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CW-cavity ring down spectroscopy of the ozone molecule in the 6625–6830 cm^{-1} region

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Abstract

The absorption spectrum of ozone, $^{16}O_3$, has been recorded by CW-cavity ring down spectroscopy in the 6625–6830 cm^{-1} region. The typical sensitivity of these recordings ($\alpha_{min} \sim 3 \times 10^{-10}$ cm^{-1}) allows observing very weak transitions with intensity down to 2×10^{-28} cm/molecule. 483 and 299 transitions have been assigned to the $2\nu_1 + 3\nu_2 + 3\nu_3$ *A*-type band and to the $2\nu_1 + 4\nu_2 + 2\nu_3$ *B*-type band, respectively, which are the highest frequency bands of ozone recorded so far under high resolution. Rovibrational transitions with J and K_a values up to 46 and 12, respectively, could be assigned. Despite well-known difficulties to correctly reproduce the energy levels not far from the dissociation limit, it was possible to determine the parameters of an effective Hamiltonian which includes six vibrational states, four of them being dark states. The line positions analysis led to an rms deviation of 8.5×10^{-3} cm^{-1} while the experimental line intensities could be satisfactorily reproduced. Additional experiments in the 5970–6021 cm^{-1} region allows detecting the (233) ← (010) hot band reaching the same upper state as the preceding cold band. From the effective parameters of the (233) state just determined and those of the (010) level available in the literature, 329 transitions could be assigned and used for a further refinement of the rovibrational parameters of the effective Hamiltonian leading to a value of 7.6×10^{-3} cm^{-1} for the global rms deviation. The complete list of the experimentally determined rovibrational energy levels of the (233), (242), and (520) states is given. The determined effective Hamiltonian and transition moment operators allowed calculating a line list (intensity cut off of 10^{-28} cm/molecule at 296 K), available as Supplementary material for the 6590–6860 and 5916–6021 cm^{-1} regions. The integrated band strength values are 1.75×10^{-24} and 4.78×10^{-25} cm/molecule at 296 K for the $2\nu_1 + 3\nu_2 + 3\nu_3$ *A*-type band and to the $2\nu_1 + 4\nu_2 + 2\nu_3$ *B*-type band, respectively, while the band intensity value of the (233) ← (010) is estimated to be 1.03×10^{-24} cm/molecule.

Keywords: Ozone; $^{16}O_3$; Cavity ring down spectroscopy; Effective Hamiltonian model; Effective transition moment operator; Vibrational assignments

1. Introduction

The study of the very dense absorption spectrum of $^{16}O_3$, in the range approaching the dissociation limit (~8000 cm^{-1}) should provide extremely valuable information on the ozone molecular properties. This work aims at extending the analysis of the near infrared high-resolution absorption spectrum of ozone to the range above 5800 cm^{-1}. As a consequence of the weakness of considered transitions (line intensities are on the order of 10^{-27} cm/molecule), high sensitive absorption techniques are required. The continuous wave cavity ringdown spectroscopy (CW-CRDS) spectrometer based on DFB laser diodes, developed in Grenoble, is particularly well suited as it provides typical sensitivity of $\alpha_{min} \sim 3 \times 10^{-10}$ cm^{-1} and requires small quantity of gas (some tens cm^3 at 10 Torr pressure) which reduces the hazards in the manipulation of this very explosive gas.

During a first measurement campaign, the CRDS spectrum between 6030 and 6800 cm^{-1} could be continuously

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recorded. Considering the amount of new observations obtained in these recordings, the analysis will be published in several contributions. A first publication [1] was devoted to two A-type bands centred at 6063.9 and 6124.3 cm^{-1} labelled $3\nu_1+3\nu_3$ and $2\nu_2+5\nu_3$ in Ref. [1], respectively. The present paper is focused on the study of the 6625–6820 cm^{-1} region which shows two newly observed bands: the A-type band near 6716 cm^{-1} assigned as $2\nu_1+3\nu_2+3\nu_3$ and the B-type band near 6764 cm^{-1} assigned as $2\nu_1+4\nu_2+2\nu_3$. These bands correspond to the highest frequency rovibrational transitions of ozone recorded so far under high resolution.

More recently, new spectra were recorded in the 5955–6030 cm^{-1} spectral region that includes a part of the P branches of the A-type bands studied in Ref. [1]. These new data confirm our previous analysis [1] and allow extending the line assignments for higher J and K_a values. However, numerous lines still remained unassigned. The forthcoming analysis will show that many of these lines can be assigned to the (233)–(010) hot band reaching the same upper state than the band centred at 6716.536 cm^{-1} and will then confirm the modelling of the corresponding rovibrational states.

