Transition frequencies of oxygen B-band lines measured with optical frequency comb assisted cavity ring-down spectroscopy

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Abstract. Transition frequencies of weak B-band lines of O₂ were measured with low uncertainties. These results were compared to data available in the literature. In order to achieve reported accuracy we took into account in the data analysis several subtle line-shape effects, such as speed dependence of collisional broadening andDicke narrowing. We found that the speed-dependent Nelkin-Ghatak profile can properly describe experimental line shapes in the investigated pressure range of up to 22 Torr. Our experimental setup consists of the Pound-Drever-Hall locked frequency-stabilized cavity ring-down spectrometer. This spectrometer provides high-resolution and very high signal-to-noise ratio of measured spectra. It was recently linked to the optical frequency comb working in the visible region of spectrum. This upgrade allows for accurate determination of the absolute frequency axis of the CRD spectrum by direct measurement of the probe laser frequency.

1. Introduction
Recent progress in the optical frequency combs (OFC) technology [1] has greatly simplified ultra precise optical frequency measurement in a broad spectral region. OFC combined with a high-quality spectrometer [2, 3] can provide experimental data on molecular transition frequencies and subtle line-shape effects needed for improving molecular constants and spectroscopic databases, such as HITRAN [4]. Precise data on transition frequencies, intensities, and collisional effects are needed in such applications as spectroscopic temperature and pressure measurements, trace gases detection, modeling of atmosphere and weather forecast, climate changes and noninvasive medical diagnostics. Remote systems for global monitoring of atmosphere composition and pollution with high spatial resolution require precise spectroscopic data on used molecular transitions.

Continuous improvements in the frequency-stabilized cavity ring-down spectroscopy (FS-CRDS) [5] led to construction of precise spectrometer [6, 7, 8, 9] operating in the visible region of the spectrum, providing data with extremely high signal-to-noise ratio (SNR) [10] and having frequency axis directly linked to the frequency-doubled OFC [11]. Such configuration allows us to investigate weak molecular oxygen B-band (b¹Σ⁺⁻→X³Σ⁻, (ν' = 1) ← (ν'' = 0)) transitions and measure their line-shape properties as well as line intensities and transition frequencies.
The oxygen B-band is particularly interesting with respect to its potential applications to remote sensing of the atmosphere because these weak transitions do not saturate at long optical paths in the atmosphere and therefore gas properties can be determined from measured line profiles. In contrast to a relatively well characterized A-band ($b^1 \Sigma_g^+ \leftarrow X^3 \Sigma_g^-$, ($\nu' = 0$) $\leftarrow$ ($\nu'' = 0$)), the weaker B-band located near 690 nm was measured by few authors, because of too low line intensities for traditional absorption techniques. Available O$_2$ B-band experimental data were measured by Fourier-transform spectroscopy [12], photo-acoustic spectroscopy [13], and CRDS [14, 15]. Also several interesting applications of the B-band spectra were proposed and realized including cloud parameters measurement [16, 17], stratospheric wind determination [18], measurement of pressure and temperature profiles of atmosphere [19], and chlorophyll fluorescence detection [20, 21].

2. Experimental setup

Our experimental setup consists of a Pound-Drever-Hall locked frequency-stabilized cavity ring-down spectrometer (PDH-locked FS-CRDS) linked to the frequency-doubled Er:fiber OFC used to measure absolute frequency of the probe laser at each point of a spectrum. The experimental setup and measurement procedure was improved comparing to this described in Ref. [11], where the absolute frequency of the probe laser was determined for the first and the last point of the spectrum.

