Temperature dependent absorption cross-sections of O₂–O₂ collision pairs between 340 and 630 nm and at atmospherically relevant pressure†

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The collisions between two oxygen molecules give rise to O₄ absorption in the Earth atmosphere. O₄ absorption is relevant to atmospheric transmission and Earth’s radiation budget. O₄ is further used as a reference gas in Differential Optical Absorption Spectroscopy (DOAS) applications to infer properties of clouds and aerosols. The O₄ absorption cross section spectrum of bands centered at 343, 360, 446, 477, 532, 577 and 630 nm is investigated in dry air and oxygen as a function of temperature (203–295 K), and at 820 mbar pressure. We characterize the temperature dependent O₂ line shape and provide high precision O₄ absorption cross section reference spectra that are suitable for atmospheric O₄ measurements. The peak absorption cross-section is found to increase at lower temperatures due to a corresponding narrowing of the spectral band width, while the integrated cross-section remains constant (within <3%, the uncertainty of our measurements). The enthalpy of formation is determined to be ΔH°₂⁰⁰ = −0.12 ± 0.12 kJ mol⁻¹, which is essentially zero, and supports previous assignments of O₄ as collision induced absorption (CIA). At 203 K, van der Waals complexes (O₂-dimer) contribute less than 0.14% to the O₄ absorption in air. We conclude that O₂-dimer is not observable in the Earth atmosphere, and as a consequence the atmospheric O₄ distribution is for all practical means and purposes independent of temperature, and can be predicted with an accuracy of better than 10⁻³ from knowledge of the oxygen concentration profile.

1. Introduction

The collision of two O₂ molecules gives rise to the formation of several absorption bands throughout the ultra-violet, visible and near infrared regions of the electromagnetic spectrum. At very low temperatures – such as those typical of molecular beams – the formation of a weakly bound van der Waals complex (binding energy, ΔE = −17.0 meV = −1.64 kJ mol⁻¹ = ΔH°; ΔH° is the enthalpy of formation at a temperature of 0 K) gives rise to O₂-dimer absorption.²⁻⁴ The molecular structure of this open-shell complex has been studied by rotationally resolved measurements and theory.² At higher temperatures, collision induced absorption (CIA) results in additional O₄-CIA absorption from O₂–O₂ collision pairs that overlaps with that of O₂-dimer. With CIA, the selection rules of molecular O₂ transitions are relaxed as a result of interactions between the electron shells of 2 O₂ molecules⁵,⁶ during collisions that are fully reversible, i.e., do not involve a bound state. Despite many decades of research⁵,⁷⁻⁹ discussions about O₄ absorptions (sum of CIA and O₂-dimer) in the atmosphere do not remain free of contradictions. For example, measurements in the atmosphere found a weak temperature dependence of the observed O₄ absorption, which – unless accounted for – can lead to errors on the order of 22% (for a ΔT = 100 K (196–296 K)) with the calculation of solar heating rates, inferred photon path lengths, and cloud height inferences from atmospheric O₄ observations.¹⁰ On the other hand, laboratory evidence⁶,¹¹ could in principle explain these observations by demonstrating apparent changes in the spectral band-shape. However, knowledge about band shapes remains limited for measurements at atmospheric pressure. The question whether O₂-dimer contributes to atmospheric O₄ absorptions is of fundamental importance for the vertical distributions of O₄ in the atmosphere.

O₄ is a greenhouse gas that absorbs incoming solar radiation, and integrated over all O₄ bands, is responsible for 2.03–2.31 W m⁻² atmospheric forcing (1.06 W m⁻² only counting bands in the visible spectral range).¹²⁻¹³ The vertical O₄ column density ~1.33 × 10¹⁴ mol³ cm⁻² (ref. 14) gives rise to weak absorptions (e.g., ~0.0007 optical density at 446 nm and ~0.015 at 577 nm for overhead sun, base e). This is due to

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the rather small absorption cross sections of O₄, \( \sigma_{O_4} \), that pose challenges to their accurate determination. Measurements of \( \sigma_{O_4} \) require it to employ either (1) very long absorption light paths (several km), or (2) high O₂ pressure (several 10 bars) to derive a measurable signal. At higher than ambient pressures, pressure broadening could alter the band shapes found in the atmosphere and has not been systematically quantified. Further, the changes in the band shape with temperature are currently not well known. Only selected bands have been measured at lower than ambient temperatures, i.e., at 196 K \(^6\), \(^1^1\) at 76 K \(^3\), \(^4\), \(^1^5\)–\(^1^7\) and at ~10 K \(^2\), \(^4\). More recent applications of high-finesse optical cavities to O₄ measurements \(^1^1,^1^8–^2^1\) provide first measurements that benefit from (1) close to atmospheric conditions, and (2) compact experimental design for straightforward temperature control, but employed monochromatic light sources. Here we present the first use of a high-finesse optical cavity coupled with (3) polychromatic light sources to determine O₄ absorption band shapes over extended wavelength ranges that are wide enough to include one or several absorption bands simultaneously (multiplex advantage).

The O₄ bands are used by Differential Optical Absorption Spectroscopy (DOAS) \(^2^2\) instruments to infer information about aerosols and clouds, i.e., satellite DOAS, \(^2^2,^2^3\) multi-axis DOAS (MAX-DOAS), \(^2^2,^2^4\) and airborne MAX-DOAS, \(^2^5–^2^7\) and further provide an internal reference gas for in situ CE-DOAS. \(^2^8\) DOAS measurements require high quality reference spectra of O₄, and are particularly sensitive to changes in the O₄ band shape. There is a need for high signal-to-noise O₄ spectra under atmospherically relevant pressure, and over the range of temperatures found in the atmosphere.

