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First pressure shift measurement of ozone molecular lines at 9.54 µm using a tunable quantum cascade laser

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ABSTRACT

Using a free-running distributed-feedback quantum cascade laser (QCL) emitting at 9.54 µm, the pressure shift parameters of four intense rovibrational transitions in the ν_3 fundamental band of ozone induced by oxygen (O_2), air and the noble gases helium (He), argon (Ar), and xenon (Xe) are obtained by employing second harmonic detection. The experimental analysis comprises a full uncertainty budget and provides line shift data which are traceable to SI. The high density of transitions in the ν_3 spectral region of ozone make this region particularly difficult to study with more commonly used techniques such as Fourier transform spectroscopy. The comparatively high spectral resolution of the QCL in the MHz range, on the contrary, allows to measure molecular shifts at relatively low pressures (from 2 to 70 hPa), thus reducing the impact of spectral congestion due to pressure broadening of molecular lines. The comparison of our results with published data shows that presently recommended values for the pressure shift are too low in this region. This observation is corroborated by semi-classical calculations using the Robert-Bonamy formalism. A slight negative J dependence, already observed in other ozone vibrational bands, is predicted. Systematic use of our technique could be very useful to support this hypothesis and to make up for the lack of shift parameters for ozone ν_3 transitions in molecular spectral databases. A subsequent stabilization of the QCL onto an optical frequency comb will open up possibilities to perform metrological measurements of Doppler-free molecular lines.

1. Introduction

Ozone (O_3) is the tri-atomic allotrope of oxygen and its chemical formula has been identified almost exactly 150 years ago first by Soret and shortly later by Schönbein [1]. The molecule plays a pivotal role in Earth's atmosphere. It is a unique absorber of ultraviolet (UV), visible and infrared (IR) radiation, thus greatly influencing the thermal structure of Earth's atmosphere, protecting Earth's surface from energetic solar UV irradiation, and playing a role in global climate – chemistry feedback. Moreover, the molecule is an irritant that is key in atmospheric oxidation chemistry.

Precise determinations of local ozone mixing ratios or abundance profiles in the atmosphere are thus of great interest and can be obtained through spectroscopic measurements in all spectral domains from the UV to the Far-IR. In the light of new studies and more stringent user requirements, the re-evaluation and new measurements of data covering all these domains are under way [2–7]. The spectral region at 10 µm is of particular interest for these measurements which is due to the absence of water absorptions in this atmospheric 'window' and the presence of the strongest fundamental (ν_3) of ozone. The inversion of atmospheric spectra, however, requires a precise knowledge of ozone spectral line parameters such as position, intensity, line broadening, and shifting parameters [3,5,8], with required relative uncertainties decreasing with the order in which parameters are listed. In most atmospheric applications, line shifting has thus be neglected altogether [9]. More recently, however, line shift data have become a concern in atmospheric applications [10]. One reason being the increasing spectral resolution in modern instrumentation that leads to increased requirements, because rather typical uncertainties in shift coefficients of about 10^{-3} cm^{-1}/atm may lead to significant residues in the retrieval of atmospheric spectra [11].

The shifting of ozone rovibrational transitions has been studied both experimentally [12–17] and theoretically [8,18, and references therein] mostly in the $\nu_1, \nu_2, \nu_1+\nu_3, \nu_1+\nu_2+\nu_3$, and $3\nu_3$ vibrational bands. For an extensive review of these

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measurements up to 1998 readers are referred to Ref. [8]. Interestingly, line shifts in the ν_3 band of ozone have only been studied non-systematically such that values for just 10 lines are reported in the literature [12,13,16]. Due to the lack of experimental data, shift parameters for ν_3 lines in the spectroscopic databases are lacking or must be based on some form of extrapolation from data in other bands. At present, all transitions belonging to this band have shift parameters arbitrarily set to $\delta = -7 \cdot 10^{-4}$ cm^{-1}/atm in HITRAN [19] or to $\delta = 0$ in GEISA [20] and in S&MPO [21]. Nevertheless, shifting parameters are vibration dependent [22], show a large variability [12–17], and the validity of these attributions thus requires experimental verification.

In this paper, we present experimental data of line shifts of O_3 in the ν_3 region induced by the different gases O_2, air, He, Ar, and Xe. The results are obtained using QCL technology, instead of the more commonly used Fourier Transform Spectroscopy (FTS) for high-resolution spectroscopic measurements. Compared to previous line shift studies [12–17] who mostly report the observed scatter as an estimate of the associated measurement uncertainty, we here provide a full uncertainty analysis with metrological traceability.

We recall that the SI unit for line shifts is Hz/Pa, when line positions are measured in units of frequency and we use the derived unit of kHz/Pa throughout the paper along with values in cm^{-1}/atm and MHz/Torr, which are the more traditional units in the radiative transfer or physical chemistry communities. The different units are linked to each other by

$$1\ \frac{\mathrm{kHz}}{\mathrm{Pa}} = \frac{72375}{21413747}\ \frac{\mathrm{cm}^{-1}}{\mathrm{atm}} \simeq 3.380 \cdot 10^{-3}\ \frac{\mathrm{cm}^{-1}}{\mathrm{atm}} \tag{1}$$

and

$$1\ \frac{\mathrm{kHz}}{\mathrm{Pa}} = \frac{4053}{30400}\ \frac{\mathrm{MHz}}{\mathrm{Torr}} \simeq 0.1333\ \frac{\mathrm{MHz}}{\mathrm{Torr}}. \tag{2}$$

The paper is organized as follows. We first present the underlying theory for the line shift calculations before the experimental set-up and the method are described in the following section. Then we present and discuss the pressure shift measurements. In the conclusion and outlook section we finally summarize the results and propose further spectroscopic applications.

