

CW-Cavity Ring Down Spectroscopy of the ozone molecule in the 5980–6220 cm^{-1} region

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Abstract

The absorption spectrum of ozone, $^{16}\text{O}_3$, has been recorded in the 5980–6220 cm^{-1} region by high sensitivity CW-Cavity Ring Down Spectroscopy ($\alpha_{\text{min}} \sim 3 \times 10^{-10} \text{ cm}^{-1}$). This study extends a first investigation with the same experimental set-up limited to the 6030–6090 cm^{-1} spectral region [M.-R. De Backer-Barilly, A. Barbe, Vl.G. Tyuterev, D. Romanini, B. Moeskops, A. Campargue, *J. Mol. Struct.* 780–781 (2006) 225–233] where the analysis of two A-type bands was reported, using FTS spectra for complementary information. The spectral extension of the recordings allows not only to enlarge considerably the observed transitions of these two bands, but more importantly, to assign four new bands: the $3\nu_2 + 4\nu_3, 5\nu_1 + \nu_2$ and $\nu_1 + 2\nu_2 + 4\nu_3$ B-type bands which were considered as dark in our previous report and the $3\nu_1 + 3\nu_2 + \nu_3$ A-type band. The high mixing of the observed states approaching the dissociation limit, leads to the breakdown of the polyad structure and ambiguities in the vibrational labelling which are discussed. Finally, 1789 transitions were assigned, and a suitable Hamiltonian model allows reproducing correctly the observations for five of the six observed bands. The list of 1004 experimentally determined energy levels is provided. The determined effective Hamiltonian and transition moment operators were used to generate a list of 5338 transitions given as Supplementary Material. It is interesting to note that the d_5 parameter of the effective transition moment is of great importance to account for the observed intensities of the B-type bands.

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1. Introduction

This work continues our systematic study of the rovibrational spectra of ozone in the infrared [1 and references herein], corresponding to the open configuration in the electronic ground state. Most of previous analyses using FTS spectra are devoted to the spectral domain below 5500 cm^{-1} . Thanks to the higher sensitivity of the CW-Cavity Ring Down Spectroscopy (CW-CRDS) technique, spectral regions approaching the dissociation limit ($\sim 8000 \text{ cm}^{-1}$) can be now investigated with high resolution. We have very recently reported a rovibrational analysis of

the ozone spectrum in the 6030–6130 [2] and 6625–6830 cm^{-1} [3] regions. In the first paper, 671 transitions were assigned to two A-type bands centred at 6063 and 6124 cm^{-1} and it was necessary to take into account three perturber dark vibrational states to correctly reproduce the observed transitions. Since that time, we were able to extend considerably the recorded spectra covering continuously the 5980–6220 cm^{-1} region. This has allowed detecting the three above mentioned bands, which corresponded to dark upper states of our previous analysis [2], and considerably extending the set of experimental rotational levels of the two “bright” states observed at 6063 and 6124 cm^{-1} . As a result, the total number of assigned transitions is now increased to 1789 lines. In addition, a new theoretical development allows a more appropriate approach of vibrational

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assignments which will be discussed in Section 3. It is worth mentioning that in our recent contribution relative to the study of the $2\nu_1 + 3\nu_2 + 3\nu_3$ A-type band near 6716 cm^{-1} [3], we have included an analysis of the $(233) \leftarrow (010)$ hot band reaching the same upper state and lying in the presently investigated region. A total of 329 observed transitions could be assigned to this hot band between 5970 and 6021 cm^{-1} and used for a further refinement of the rovibrational parameters of the (233) state.

2. Experiment

The fibered Distributed Feed-Back (DFB) diode laser CW-CRDS spectrometer was described in detail in Refs. [2,3]. The $5980\text{--}6830\text{ cm}^{-1}$ region can be continuously covered by the help of 40 fibered DFB diode lasers, each of them having a typical tuning range of 7 nm ($\sim 30\text{ cm}^{-1}$). The typical sensitivity of our spectrometer is $\alpha_{\min} \sim 3 \times 10^{-10}\text{ cm}^{-1}$ while the estimated wavenumber accuracy is better than $2 \times 10^{-3}\text{ cm}^{-1}$, in agreement with the maximum differences obtained for the values of the energy levels determined from wavenumbers of different transitions reaching the same upper energy level. Impurities such as H_2O , CO_2 or CO present in the ozone sample were used for checking and refining the absolute calibration [4] provided by a lambda-meter. Experimental line positions were derived from the recorded spectra by using the Multifit procedure [5], which also provides line intensities. As a consequence of the slow decomposition of ozone which determines the uncertainty on the O_3 concentration, we estimate the abso-

lute accuracy on the line intensity values to be about 20%, while the relative precision is at least ten times better. An overview of the analysed spectrum is displayed in Fig. 1. It corresponds to the spectral acquisition with eight DFB laser diodes.