2. Experimental

The absorption cross-sections of O₂–O₂ collision pairs were measured using Cavity Enhanced Differential Optical Absorption Spectroscopy (CE-DOAS) \(^2^8,^2^9\). We utilized a broad-band light source to measure all wavelengths of a single band simultaneously rather than step-scanning a laser as with ring-down apparatus. \(^1^1,^1^8–^2^0\)

The absorption cross-section of O₄ absorption, \( \sigma_{O_4} \), is usually expressed in units of cm\(^5\) mol\(^-2\), owing to the fact that the equilibrium constant \( K_{eq} \) is not well known:

\[
2O_2 \leftrightarrow O_4; \quad K_{eq} = [O_4]/[O_2]^2
\]

(1)

The values of \( \sigma_{O_4} \) are instead conveniently calculated using the following equation:

\[
\text{Absorbance (optical depth)} = OD = \ln \left( \frac{I_0}{I} \right);
\]

(2)

where the observed optical depth (OD) is found from Beer’s law and solved for the binary absorption coefficient (hereafter referred to as the cross-section):

\[
\sigma_{O_4} = \frac{OD}{O_{2\text{mix}}^2 N_d l}
\]

(3)

where \( O_{2\text{mix}} \) is the oxygen mixing ratio (here: 20.95% v/v), \( N_d \) is the number density and \( l \) is the absorption length.

2.1 Experimental set up

2.1.1 Temperature controlled cavity. Measurements were carried out using a custom built temperature controlled high finesse optical cavity as shown in Fig. 1. A key feature of this cavity is that the high reflectivity mirrors (see Table S1, ESI†) are placed inside the cold region to minimize temperature gradients along the light path between the mirrors. The cold cavity was constructed of aluminum, and consists of an 86 cm long, 3.81 cm diameter tube. The tube is joined at the ends to a 2.54 cm long 10.2 cm diameter tube that houses the mirror mounts inside a cooled region sealed by quartz windows to the ambient air. In the final assembly, the mirrors are placed 87.0 (±0.1) cm apart. The tube is encased in a temperature jacketed cell, while the end regions are surrounded by copper tubing soldered to the aluminum and connected to the cooling fluid. Methanol was used as the cooling fluid in an ultra-low temperature bath (NESLAB Endocal ULT-80), and is supplied near one end of the cavity assembly to lower temperatures homogeneously over the full cavity length from room temperature.
(295 K) down to 203 K. Seven thermocouples (Type K, Omega Engineering, CASS-116E-24) were permanently installed in the cavity in the center, mid-way between the center and at the end of the cavity, and just on the inside and outside of the mirror region and signals were recorded using a National Instruments data acquisition module (USB-DAQ). Pressure was measured at the exit of the cell using a Honeywell (model PPT0015) pressure transducer. During the design of the apparatus, attention was paid to place the mirrors as close as possible to the exit of the cavity to minimize temperature gradients. Heated quartz windows (held at 293 K) close off the mirror mount region to outside air and the outside of the windows was flushed continuously with ~10 liters per minute of dried room air. Sample gas flow was measured with a mass flow meter (Sierra Instruments) and dried in a dry-ice (CO\textsubscript{2}) trap to remove residual water vapor before adding it through the jacket of the cell. Nitrogen (Airgas, 99.9998%), air (Airgas breathing quality air, O\textsubscript{2} mixing ratio of 20.95%), argon (Airgas, 0.99998%), oxygen (Airgas, industrial grade >99.9% purity) and helium (Airgas, 0.99998%) were supplied to the cavity in sequence during the measurements.

2.1.2 Experimental conditions. For each wavelength range, measurements were taken starting at room temperature with the following cycle of gases: He then N\textsubscript{2} to measure the mirror reflectivity curve\textsuperscript{28,31} followed by addition of either air or pure oxygen to measure the collision pair absorbance (see Table S1, ESI\textsuperscript{1}). This was followed by the addition of either N\textsubscript{2} or Ar as a reference. N\textsubscript{2} is used as the I\textsubscript{0} for measurements in air while Ar was used for measurements in pure O\textsubscript{2} due to the more similar Rayleigh scattering cross-section of O\textsubscript{2} and Ar. A typical cycle of gases at one temperature was as follows: 15 minutes each of He, N\textsubscript{2}, Air, and N\textsubscript{2} (for stronger bands at 477, 577 and 630 nm) or 15 minutes each of He, N\textsubscript{2}, O\textsubscript{2}, and Ar (for weaker bands at 446 and 532 nm, or lower reflectivity mirrors at UV wavelengths).

The cavity was cooled to take individual measurements at set points of 293, 273, 253, 233, 213 and 200 K. The actual temperature in the cavity at the lower temperatures was higher than the desired set point of the chiller bath (less than 1 K), but was held constant at each level for the measurements. The individual temperature sensors showed deviations from each other that were smaller than 4 K at 203 K. The path length weighted temperature uncertainty across the entire length of the cavity was smaller than 0.3 K (see Fig. S1, ESI\textsuperscript{1}). Each temperature and wavelength range was sampled independently at least two times for reproducibility.

2.1.3 Mirror and LED combinations. Five different pairs of high reflectivity mirrors were used to cover the ultra-violet and visible range from 330-660 nm (360, 455, 532, 580 and 630 nm) centering on each of the oxygen collision pair absorption bands. Light emitting diodes (LEDEngin, for specific model information see details in the ESI\textsuperscript{1}, Table S1) centered at each mirror wavelength were used as the light sources for the visible wavelengths. The LEDs were mounted on a single stage Peltier cooling stage, equipped with a PID temperature control to stabilize temperature at 20 ± 0.01 °C. In the ultraviolet spectral range, a Xe-arc lamp (Hamamatsu L2273, 150 W, 2 mm arc) was used.