2. Line shift calculation

Line shifts have been calculated using the semi-classical formalism of Robert and Bonamy (RB, hereafter) [22]. The method, as well as the advantages of using the RB formalism rather than the older Anderson-Tsao-Curnutte (ATC) theory [23,24] is well described by Lynch et al. [25]. Hence, we present only a short account for providing a basic understanding and explaining the approximations made in the calculations.

The line shift δ_{if} for the transition $f \leftarrow i$ is calculated using the following equation:

$$\delta_{if} = \frac{n_2 \bar{v}}{2\pi c}\left\langle \int_{r_0}^{\infty} 2\pi r_c\, \mathrm{d}r_c \left(\frac{v'_c}{\bar{v}}\right)^2 \sin S_1 e^{-\Re(S_2)} \right\rangle_2 \tag{3}$$

where n_2 is the perturber number density, $\bar{v}$ the mean relative velocity of the two colliders, c the speed of light, and following the framework of the RB formalism [22], the parabolic trajectory is described by the distance of closest approach r_c and the effective velocity at this distance v'_c, $r_0$being the minimum value of r_c obtained for a zero impact parameter. $\langle \ldots \rangle_2$ means an average over the rotational states of the perturber, $\Re$ means real part, and S_1 and S_2 are the usual scattering terms depending on the intermolecular potential including electrostatic and atom-atom terms.

To obtain this equation, the following assumptions have been made:

- following the original paper of RB [22, see Eq. (13)], the imaginary part $\Im(S_2)$ has been neglected. Lynch et al. [25] have shown that this can lead to an error of about 10% in the case of N_2 broadening of water lines.
- The S_1 term that depends only on the isotropic part of the interaction potential is given by:

$$S_1 = -\frac{\alpha_2 \bar{v}}{r_c^5 v'_c}\frac{3\pi}{8\hbar}\left[\frac{3}{2}\frac{I_1 I_2}{I_1 + I_2}(\alpha_{1f} - \alpha_{1i}) + \left(\mu_f^2 - \mu_i^2\right)\right], \tag{4}$$

  where $\alpha_1$and α_2 are ozone and perturber polarizabilities, I_1 and I_2 the respective first ionization energies and μ_f and μ_i the ozone electric dipole moment in the initial ($\nu_3 = 0$) and final ($\nu_3 = 1$) vibrational states.
- $\Re(S_2)$ is calculated following previous studies of line broadening in ozone [26], taking into account an electrostatic interaction potentiel up to the quadrupole-quadrupole term and a Lennard-Jones type atom-atom potential:

$$\begin{aligned} V_{at-at} &= 4\sum_{i,j}\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \\ &= \sum_{i,j}\left(\frac{d_{ij}}{r_{ij}^{12}} - \frac{e_{ij}}{r_{ij}^{6}}\right) \end{aligned} \tag{5}$$

  where ϵ_{ij} and σ_{ij} are the Lennard-Jones parameters for the interaction of the i^{th} atom of the active molecule with the j^{th} atom of the perturber.

The S_1 term has been calculated using the ionization potentials listed in the CRC handbook of physics and chemistry [27]. Rare gas polarizabilities and those of N_2 and O_2 are also given in the CRC handbook [27]. The vibrationally dependent dipole moment and polarizability of ozone have respectively been taken from Refs. [28,18]. For convenience, we summarize the values of the molecular parameters used in the calculations in Table 1. Atom-atom interaction parameters are listed separately in Table 2. Based on Eq. (5), values of d_{OO} and e_{OO} for the ozone molecule have been calculated from the corresponding σ_{OO} and ϵ_{OO} values that have been extracted from the parameters given in Ref. [26] for O_3–O_2 and O_3–N_2 pairs, using standard combination rules. They have then been combined with values for N_2 [29], O_2 [29], Ar [30], He [30] and Xe [31]. Molecular trajectory calculations were made using an isotropic 6–12 Lennard Jones potential whose ϵ and σ parameters are also given in Table 2.

3. Experimental setup

Fig. 1 shows a scheme of the experimental setup, emphasizing on the optical components. Our electromagnetic source is a distributed feedback quantum cascade laser (DFB-QCL, *Alpes Laser*), centered at 1049 cm^{-1} (9.54 μm) and covering the spectral range between 1046.2 and 1053.1 cm^{-1}. The QCL operates at temperatures ranging from −25 to +20 °C at a maximum current of 1.48 A. The threshold current changes from 0.88 A at −25 °C to 1.31 A at +20 °C. The QCL is driven by a home-made, low-noise stabilized current source while temperature is stabilized to better than ±0.1 K using a Peltier module controlled by a thermoelectric cooler (TC-3, *Alpes Laser*). Heat generated by the Peltier element is dumped into a closed-circuit water chiller (ThermoCube, *Solid State cooling*). Moreover, in order to minimize the thermal resistance and to allow efficient dissipation of heat, the laser housing is fixed on a monolithic copper support which is screwed on the optical table. Under

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