2. Experiment

2.1. Ozone preparation

The ozone sample was prepared using a silent electric discharge (12 kV, 400 Hz) at 77 K. This system already described [2] allows obtaining a quasi-complete conversion of oxygen to ozone. After this conversion, by measuring the slow pressure increase due to the $2O_3 \rightarrow 3O_2$ conversion, the ozone pressure can be evaluated with the assumption that the total pressure of impurities in the cell is small.

2.2. The CW-CRDS spectrometer

The fibered distributed feed-back (DFB) diode laser CW-CRDS spectrometer was described in details in Ref. [3]. It allows to cover continuously the 5955–6800 cm^{-1} region by the help of 40 fibered DFB diode lasers, each of them having a typical tuning range of 7 nm (~30 cm^{-1}). The considered spectral region corresponds to the important 1.5 μm atmospheric window of transparency used for telecommunication. This spectrometer was previously applied to the high sensitive absorption spectroscopy of a series of molecules of atmospheric interest: $^{13}CO_2$ [4], H_2O [5] and $^{12}CO_2$ [6]. The reader is referred to Refs. [1,4] for more details about the data acquisition system.

An overview of the CW-CRDS spectrum of ozone between 6690 and 6725 cm^{-1} is presented in Fig. 1. Many lines due to carbon dioxide and water, present as impurities in our sample, could be identified using the last HITRAN database edition [7]. They were also used to check the accuracy of the wavenumber calibration of the CW-CRDS spectra.

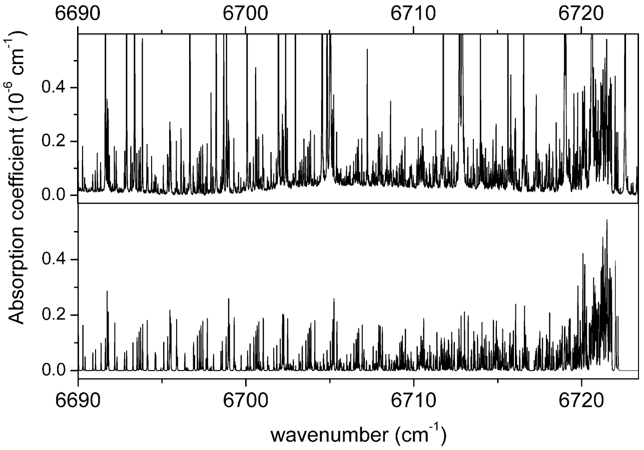

Fig. 1. Upper panel: overview of the CW-CRDS spectrum of the weak $2\nu_1+3\nu_2+3\nu_3$ A-type band of ozone centred at 6716 cm^{-1}. All the strong lines are due to H_2O or CO_2. The partial pressures were the following: $P(O_3) = 28.8$ Torr, $P(CO_2) = 1.0$ Torr, $P(H_2O) = 0.12$ Torr. The very compressed R branch near 6720 cm^{-1} is clearly observed. Lower panel: spectrum simulated by using the effective Hamiltonian and transition moment operators determined in this work (Tables 2 and 4, respectively).

The pressure, measured by a capacitance gauge (Baratron), as well as the ringdown cell temperature were continuously recorded during the experiments. Various pressures ranging between 3 and 30 Torr were adopted. Under these conditions, the conversion of ozone into oxygen ($2O_3 \rightarrow 3O_2$) is sufficiently slow to allow for the scan of several diode lasers before renewing the gas sample. In these pressure conditions, collisional broadening (FWHM $\sim 2.6\times10^{-3}$ cm^{-1} at a pressure of 10 Torr) is significantly lower than the Doppler broadening (FWHM $\sim 11\times10^{-3}$ cm^{-1}) and the observed line profile is mostly Gaussian as the diode laser linewidth contribution (a few MHz) is negligible.

The wavenumber calibration of the spectrum was based on the values provided by a lambdameter (Burleigh WA1640). It improves the method using an etalon signal adopted in Ref. [1]. The lambdameter records on the fly the wavelength of the laser source. Then, during one lambdameter scan (1 s), the laser frequencies are integrated leading to an error on the frequency determination which depends on the speed of the laser scan. Even if hardware improvements have been performed in order to improve the linearity of the DFB laser frequency scan, its speed varies over the 7 nm tuning range and the frequency error is not a constant. The reader is referred to Ref. [8] for a detailed description of the procedure followed to correct this systematic shift on the wavelength values.

After this speed correction, the entire spectrum can be simply frequency stretched (with an origin at 0) in agreement with highly accurate positions of reference line (CO_2 or H_2O) observed in the CRDS spectrum. As a result, reproducibility better than 2×10^{-4} cm^{-1} could be achieved in the overlapping part of two successive spectral regions. Maximum deviation of 2×10^{-3} cm^{-1} were observed for CO_2 reference lines which is then the