A full description of light sources and cavity mirrors is provided as part of the ESI\textsuperscript{1} (Table S1). The control of the temperature of the LED cooling led to a peak to peak variability in the flux of <0.02% over one hour. The Xe arc was much less stable. Attempts to adjust the spectra for power fluctuations by scaling to out of band light levels\textsuperscript{31} were found to increase the overall error and abandoned. It was decided to minimize measurement time between different gases, and intensity drifts were accounted for by the background/offset correction as described in Section 2.2.

2.1.4 Spectrometer and detector. The light from the LED or Xe-arc was collimated using a 50.8 mm f/1 lens into the cavity. The measurement light was passed through a set of optical filters placed before and after the cavity to remove out of band light. Light exiting the cavity was focused onto a 1.35 mm diameter optical fiber (Ceramoptic) using a 25.4 mm f/4 lens.

The light from the mono-fiber was transferred to a fiber bundle (36 × 145 μm), which was arranged vertically on the slit of the Acton SP2300i spectrometer equipped with a 1200 g mm\textsuperscript{-1} grating (500 nm blaze wavelength), and coupled to a PIXIS400b (Roper Scientific) CCD camera.\textsuperscript{24,28} Custom LabView data acquisition software was used to collect spectra and control the temperature of the spectrometer (spectrometer housing temperature, 34 ± 0.02 °C; Spectrometer and electronics rack, 26.0 ± 0.8 °C) as well as the LED temperature. The resolution of the measurements ranged from 0.32–0.45 nm full width at half maximum (FWHM) resolution from the measured widths of atomic emission lines, and depending on the wavelength range of interest (UV to red). Instrument line functions were measured using Hg, Xe, Kr or Ne atomic emission lines for each wavelength range. The line functions were slightly asymmetric with the tail towards the shorter wavelengths, but do not limit the apparent band shape of O\textsubscript{4} bands (which were typically about 10 times wider). The change in the resolution across the detector is exemplified as the change in the FWHM of Xe atomic line emissions for the blue cavity (455 nm centered) [0.368 nm FWHM, 450.22 nm, pixel 257; 0.360 nm FWHM, 473.54 nm, pixel 748; 0.355 nm FWHM, 484.47 nm, pixel 952]. For measurements near 630 nm, we used a 600 g mm\textsuperscript{-1} grating (300 nm blaze wavelength) giving a resolution of 0.68 nm FWHM. This was necessary to better capture the entire absorption band at 630 nm, which is significantly wider than other bands (for specifics on the wavelength range and resolution of each cavity see Table S1, ESI\textsuperscript{1}).

The wavelength pixel mapping was determined by recording solar stray-light spectra from connecting the optical fiber at the exit of the cavity to a small telescope, and pointing it out of the window. The Fraunhofer lines were compared to the Kurucz spectrum,\textsuperscript{32} using the WinDOAS software.\textsuperscript{33} From these comparisons we determine the reported wavelength stamp to be accurate within 0.01 nm.

2.2 Data analysis

The mirror reflectivity curve of each cavity at each temperature was measured with respect to wavelength as in Washenfelder \textit{et al.}\textsuperscript{31} and Thalman and Volkamer\textsuperscript{23} from the difference in the
Rayleigh scattering of He and N\textsubscript{2} according to the following equation:

\[ R(\lambda) = 1 - \frac{d N_{\text{He}}(\lambda)}{d N_{\text{N}_2}(\lambda)} z_{\text{Ray}}(\lambda) \frac{N_{\text{He}}(\lambda)}{N_{\text{N}_2}(\lambda)} \]  

(4)

where \( R \) is the mirror reflectivity, \( d \) is the cavity length; \( I \) is the intensity spectra for each gas and \( z \) is the extinction due to N\textsubscript{2} or He gas, respectively (cm\textsuperscript{-1}), all with respect to wavelength. Ten to fifteen minutes of spectra were accumulated for each gas and averaged to decrease the photon shot noise in the averaged spectra. Measurement spectra were analyzed in two ways: (1) comparing absolute intensities as done in BBCEAS\textsuperscript{31,34,35} was employed for the weaker O\textsubscript{4} absorptions in air, or (2) using the Beer–Lambert law as defined in eqn (3).

With the first approach, BBCEAS fitting based on the following equation derives the extinction in the cavity:

\[ z(\lambda) = \left( \frac{1 - R(\lambda)}{d} \right) \left( I_0(\lambda) - I(\lambda) \right) \frac{I(\lambda)}{I_1(\lambda)} \]  

(5)

The extinction was then divided by the square of the oxygen concentration to calculate the absorption cross-section (cm\textsuperscript{-1}). The extinction was then divided by the square of the oxygen concentration to calculate the absorption cross-section (cm\textsuperscript{-1}).

With the second analysis approach, eqn (2) and (3) are employed as in traditional absorption spectroscopy. Corrections are needed as (a) the path length varies strongly as a function of wavelength, and (b) O\textsubscript{4} absorption may become self-limiting to path length if the O\textsubscript{4} absorptions exceed a few percent optical density. Both corrections were applied simultaneously by means of the following equation from Platt et al.\textsuperscript{39}

\[ L(\lambda) = \frac{d}{1 - R(\lambda) + d N_3 \sigma_{\text{Ray}}(\lambda) + d O_2 \sigma_{\text{O}_2}(\lambda)} \]  

(6)

The correction for self-limitation becomes significant in our data whenever the O\textsubscript{4} absorption term (last term in denominator to eqn (6)) contributed more than \( \sim 3\% \) to the path-length as determined. Under these conditions we employed eqn (6) iteratively to calculate a path length correction to the optical density and derive the absorption cross-section. The calculated cross-section from the first iteration is used to re-calculate the path length equation and the cross-section is retrieved accounting for the reduction in the light path (eqn (3)). This cycle typically converges to relative changes between iterations of less than 1% within 3 iterations.