In Fig. 1 a scheme of the experimental setup is presented. The ring-down cavity is actively locked to the stabilized HeNe laser with use of the FM technique. The cavity mirrors are designed to provide moderate reflectivity of about 98% for the HeNe laser wavelength which enables to use the FM locking scheme, and the feedback loop controls the cavity length by the PZT actuator [22, 23]. The probe laser (ECDL) is locked to the high-finesse ($F^* = 12600$) ring-down cavity with the PDH technique. 20 MHz modulation of the optical frequency is realized by an electro-optic modulator (EOM) and the PDH error signal is generated using the silicon detector (PDH det). The PDH-lock feedback loop controls the ECDL diode current and diffraction grating angle. The ring-down event is started by switching off the acousto-optic modulator.
by exceeding a given threshold of the transmission signal registered by the silicon detector (RD det). The PDH lock is repetitively interrupted for the ring-down event and relocked again, see Refs. [7, 8] for details. The scanning Fabry-Perot interferometer (FPI) serves for monitoring a single-mode operation of the ECDL laser. To measure a spectrum the ECDL is tuned and relocked to consecutive TEM$_{00}$ modes of the RD cavity and typically 1000 ring-down events are acquired per each spectrum point.

In order to measure absolute frequency of the probe laser at each point of the spectrum it is compared to the OFC equipped with a frequency doubler to reach the probe wavelength of about 687 nm. The approximate frequency of the ECDL is measured by commercially available wavemeter ($\lambda$) with uncertainty of 65 MHz which is smaller than the repetition rate of the OFC ($f_r = 250$ MHz). Together with the beat note frequency between ECDL and the intermediate ultra stable laser (US laser) [24], measured by the detector (BN2 det), the wavemeter reading is used to determine absolute mode number $n$ of the OFC closest to the optical frequency of the intermediate US laser. The US laser is an extremely narrow bandwidth (< 10 Hz) laser with a very slow frequency drift of about 300 Hz/s. Therefore the beat note frequency between OFC and US laser is almost constant during a spectrum measurement. Such approach simplifies automation of the absolute frequency measurements because there is no need to change the repetition rate $f_r$ and the offset frequency $f_o$ of the OFC during the spectrum measurement. The high-bandwidth BN2 detector allows to measure the frequency difference between the US and the ECDL lasers in a ±20 GHz range. The wavemeter readings together with beat notes from BN1 and BN2 detectors and OFC $f_r$ and $f_o$ frequencies gives the ECDL frequency at each spectrum point. This procedure enables fast determination of the absolute frequency of the probe laser with an uncertainty smaller than 0.5 MHz.

3. Results and discussion
Our experimental transition frequencies $\nu_0$ were determined as extrapolation to zero pressure of the line center determined from fits of the speed-dependent Nelkin-Ghatak profile (SDNGP) [25, 26] to the measured line profiles at different pressures, up to 22 Torr of pure O$_2$. Example spectrum with residuals from fits of the Voigt profile (VP) and SDNGP is presented in Fig. 2. The "W" shape of residuals from the VP fits is characteristic for profiles in which Dicke narrowing

![Figure 2](image-url)
and/or the speed-dependence of the collisional broadening play an important role. Both these effects are taken into account in the SDNGP, which can properly describe the observed line shapes of the $O_2$ B-band transitions [10]. It should be noted however that the difference of transition frequencies obtained from fits of the VP and SDNGP are below 150 kHz, which is less than standard uncertainties of $\nu_0$.

In Fig. 3 our absolute transition frequencies $\nu_0$ of the oxygen B-band transitions are compared to available literature data from the HITRAN database [4], Cheah et al. [12] and Gordon et al. [27]. Comparing to results presented in Ref. [11] this graph has been extended by adding three lowest rotational energy $J''$ transitions investigated using the new experimental setup. Results of Gordon et al. [27] are the closest ones to our line positions, however observed differences of up to 40 MHz are much bigger than reported in [27] (0.3 - 3) MHz uncertainties and standard uncertainties of our $\nu_0$ which are below 0.5 MHz for $J'' \leq 6$ and below 1.2 MHz in most other cases. Results from HITRAN [4] are systematically higher than ours by (140 - 300) MHz however this difference is still within the range of uncertainties given in [4]. Transition frequencies of Cheah et al. [12] have relatively big scatter for higher $J''$, but for lower $J'' (\leq 18)$ they are different from our results by up to 50 MHz. It’s worth noting that differences between our results and those from Ref. [12] are not correlated with differences between our results and data from Ref. [27]. Clearly further investigation and measurement of more transitions with high a signal-to-noise ratio of spectra, such as presented in this paper, is required to solve observed discrepancy between data from different laboratories.

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