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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 N2–O2 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 CO2 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 O2 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 CO2 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 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 by 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 (O₂N₂ CIA) seems better understood than the CIA due to oxygen oxygen collisions (O₂O₂ CIA) for which no satisfactorily 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 O₂O₂ CIA at atmospheric relevant densities using cavity ring-down spectroscopy (CRDS). Accurate data were taken with a 0.07 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 the co-authors 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 O₂O₂ CIA at atmospheric relevant densities using cavity ring-down spectroscopy (CRDS). Accurate data were taken with a 0.07 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 the co-authors from 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 O₂−N₂ 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 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 N₂ is assumed to be additive. The collision contribution is weighed by the volume fractions, (V_k). The total broadening for a given line (γ_j) is thus given by

\[ γ_j = V_Oγ_jO_2 + (1 - V_O)γ_jN_2, \]

where \( V_k \) is the volume fraction of gas \( k \) and \( γ_jk \) 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:

\[ φ(ω) = \frac{1}{π} \frac{1}{r(ω - L_0) + Γ(ω)} \sum_{q, q', j} ρ_j x_{qj} x_{q'j'} \left[ \frac{1}{r(ω - L_0) + Γ(ω)} \right] x_{q'j}, \]

In this equation, \( ρ_j \) are the (temperature dependent) initial state populations, \( x_{qj} \) are the reduced dipole moments. The products \( ρ_j |x_{qj}|^2 \) provide the line strengths as found in HITRAN [9,23], \( ω \) 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 \( Γ \) contains all collisional effects and is called the relaxation matrix. The diagonal of the relaxation matrix describes line 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]:

$$
\Gamma_{qjq'j'} = (1 - r)\delta_{qq'}\bar{\tau}^{-1}\left(\delta_{jj'} - A_q^{-1}\rho_j\chi_{qq'}\chi_{jj'}\right)$$

$$
+ r\bar{\tau}^{-1}\left(\delta_{qq'}\delta_{jj'} - A_q^{-1}\rho_j\chi_{qq'}\chi_{jj'}\right) + \delta_{jj'}\Delta\tilde{\nu}_j,
$$

(3)

In this equation $\bar{\tau}^{-1}$ is the averaged collision frequency, which is obtained from the pressure broadening parameters from HITRAN, and $\Delta\tilde{\nu}_j$ is the pressure shift of line $j$. We use these pressure shifts as found in the 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$_2$ mixed with N$_2$, three mixtures were used, two of which were quantified by the Netherlands Institute for Standards (NMI). The mixing ratios 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 ($R \approx 0.99995$) 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$_2$N$_2$ CIA due to possible errors in the O$_2$O$_2$ CIA, measurements on gas mixtures were alternated with measurements on pure O$_2$. We found that this procedure gave the same results when using the averaged CIA spectrum of O$_2$O$_2$ deduced in FS.

4. Results

CRDS determines total extinction coefficients as a function of density. The extinction coefficients contain contributions from Rayleigh scattering, from the allowed magnetic dipole absorption of O$_2$, from the O$_2$O$_2$ CIA and from the O$_2$N$_2$ 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 quadratically. 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$_2$N$_2$ 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 O2O2 CIA and O2N2 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 O2O2 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 D02DN2, 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 between the lines of the R-branch. Due to the close proximity of the individual lines in the R-branch (±2 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 Figure 1 the O2N2 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 cm⁻¹ amg⁻¹. We note that the O2N2 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 O2N2 CIA values should be positive. We have looked at various possible sources for this effect. For the Q-branch, setting the 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 O2O2 CIA values by those published by Tran et al. does not mitigate this problem. In principle, we have only one free parameter, the interbranch coupling parameter, r. This parameter also affects the O2O2 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).

In Figure 1 the O2N2 CIA for the three mixtures is shown. Circles: mixture one. Triangles: mixture two. Squares: mixture three.