Molecular oxygen overtone bands overlap with O\textsubscript{4} bands near 579 and 630 nm. They were accounted to retrieve the collision pair absorption cross-section by convolving the HITRAN\textsuperscript{38} database output for the 628.8 nm \( \gamma \) overtone band of the O\textsubscript{2} \([b^1\Sigma_g^+(v' = 2) \leftrightarrow X^1\Sigma_g^-(v'' = 0)]\) using the instrument line function. We performed high resolution cross section modeling in intensity space for the appropriate slant column density of O\textsubscript{2} to represent distortions of the apparent band shape of O\textsubscript{2} at the limited instrument resolution prior to convoluting the spectra to obtain the best possible match with our measurements.\textsuperscript{39} Separate cross section spectra were calculated at each temperature at the appropriate oxygen slant column densities. For lack of data for the 2nd overtone of O\textsubscript{2} \([\lambda, 579.7 \text{ nm}, [b^2\Sigma_g\, g(v' = 3) \leftrightarrow X^2\Sigma_g\, g(v'' = 0)]]\) in HITRAN, room temperature spectra were fitted using the Hermans band shape and the residual used as the cross-section for the O\textsubscript{2} band. This correction worked well for the much weaker 2nd overtone band. However, it was found that residuals remained visible for the much stronger 1st overtone; necessitating the further smoothing of O\textsubscript{4} spectra near the blue shoulders of the 630 nm O\textsubscript{4} band. We accomplished this by fitting a high order (6+) polynomial to the peak and replacing a limited region near the peak with the polynomial.

Rayleigh scattering cross-sections for N\textsubscript{2}, Ar, O\textsubscript{2} and air were taken from the refractive index based theory as given in Bates,\textsuperscript{40} S neep and Ubachs\textsuperscript{41} and in Bodhaine et al.,\textsuperscript{42} while the Rayleigh scattering cross-section of He gas was from the expression given in Washenfelder et al.\textsuperscript{43}

The overall error in the measurements of peak and integrated \( \sigma_{\text{O}_4} \) is the sum of contributions resulting from measurements of temperature and pressure, geometry, and corrections to spectra and are detailed in Table 1. The statistical error was either limited by (a) the spectra to spectra variability of the peak and integrated \( \sigma_{\text{O}_4} \) within a single sequence of gas fillings (usually accumulations of 30 seconds worth of scans) and is generally <1%; it was mostly found to be limiting when using the Xe-arc lamp, and represents the precision in the method of background correction for light source drift as described earlier in this section, or (b) the variation in the peak and integrated

<table>
<thead>
<tr>
<th>Error description</th>
<th>Maximum correction (%)</th>
<th>Relative error\textsuperscript{a} (%)</th>
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<td>Temperature inhomogeneity</td>
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</tr>
<tr>
<td>Temperature measurement</td>
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<tr>
<td>Pressure measurement</td>
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<td>Rayleigh scattering cross-sections</td>
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<td>Oxygen mixing ratio (air/O\textsubscript{2})</td>
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<tr>
<td>360 nm</td>
<td>&lt;20</td>
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<tr>
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<td>446 nm</td>
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<tr>
<td>532 nm</td>
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<tr>
<td>O\textsubscript{2} band subtraction</td>
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<td>580 nm</td>
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<td>2.3</td>
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<tr>
<td>Overall error</td>
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\textsuperscript{a} Relative error is calculated after correction.
\( \sigma_{O_4} \) values between separate gas fillings during repeat runs; it represents the variability in temperature set points and the reproducibility of the cavity and is generally \(< 3\%\), and was typically found to be limiting with the LED light sources (2–4\%). The 3\( \sigma \) variability of peak and integrated \( \sigma_{O_4} \) within a single run is comparable to the variability between repeat measurements. For the reporting of data the 1\( \sigma \) variability (for \( n > 2 \)) or the range (\( n = 2 \)) for repeat runs are reported as the uncertainty.

3. Results

The absorption cross-section spectrum of \( O_4 \) is shown in Fig. 2, and compared to the literature cross-sections of Hermans\(^{36,37}\) and Greenblatt et al.\(^6\) Notably, the Hermans spectrum is recorded at much higher resolution (\( \sim 0.02 \) nm FWHM), and should be directly comparable to our data. The spectrum by Greenblatt was recorded at 0.6 nm FWHM resolution, which is about five to 20 times better resolution than the line width of \( O_4 \) bands (see Table 2). Both spectra are compared here with no further treatment of the data. In this work bands at 340, 360, 380, 446, 477, 532, 577 and 630 were observed with signal to noise for most bands of \( > 100 \). Our measurements show small differences when compared to Hermans, but much larger differences due to variations in the band shape with respect to Greenblatt that are illustrated in the top panel. Generally, we reproduce the spectral shape for Hermans within better than 5\% for the stronger bands. Larger relative differences are found for the weaker \( O_4 \) bands near 446, as is shown in the inset of Fig. 2.

The residual wiggles that appear as differences to our spectrum are about 15 times larger than the 1\( \sigma \) RMS noise in our data, and thus are highly significant. However, the larger differences are observed to the spectrum of Greenblatt et al.,\(^6\) which shows clear indications for line broadening when comparing the bands at 360 nm, 380 nm, 477 nm, 580 nm and 630 nm. More broad (unstructured) differences are observed for the weaker bands at 344 nm, 446 nm and 532 nm.