3. Assignments, model and analyses

3.1. Vibrational assignments

As already remarked in the previous study [3], a conventional normal mode labels (ν_1, ν_2, ν_3) appears to be ambiguous for some states in the considered energy range, as a result of strong mixing of the basis normal mode wave functions, due to anharmonic interactions.

A recent theoretical work [6] allows calculating various normal mode contributions to a wave function of a rovibrational state starting from a molecular potential energy surface (PES). The vibrational eigenstates of $^{16}\text{O}_3$ were calculated from the molecular PES of Refs. [7,8], which currently provides the most accurate vibrational predictions for the $^{16}\text{O}_3$ molecule. Corresponding mixing coefficients P_n which represent squares of wave function expansion coefficients in the zero-order normal mode basis are given in Table 1 for all vibrational levels involved in the studied energy interval. As in our previous study, we have adopted a vibration normal mode assignment based on this procedure keeping in mind that resulting notations are somewhat arbitrary for situations where no truly dominant normal mode contribution appears. It was already mentioned [3]

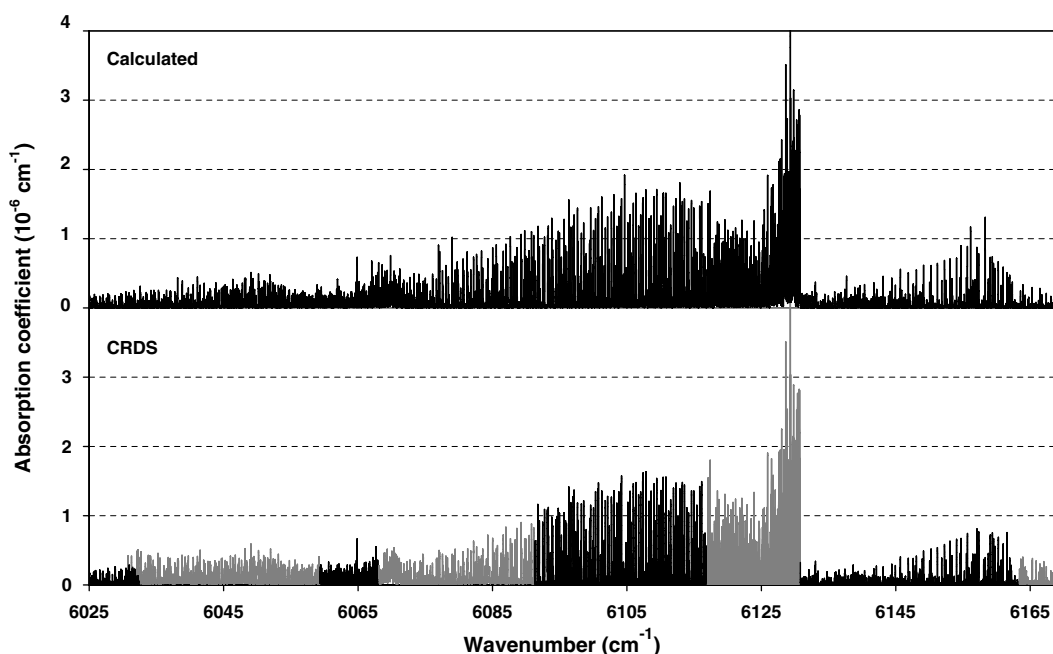


Fig. 1. Overview of the absorption spectrum of ozone between 6025 and 6170 cm^{-1} . The spectrum is dominated by the $2\nu_1 + 2\nu_2 + 3\nu_3$ A-type band which shows a compressed R branch near 6130 cm^{-1} . (Lower panel) Experimental spectrum recorded by CW-CRDS with a sample pressure of about 20 Torr. The black and grey colours shows that the whole spectrum is in fact the addition of eight spectra recorded with different DFB diodes. In this spectrum, all the absorption lines due to impurities (H_2O , CO_2 and CO) have been removed for sake of clarity. (Upper panel) Spectrum simulated by using the effective Hamiltonian and transition moment operators determined in this work (Tables 5 and 6, respectively).

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