Table 2. The refractive index (n) and King correction factor (F) for both O2 and N2 at 288.15 K and 1 atm. From these the Rayleigh scattering (σ) cross-section can be derived using $\sigma = (24\pi^2\ldots^3 / N^2) [(\sigma^2 - 1)/(\sigma^2 + 2)]F$, 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.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Refractive Index [26] (n - 1) × 10⁶</th>
<th>King Correction Factor [26] (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>21351.1 + 21.8567 × 10¹² / 4.09 × 10⁹ - ((\frac{\nu}{cm^{-1}}))^2</td>
<td>1.096 + 1.385 × 10⁻¹¹ ((\frac{\nu}{cm^{-1}}))² +1.448 × 10⁻²³ ((\frac{\nu}{cm^{-1}}))⁴</td>
</tr>
<tr>
<td>N₂</td>
<td>6855.2 + 324.3157 × 10¹² / 1.44 × 10⁹((\frac{\nu}{cm^{-1}}))^2</td>
<td>1.034 + 3.17 × 10⁻¹² ((\frac{\nu}{cm^{-1}}))²</td>
</tr>
</tbody>
</table>

Figure 1. The O2N2 CIA for the three mixtures (see Table 1). Circles: mixture one. Triangles: mixture two. Squares: mixture three.
or modifications of the line parameters may remove the unphysical negative values. We note that all mixtures consistently give near zero O2N2 CIA values below 13,000 cm\(^{-1}\) and above 13,200 cm\(^{-1}\), in contrast to the O2O2 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 Figure 3 we show the averaged O2N2 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 O2N2 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 cm\(^{-1}\) (20 cm\(^{-1}\) FWHM), a procedure suggested by Tabisz et al. [12] for generating CIA spectra. The resulting fit is displayed in Figure 3 and reproduces the observed contour of the P-branch remarkably well. The total integrated absorption including the part under the R-branch yields \((1.24 \pm 0.3) \times 10^{-5}\) amg\(^{-2}\), which agrees reasonably well with the value obtained with the value of \((0.96 \pm 0.1) \times 10^{-5}\) 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 cm\(^{-1}\) resolution FT instrument at several pressures between 50 and 150 amg (see Figure 3). Their O2N2 CIA spectrum predicts smaller values below the R-branch \((0.42 \pm 0.1) \times 10^{-5}\) amg\(^{-2}\) than below the P-branch \((0.54 \pm 0.1) \times 10^{-5}\) amg\(^{-2}\). Integrating our spectrum from 129,750 cm\(^{-1}\) to 13,123 cm\(^{-1}\) yields \((0.63 \pm 0.3) \times 10^{-5}\) 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 O2O2 CIA spectrum which may also affect their O2N2 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.

When comparing the spectrum of O2N2 CIA with the O2O2 CIA (see Figure 4), large differences can be seen. The largest difference is that in Tran et al. a smoothing has been applied to the O2O2 CIA spectrum which may also affect their O2N2 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.

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 (Figure 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 transition, our results indicate that for the O2N2 CIA spectrum the average photon energy is equal to the average of the allowed dipole transition. Here, the average photon energy is defined as

$$\langle \tilde{v} \rangle = \frac{\int_0^\infty \tilde{v} \alpha(\tilde{v}) d\tilde{v}}{\int_0^\infty \alpha(\tilde{v}) d\tilde{v}},$$ (4)

where $\alpha(\tilde{v})$ is the absorption at wavenumber $\tilde{v}$. 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 O2N2 CIA.
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 total extinction. The relative contribution is largest in the region above the R-branch bandhead and the windows in 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 amg in this case. It is of interest to note that in the minima in 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 CO₂ 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 O₂O₂ 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 O₂N₂ CIA.

Using cavity ring-down spectroscopy in combination with density ramps, we determined absolute absorption coefficients for mixtures of O₂ and N₂ in the oxygen A-band (760 nm) at room temperature as a 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 O₂O₂ CIA and deduced the O₂N₂ 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 O₂N₂ 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 cm⁻¹.

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

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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 O₂. We acknowledge the financial support from NWO (Echo project).

Note

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

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