The temperature dependence in the absorption cross-sections is illustrated for selected temperatures (200, 253 and 295 K) in Fig. 3. The differences between cross sections are plotted in the top panel (calculated as \( \sigma_{O_4}(T) - \sigma_{O_4}(295 \) K)). The changes in band shape are observed for all bands at all temperatures studied. The peak cross section, band width and integrated cross section are tabulated for the individual bands and temperature studied in Table 2. As can be seen in Fig. 3, the peak \( \sigma_{O_4} \) increases with decreasing temperature for all bands and the changes in the peak \( \sigma_{O_4} \) vary between 10 and 20\% over the temperature range studied, for all bands. The two difference spectra in the top panel compare a change over 42 K (253 K, light blue line) with that over 50 K (203 K, dark blue line). While the first range is only \( \sim 25\% \) larger, the \( \sigma_{O_4} \) changes are 2 to 5 times larger at colder temperatures. Thus, changes in spectral band shapes of \( \sigma_{O_4} \) are relatively minor at typical ambient temperatures, and down to temperatures below 253 K.

The widths of the \( \sigma_{O_4} \) bands are generally poorly described by fitting mathematical functions to represent the spectra (see discussion in ref. 11). As such we are listing the width in Table 2 as the FWHM, taking the half height on either side of the

![Fig. 2](https://example.com/f2.png) Comparison of \( O_4 \) absorption cross-sections to literature spectra at room temperature. For improved display the Hermans and Greenblatt cross-sections are offset. The inset shows a zoom of the weakest \( O_4 \) band near 446 nm and difference to other spectra. The experimental error for this band is \( \sim 0.05–0.2 \times 10^{-47} \) cm\(^5\) mol\(^{-2}\) (see Table 2).
This width is observed to decrease with temperature for all bands. Similar findings had been reported for the 360, 477, 532, 577 and 630 nm bands in the literature\textsuperscript{6,11,21,44} while this is the first reported decrease in the width for the 380 and 446 nm bands.

Fig. 4 illustrates the different behavior for the peak \( \sigma \) and for the integrated \( \sigma \) over any individual band for the 4 most prominent wavelengths relevant to DOAS measurements, and compares our data with literature values. A similar behavior is observed for all other bands that were studied. While the integrated \( \sigma \) scatters for all bands around a slope of zero (Fig. 4, lower trace in all four panels), i.e., do not show any significant change with respect to temperature, the peak \( \sigma \) increases with decreasing temperature as described above.

\begin{table}[h]
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\begin{tabular}{|c|c|c|c|c|c|}
\hline
Band & Temp (K) & Peak (nm) & Peak \( \sigma \) & Width (nm) & Integrated \( \sigma \) \\
\hline
\( ^1\Sigma_g^+ + ^1\Sigma_g^+ \) (v = 2) & 295 & 343.9 & 0.95(4) & 3.21 & 339.8–347.2 \\
& 273 & 343.85 & 0.95(4) & 4.0 & 0.252 \\
& 253 & 344.0 & 0.98(4) & 3.04 & 0.269 \\
& 233 & 343.95 & 1.07(4) & 3.07 & 0.293 \\
& 213 & 344.0 & 1.13(4) & 3.02 & 0.316 \\
& 203 & 344.0 & 1.20(4) & 2.94 & 0.316 \\
\hline
\( ^1\Sigma_g^+ + ^1\Sigma_g^+ \) (v = 1) & 295 & 360.97 & 4.29(6) & 4.3 & 349.5–368.0 \\
& 273 & 4.42(7) & 4.07(3) & 1.64(5) \\
& 253 & 4.58(7) & 3.85(13) & 1.66(4) \\
& 233 & 4.86(4) & 3.75 & 1.65(4) \\
& 213 & 5.12(20) & 3.63(1) & 1.69(5) \\
& 203 & 5.32(20) & 3.63 & 1.76(10) \\
\hline
\( ^1\Sigma_g^+ + ^1\Sigma_g^+ \) & 295 & 380.32 & 2.43(3) & 4.04(7) & 370.0–386.1 \\
& 273 & 2.56(8) & 3.88(6) & 7.6(3) \\
& 253 & 2.68(8) & 3.71(3) & 7.5(3) \\
& 233 & 3.1(2) & 3.61(4) & 8.7(6) \\
& 213 & 3.3(2) & 3.42(2) & 8.7(5) \\
& 203 & 3.5(3) & 3.32(2) & 9.1(10) \\
\hline
\( ^1\Sigma_g^+ + ^1\Delta_g \) (v = 2) & 293 & 446.52 & 0.520(20) & 4.496 & 433.5–453.8 \\
& 273 & 446.43 & 0.552(5) & 4.35 & 0.153(2) \\
& 253 & 446.53 & 0.53(2) & 3.88 & 0.136(10) \\
& 233 & 446.48 & 0.587(14) & 3.93 & 0.151(1) \\
& 213 & 446.43 & 0.618(23) & 3.61 & 0.150(20) \\
& 203 & 446.43 & 0.639(15) & 3.6 & 0.150(30) \\
\hline
\( ^1\Sigma_g^+ + ^1\Delta_g \) (v = 0) & 293 & 477.02 & 6.598(97) & 5.39 & 459.4–487.6 \\
& 273 & 476.88 & 6.75(3) & 5.37 & 2.02(4) \\
& 253 & 476.88 & 6.91(4) & 5.08 & 1.91(9) \\
& 233 & 476.98 & 7.01(6) & 4.66 & 1.89(3) \\
& 213 & 476.83 & 7.36(3) & 4.52 & 1.91(2) \\
& 203 & 476.84 & 7.67(20) & 4.04 & 1.92(1) \\
\hline
\( ^1\Delta_g + ^1\Delta_g \) (v = 2) & 293 & 532.7(1) & 1.09(6) & 8.89 & 511.5–544.3 \\
& 273 & 532.7(1) & 1.11(6) & 8.58 & 0.385(40) \\
& 253 & 532.9(1) & 1.10(6) & 8.26 & 0.364(50) \\
& 233 & 532.7(3) & 1.27(7) & 7.97 & 0.398(20) \\
& 213 & 532.8(1) & 1.36(7) & 7.48 & 0.400(33) \\
& 203 & 532.8(3) & 1.37(6) & 7.31 & 0.408(23) \\
\hline
\( ^1\Delta_g + ^1\Delta_g \) (v = 1) & 293 & 577.6 & 11.2(1) & 11.2(2) & 552.0–595.0 \\
& 273 & 577.5 & 11.3(6) & 10.82(3) & 4.25(1) \\
& 253 & 577.7 & 11.5(1) & 10.51(3) & 4.17(5) \\
& 233 & 577.7 & 12.3(1) & 9.99(3) & 4.26(5) \\
& 213 & 577.7 & 13.2(1) & 9.56(3) & 4.43(2) \\
& 203 & 577.7 & 13.8(1) & 9.25(5) & 3.51(2) \\
\hline
\( ^1\Delta_g + ^1\Delta_g \) (v = 0) & 293 & 630.2(4) & 7.11(2) & 13.75(4) & 600.0–654.0 \\
& 273 & 630.1 & 7.27(7) & 13.25 & 2.79(8) \\
& 253 & 630.0 & 7.44(30) & 12.76 & 2.8(2) \\
& 233 & 630.1 & 7.69(30) & 12.48 & 2.74(10) \\
& 213 & 630.1 & 8.1(3) & 12.24 & 2.85(8) \\
& 203 & 630.1 & 8.43(20) & 12.00 & 2.94(5) \\
\hline
\end{tabular}
\caption{Results}
\end{table}

