $r$ , affects both the O<sub>2</sub>O<sub>2</sub> CIA and the O<sub>2</sub>N<sub>2</sub> CIA values. The  
36 systematic negative values cannot be altered without resulting in an unphysical O<sub>2</sub>O<sub>2</sub> CIA  
37 spectrum." and it now reads: "In principal, we have only one free parameter, the interbranch  
38 coupling parameter,  $r$ . This parameter also affects the O<sub>2</sub>O<sub>2</sub> CIA and variation showed that the most  
39 consistent data were obtained keeping the value fixed to that found in our work on pure oxygen  
40 ( $r=0.8$ )."

41 **Page 4, line 52:** *Here I think there may be a serious problem. First, let me say that I guess*  
42 *the correct sentence is "do not behave" and not "no not behave". If this is right, I see absolutely no*  
43 *reason why the LM-model would not predict a quadratic dependence for N<sub>2</sub> while it was the case*  
44 *for O<sub>2</sub>. in fact this quadratic dependence comes from the fact that absorption in the troughs*  
45 *between lines is considered at distances from line centers significantly greater than the widths. As*  
46 *long as this is the case, a quadratic dependence is obtained with a LM model, regardless of the*  
47 *relaxation matrix. Furthermore, the relaxation matrices for collisions with O<sub>2</sub> and N<sub>2</sub> should be*  
48 *quite alike. But maybe the sentence does not apply to the LM absorption but to the total absorption,*  
49 *including the Rayleigh... This really needs to be clarified.*

50 The referee was surprised about a non quadratic nature of our extinction in the case of O<sub>2</sub>-N<sub>2</sub>  
51 mixtures. He/she is correct that we should not suggest a fundamental difference, therefore  
52 we rephrased this part as: "The experiments with mixtures are performed to higher densities than  
53 our experiments in pure oxygen. Due to the presence of oxygen isotopologues and the use of higher  
54 pressures, small deviations from pure quadratic behaviour (order of 0.5-1.5%) were found.

1  
2 Subtraction of the calculated LM values correct for this effect. "

3 **Page 5, line 54:** *The authors discuss here the effect of an error on pressure on the retrieve*  
4 *CIA and find that the consequences are negligible as can be expected from the accuracy of the*  
5 *pressure measurement. I am convinced that, as stated by the authors; the CIA is mostly sensitive to*  
6 *the description of the contribution (affected by LM) of the allowed lines. For instance, a change of*  
7 *2% of the line intensities (and similarly of the half width) will change the allowed absorption in the*  
8 *troughs by 2% and then affect the retrieved CIA. Furthermore, any error in the LM model will have*  
9 *consequences on the CIA. The negative values obtained likely mostly result from these uncertainties,*  
10 *which have emphasized effects on the CIA since the allowed contribution is dominant. This should*  
11 *be clearly stated. In fact, the authors may consider comparing the CIA retrieved after changes of*  
12 *the intensities and/or half widths, and or value of the r parameter.*

13 We agree with the referee that the line parameters are important on the influence of the CIA  
14 spectrum. We also agree that the LM model probably needs some improvements, but we have  
15 already mentioned that in our previous paper. Finally, we decided only to mention the influence of  
16 the pressure, since this is a possible source of errors.

17 **Page 6, line 52:** *The residual shape in the Rayleigh probably comes from uncertainties on*  
18 *the measurements. In fact, it is well known that, if a finite number of densities is used, there are*  
19 *correlations between the liner and quadratic coefficients obtained from a polynomial fit. A small*  
20 *change of the values for high densities, for instance, will translate in all three parameters of the*  
21 *second order polynomial. In fact, the residual "P branch shape" in Fig. 2 is only obvious for the*  
22 *circles and, furthermore, much smaller than the error bars. The authors this should not put to much*  
23 *emphasis on this discussion.*

24 We thank the referee for pointing this out and we are familiar with mentioned effect, but we decided  
25 not to change the text.

26 **Page 7, Figure 3 and discussion starting on line 24:** *Using the allowed band to compute*  
27 *the shape of the CIA is extremely surprising to me. In fact, the calculated shape, that clearly shows*  
28 *two distinct branches, does not look like any CIA observed previously for CIA bands of O2, N2,*  
29 *CO2, ... I am surprised that this procedure could have been suggested by Tabisz. The case of the*  
30 *pure O2 CIA in the A band clearly demonstrates that this is not correct. I thus think that this part of*  
31 *the paper should be removed and that a comparisons with the total band intensity of Tran et al is*  
32 *impossible. Nevertheless, one comparison can be made: it consists in calculating the area below the*  
33 *CIA in the spectral region common to both the present paper and Tran et al. The authors could thus*  
34 *integrate their CIA in the intervals where they have measured values, ie [12950,13125] +*  
35 *[13175,13275] and do the same thing with Tran's data and compare the values. From a look at Fig.*  
36 *3 my guess is that these two values will be quite consistent*

37 The method described by Tabisz is given at: Tabisz et al. Canadian Journal of Physics, 1969; 2859-  
38 2870. On page 2867 a description of the method identical to ours is given to fit the A-band CIA  
39 spectrum.

40 Furthermore, we disagree with the referee concerning the application of the model. The O2 CIA is  
41 different from the N2 and CO2 shapes, indicative that a second process is occurring in pure O2. It is  
42 not clear which process this is, although suggestions are put forward with regard to the short range  
43 interactions. This process seems absent for CIA resulting from O2N2 and O2CO2 collisions.

44 However, we did follow the suggestion to include a comparison based on part of the spectrum. As  
45 such we incorporated values for the P- and R-branch for the CIA spectrum obtained by Tran et al  
46 and compared the value obtained for the P-branch with our spectrum integrated over the P-branch.  
47 This is expressed in the manuscript in the following way: "Their O2N2 CIA spectrum predicts  
48 smaller values below the R-branch  $((0.42 \pm 0.1) \times 10^{-5} \text{ amg}^{-2})$  than below the P-branch  $((0.54 \pm 0.1)$   
49  $\times 10^{-5} \text{ amg}^{-2})$ . Integrating our spectrum from 129750  $\text{cm}^{-1}$  to 13123  $\text{cm}^{-1}$  yields  $(0.63 \pm 0.3) \times$   
50  $10^{-5} \text{ amg}^{-2}$ , reducing the difference between the two experiments."

51 Finally, we noted that the value obtained for our full integrated spectrum was still in atmosphere  
52 instead of amagat, which we now replaced by the correct value.

53 **Page 7, discussion starting on line 46:** *My knowledge on CIA is not sufficient to evaluate*

1  
2 *the validity of this discussion but I found it a little “strange”. The opinion of specialists in CIA*  
3 *(R.H. Tipping ?) my be of interest. One thing: my memory may be wrong but I do not remember any*  
4 *such discussion in Tran’s paper (see Line 30 on page 8).*

5 The referee is correct in noticing that this discussion is absent in the paper of Tran. We changed the  
6 sentence to: "In comparison, the CIA spectrum reported by Tran et al. implies that the average  
7 photon energy is smaller than that of the allowed magnetic dipole spectrum, as the CIA coefficients  
8 below the R-branch are smaller than below the P-branch."  
9

10 *Page 9 discussion starting on line 43: See remark above*

11 We hope our explanation above for Page 7, Figure 3 and discussion starting on line 24 is sufficient  
12 to support this conclusion.  
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