\( ^a \) Locations and widths for the 630 band are approximate due to oxygen subtraction. \( ^b \) Wavelength range over which the absorption band has been integrated. \( ^c \) The number in parentheses is the 1\( \sigma \) error in the last digit of the reported value.

absorption band to determine the width. This width is observed to decrease with temperature for all bands. Similar findings had been reported for the 360, 477, 532, 577 and 630 nm bands in the literature\textsuperscript{6,11,21,44} while this is the first reported decrease in the width for the 380 and 446 nm bands.

Fig. 4 illustrates the different behavior for the peak \( \sigma \) and for the integrated \( \sigma \) over any individual band for the 4 most prominent wavelengths relevant to DOAS measurements, and compares our data with literature values. A similar behavior is observed for all other bands that were studied. While the integrated \( \sigma \) scatters for all bands around a slope of zero (Fig. 4, lower trace in all four panels), i.e., do not show any significant change with respect to temperature, the peak \( \sigma \) increases with decreasing temperature as described above.
Detailed values for each temperature are reported in Table 2. The lack of any significant temperature dependence in the integrated $\sigma_O$, suggests that $O_2$-dimer absorption does not contribute to the observed $O_4$ absorption over the range of temperatures investigated.

To corroborate this further, we have segregated our data for measurements in air and $O_2$. The similarity of data in air and $O_2$ is illustrated in Fig. 5, where data from Table 2 have been renormalized and pooled for all wavelengths. First, for any given wavelength, the integrated cross sections have been normalized to the average across all temperatures for this wavelength (grey symbols). The relative difference to this global average integrated cross section was then plotted over temperature (grey symbols). Second, the normalized data from different wavelengths have been pooled at any given temperature according to (1) spectra recorded in air (dark blue), (2) $O_2$ (light blue), and (3) all data (black); measurements of 343, 380, 446 and 532 nm bands were in $O_2$, the 477, 577 and 630 nm bands in air.

**Fig. 3** Temperature dependence of the band shapes at 295 K, 253 K and 203 K. The ‘difference’ (top panel) is calculated as: $\pi(T) - \pi(295 \text{ K})$.

**Fig. 4** Comparison of peak and integrated cross-sections to available literature values at four wavelengths.
and the 360 nm band in both O\(_2\) and air. The regression line equations for these data pools are (1) slope: \(-0.028 \pm 0.025\); \(R^2 = 0.25\), (2) \(-0.047 \pm 0.03\); \(R^2 = 0.38\), and (3) \(-0.023 \pm 0.02\); \(R^2 = 0.24\), respectively. In particular, no significant difference between air and O\(_2\) is observed in the slopes, and slopes are further found compatible with zero (within 2\(\sigma\)). More importantly, at the coldest temperature, the integrated sigma difference in air is actually higher than that in pure O\(_2\). We conclude that over the full range of temperatures, the maximum contribution of O\(_2\)-dimer to the O\(_4\) absorption is less than 3% in both air and O\(_2\). This lack of an apparent difference between air and O\(_2\) is observed in the slopes, and slopes are further found compatible with zero (within 2\(\sigma\)). More importantly, at the coldest temperature, the integrated sigma difference in air is actually higher than that in pure O\(_2\). We conclude that over the full range of temperatures, the maximum contribution of O\(_2\)-dimer to the O\(_4\) absorption is less than 3% in both air and O\(_2\). This lack of an apparent difference between air and O\(_2\) is observed in the slopes, and slopes are further found compatible with zero (within 2\(\sigma\)). More importantly, at the coldest temperature, the integrated sigma difference in air is actually higher than that in pure O\(_2\). We conclude that over the full range of temperatures, the maximum contribution of O\(_2\)-dimer to the O\(_4\) absorption is less than 3% in both air and O\(_2\). This lack of an apparent difference between air and O\(_2\) is observed in the slopes, and slopes are further found compatible with zero (within 2\(\sigma\)).

The thermally averaged enthalpy of formation can be found from the slope of \(\ln(\alpha)\) vs. \(1/T\). The results of this analysis yield \(\Delta H^\text{250} = -0.12 \pm 0.12 \text{ kJ mol}^{-1}\).

## 4. Discussion

### 4.1 Comparison to literature spectra

The reported values for our peak and integrated \(\sigma_{O_4}\) values compare within 5% of those reported by Hermans\(^6\) as well as Greenblatt et al.\(^6\) at room temperature. A selection of available literature values for peak and integrated \(\sigma_{O_4}\) at 360, 477, 577 and 630 nm are shown in Fig. 4 (a complete listing of prior literature peak, integrated \(\sigma_{O_4}\) values as well as the widths of the bands is provided in ESI, Table S2).\(^{3,6-8,11,12,15-21,36,37,44-48}\) Prior studies in the atmospheric temperature range of 180–320 K have observed the overall increase of peak \(\sigma_{O_4}\) values with respect to temperature.\(^6,8,11,12,20,44\) Our work is consistent with this finding (Fig. 4). It further reproduces the change in peak \(\sigma_{O_4}\) with respect to temperature within 5% for all bands investigated by Pfeilsticker et al.\(^12\) from atmospheric spectra (a digitized version of their Fig. 3 is overlaid with the peak values of this work as Fig. S2 in the ESI).\(^*\) Notably, we follow the changes in spectral band shape with good temperature resolution. It becomes apparent that the band width narrows at lower temperatures. This change is more pronounced at lower temperatures than near room temperature, and corresponds to an increase in the peak \(\sigma_{O_4}\) as is visible in Fig. 5. The integrated \(\sigma_{O_4}\) remains constant. See also the related discussion in Section 3, and Fig. 3.

For a discussion of the comparison with room temperature spectra by Hermans and Greenblatt et al., see Section 3. Observations of the integrated \(\sigma_{O_4}\) over this temperature range are less common.\(^6,11,44\) These previous studies for 477, 532, 577 and 630 nm show either no increase\(^6,44\) or a slight decrease\(^11\) in the integrated band strength (Fig. 4). Early studies at very low temperatures (87–113 K)\(^{15-17}\) observed a very large increase in both peak and integrated \(\sigma_{O_4}\) as well as extreme skewing of the band shape (especially the 477 nm band).\(^17\)

### 4.2 van der Waals dimer vs. collision induced absorption (CIA)

Previous studies\(^2,3,10,49,50\) have used a variety of approaches to quantify \(\Delta H^\text{f}\) of O\(_2\)-dimer, and estimate the equilibrium constant.\(^30\) Aquilanti et al.\(^1,51\) conducted molecular beam experiments and observed the angular dependence of molecular scattering of oxygen at cold rotation temperatures (~12 K) and a value of \(-1.64 \pm 0.1 \text{ kJ mol}^{-1}\) for the bond energy of lowest energy configuration and \(-1.14 \pm 0.08 \text{ kJ mol}^{-1}\) for the average of all configurations.\(^51,52\) Long and Ewing\(^3,9\) were first to report a value of \(\Delta H^\text{f} = -2.2 \pm 0.3 \text{ kJ mol}^{-1}\) from the increase in the integral of rotational absorptions on top of the collision induced oxygen bands at 6.2 \(\mu\)m. Significant O\(_2\)-dimer absorption was only observed at temperatures below 100 K.\(^50\) A similar study by Orlando et al.\(^50\) yielded a value of \(\Delta H^\text{290} = -4.6 \pm 2 \text{ kJ mol}^{-1}\) for temperatures between 225–356 K. Horowitz et al.\(^49\) observed the decrease in ozone formation from oxygen photolysis at 214 nm from 297–387 K, and determined a value of \(\Delta H^\text{442} = -0.8 \pm 1.6 \text{ kJ mol}^{-1}\). Pfeilsticker et al.\(^10\) reported observations of the change in the peak absorption of O\(_3\) bands (360 nm to 630 nm) in the atmosphere by balloon-borne DOAS measurements over the temperature range of 200–295 K (average temperature = 248 K). The authors inferred \(\Delta H^\text{280} = -1.20 \pm 0.08 \text{ kJ mol}^{-1}\) based on the increase in the observed \(\sigma_{O_4}\) absorption assuming that the band shape is independent of temperature, and stated that this should be understood as...
representative of the atmospheric conditions rather than as a characteristic of the truly bond dimer.\textsuperscript{10} Our analysis reproduces a very similar value if based on the maximum signal (see Fig. S2, ESI†), but we note that the derived parameter in ref. 10 is actually not related to the enthalpy of formation. Notably, the authors observed no change in the spectral band-shape of O\textsubscript{4} with temperature (see Section 4.3). Observations of non-zero values of $\Delta H^T$ at temperatures above 200 K\textsuperscript{10,50} are currently taken as evidence for a weak temperature dependence of O\textsubscript{4} in the atmosphere. Our value of $\Delta H^{250} = -0.12 \pm 0.12$ kJ mol\textsuperscript{-1} is zero within measurement uncertainty, and consistent with previous studies that found negligible $\Delta H^T$ at temperatures above 100 K,\textsuperscript{10} and confirm previous observations that suggest no dimer is formed at temperatures above 100 K.\textsuperscript{1,3,6,51,52}

Greenblatt et al.\textsuperscript{6} noted that their observed change in the integrated $\sigma_0$, due to O\textsubscript{2}-dimer was smaller than expected based on the $\Delta H^0$ reported by Long and Ewing;\textsuperscript{7} indeed they\textsuperscript{6} observed no change in the integrated $\sigma_0$ with $\pm 15\%$ uncertainty (360, 380 and 477 nm bands). Our data confirm these findings with lower error. The integrated $\sigma_0$ did not increase by more than $3\%$ in neither air, nor O\textsubscript{2} (see Section 3, and Fig. 5) despite O\textsubscript{2}-dimer absorption should be $\sim 22.78$ times more pronounced in O\textsubscript{2} over air. From this we conclude that O\textsubscript{2}-dimer contributes less than $0.13\%$ to the O\textsubscript{4} absorption at 203 K in air.

Our data are consistent with the previous conclusions reached by Greenblatt et al.\textsuperscript{6} and Sneep et al.,\textsuperscript{11} that in O\textsubscript{2} and at moderately warm temperatures the UV-visibility absorption bands of O\textsubscript{4} are not significantly influenced by O\textsubscript{2}-dimer, and support their assignments of O\textsubscript{4} bands as CIA.\textsuperscript{53} We conclude that O\textsubscript{2}-dimer is not observable in the atmosphere. As a consequence, atmospheric predictions of the O\textsubscript{4} vertical profile only depend on air density, and can be predicted with very small uncertainty $\sim 10^{-3}$. Knowledge about how O\textsubscript{4} is distributed in the atmosphere is hence primarily limited by the accuracy at which air temperature, pressure and humidity (as it affects the oxygen partial pressure) are known.

4.3. DOAS reference spectra

The weak temperature dependence of spectral band shapes near the upper range of temperatures that we have probed suggests that our room temperature spectrum is representative of the atmospheric O\textsubscript{4} absorption also at temperatures well above those found in the atmosphere. Only a limited volume of the atmosphere actually experiences colder temperatures than we have probed. Notably, the tropical free troposphere or the polar atmospheres during winter can experience slightly lower temperatures than those that were probed here.

The band shape change is particularly relevant at colder temperatures typical of airborne DOAS applications, or in polar atmospheres. Assuming a constant band shape can lead to errors in measured O\textsubscript{4} slant column densities as high as $20\%$ at the lowest possible atmospheric temperatures.\textsuperscript{10} Accounting for temperature effects of spectral band shape now allows us to eliminate this uncertainty. We recommend including two O\textsubscript{4} cross section spectra of different temperatures for simultaneous fitting as part of the DOAS least-squares analysis.

The respective temperatures of the two O\textsubscript{4} reference spectra should be chosen to bracket the range of atmospheric temperature extremes, and be fitted simultaneously to represent the actual temperature as a linear combination of both temperature extremes. In this way, systematic residual structures can be minimized, and accurate O\textsubscript{4} SCD measurements be made with errors of few percent under most conditions.

The optical resolution of our O\textsubscript{4} spectra is generally about 10–30 times better than the width of the observed spectral features (compare Table S1, ESI† with Table 2). As such we believe that our spectra can be considered as ‘fully resolved’, i.e., provide reference spectra that can easily be adopted to any DOAS instrument by convolution with the respective instrument line function, and over the full range of atmospherically relevant temperatures.

5. Conclusions

Absorption cross-section spectra of O\textsubscript{2}–O\textsubscript{2} collision pairs (O\textsubscript{4}) have been measured for 8 O\textsubscript{4} bands in air and O\textsubscript{2}, at six temperatures (i.e., 203, 213, 233, 253, 273, and 293 K), and at ambient pressure. The accuracy of the line strength is better $3\%$ for most bands, and limited in part by our knowledge of the Rayleigh cross sections of N\textsubscript{2} (and He) that limit knowledge of our mirror reflectivity. Our measurements combine (i) high signal-to-noise O\textsubscript{4} spectra ($60 < S/N < 1000$), (ii) small temperature variations through the optical cavity ($\Delta T < 0.3$ K for all temperatures), and (iii) temperature controlled polychromatic light sources (light emitting diodes for most bands) to assess effects of temperature on the spectral band shape. The accuracy in our wavelength calibration is $\pm 0.01$ nm.

We conclude:

(1) Changes in the spectral band shapes are observed for all bands, and visible for all pairs of temperatures investigated. For the same temperature increment, these changes become disproportionately larger in spectra recorded at temperatures below 253 K. However, the integrated absorption cross section is independent of temperature to within $3\%$ over the full range of temperatures investigated. Even at 203 K no indications are found for additional absorption from bound van der Waals complexes (O\textsubscript{2}-dimer).

(2) Near room temperature, the absorption cross section and band shape reported by Hermans\textsuperscript{17} were reproduced within $5\%$ for the stronger O\textsubscript{4} bands. At $\sigma_0$, below $6 \times 10^{-47}$ cm$^5$ mol$^{-2}$ (weak bands at 343, 446 and 532 nm) we observe larger differences (up to $20\%$ at 446 nm).

(3) Our measurements confirm previous findings\textsuperscript{6,11,44} that the integrated $\sigma_0$ is independent of temperature with $\sim 5$ to 10 times higher accuracy. We provide first measurements of the lack of a temperature dependence for the O\textsubscript{4} bands at 446 and 630 nm that had not previously been reported.

(4) O\textsubscript{2}-dimer is not observable in the Earth atmosphere. Our determination of $\Delta H^{298}$ being essentially zero with very little error implies that O\textsubscript{2}-dimer is not observable at atmospheric temperatures. We estimate that the O\textsubscript{4} vertical profile scales with an error better than $10^{-3}$ with air density in the atmosphere.
Future theoretical studies might benefit from the changes we have observed in spectral band shapes, which seem to indicate that long-range collision interactions between two O₂ molecules extend well beyond 1 nm (distance between O₂ molecules). The optical resolution employed in our work (∼0.3 nm FWHM) – while sufficient to resolve the studied O4 bands – is insufficient to provide a good correction of O₂ bands near 628 nm [b^2S_g (^4P_u = 2)<→ X^2S_g (^4P_u = 0)]. The representation of these bands in the HITRAN database 38 was found to insufficiently remove the observed O₂ absorption, and limits our analysis of the spectral band shape for O₄ at 630 nm. Future studies of these weak O₂ bands at higher optical resolution seem feasible under atmospheric conditions by means of optical cavities, and will be beneficial to improve the HITRAN database, and confirm the approximate band shape reported for this O₄ band.

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