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# CW-cavity ring down spectroscopy of the ozone molecule in the 6220–6400 $cm^{-1}$ region

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## Abstract

The absorption spectrum of ozone, $^{16}O_3$, has been recorded in the 6220–6400 $cm^{-1}$ region by high sensitivity CW-cavity ring down spectroscopy ($\alpha_{min} \sim 3 \times 10^{-10}$ $cm^{-1}$). 1836 rovibrational transitions have been assigned to the $2\nu_2 + 5\nu_3$, $5\nu_1 + \nu_3$ and $2\nu_1 + 2\nu_2 + 3\nu_3$ A-type bands centred at 6305, 6355 and 6387 $cm^{-1}$, respectively. In addition, 99 lines of the very weak $\nu_1 + 2\nu_2 + 4\nu_3$ and $4\nu_1 + 3\nu_2$ B-type bands are identified. The modeling of the observed spectrum in the effective Hamiltonian approach was particularly laborious and complex as several rovibrational interactions of both Coriolis and anaharmonic type were found to be of importance, in particular for the (124) vibrational state. Nevertheless, it has finally been possible to fit the 990 experimentally determined energy levels with an *rms* deviation of $8.29 \times 10^{-3}$ $cm^{-1}$ and to derive the transition moment parameters allowing a satisfactory reproduction of the observed intensities. As the differences in positions between the final calculations and observations are still larger than the experimental accuracy, we provide the list of all energy levels derived from the observation, in addition to their differences with the calculated ones. These experimental energy levels, with the transition moment parameters were used to generate a line-list of 2451 transitions, reproducing the observed spectrum. This list is given as Supplementary Material.

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

## 1. Introduction

This work continues our systematic study of the infrared rovibrational spectrum of ozone in the electronic ground state [1 and references herein]. Thanks to the high sensitivity of the CW-Cavity Ring Down Spectroscopy (CW-CRDS) technique, weak combination bands in spectral regions approaching the dissociation limit (~8000 $cm^{-1}$) are now observable with high spectral resolution. The CW-CRDS spectrometer developed in Grenoble has allowed for the new observations of a number of bands of $^{16}O_3$ in the 5940–7000 $cm^{-1}$ region which are reported in several contributions. For instance, in the 6030–6130 [2], 6625–6830 [3] and 5980–6220 $cm^{-1}$ [4] regions, a total of 10 bands were rovibrational assigned. The present paper is devoted to the 6220–6400 $cm^{-1}$ spectrum dominated by three A-type bands as illustrated on the overview spectrum of Fig. 1.

## 2. Experiment

The experimental set-up has been described in detail in Refs. [2–4]. Let us just recall that the 5940–7000 $cm^{-1}$ region can be continuously covered by the help of 50 fibered DFB diode lasers, each of them having a typical tuning range of 7 nm (~30 $cm^{-1}$). The estimated wavenumber accuracy is better than $2 \times 10^{-3}$ $cm^{-1}$, 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 the checking and refinement of the absolute wavenumber calibration [5]. Experimental line positions

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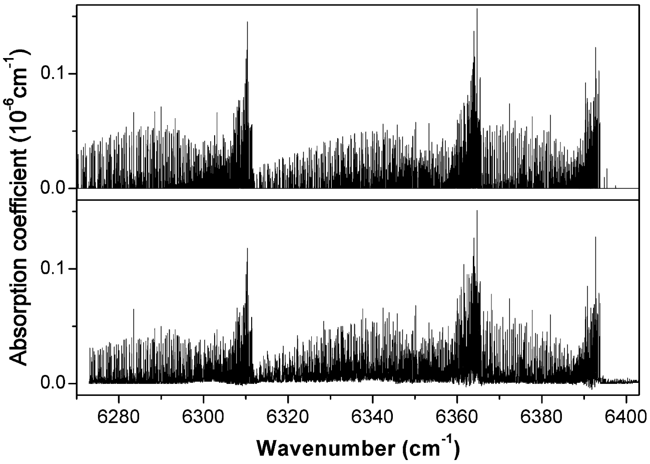

Fig. 1. Overview of the absorption spectrum of ozone between 6270 and 6400 cm$^{-1}$. The spectrum is dominated by the $2\nu_2 + 5\nu_3$,$5\nu_1 + \nu_3$ and $2\nu_1 + 2\nu_2 + 3\nu_3$ A-type bands which show compressed *R* branch head near 6308, 6364 and 6392 cm$^{-1}$, respectively. For sake of clarity, the absorption lines due to impurities ($H_2O$, $CO_2$, CO) have been removed from the observed spectrum. *Lower panel:* Experimental spectrum recorded by CW-CRDS. *Upper panel:* Simulated spectrum using the effective Hamiltonian and transition moment operators determined in this work (Tables 5 and 6, respectively).

were derived from the recorded spectra by using the MultiFiT procedure [6], which also provides line intensities. As a consequence of the slow decomposition of ozone which fixes the uncertainty on the $O_3$ concentration, we estimate the absolute accuracy on the line intensity values to be about 25%, while the relative precision is at least ten times better. Note that for the sake of clarity, impurity lines ($CO_2$, $H_2O$ and CO) were removed from the experimental spectrum of Fig. 1.

## 3. Theory

The expressions of the matrix elements of the effective Hamiltonian and of the transition moment operators expanded in powers of the elementary rotational operators are given in Eqs. (1–5) of our preceding paper [4]. The reader is referred to these equations for the definition of the effective parameters used below.

All the remarks concerning the limitations of the normal mode assignments given in Refs. [3,4] remain valid: as a result of a strong mixing of the basis normal mode wave functions due to anharmonic interactions, the conventional normal mode label ($v_1$, $v_2$, $v_3$) is ambiguous for some states of the considered energy range. The various normal mode contributions to a wave function of a vibrational state were calculated from the $^{16}O_3$ molecular potential energy surface (PES) of Refs. [7,8]. We give in Table 1 the theoretical predictions [9] of the six band centres involved on the studied interval, with the corresponding fraction,$P_n$, which represents the square of the wave function expansion coefficients in the zero-order normal mode basis. All the levels predicted between 6300 and 6400 cm$^{-1}$ are represented in Fig. 2, with the various resonances involved in the effective Hamiltonian (see below).

The values listed in Table 1 show that the bands centred at 6306, 6356 and 6367 cm$^{-1}$ and to a less extent at 6321 cm$^{-1}$ can be unambiguously assigned as the corresponding upper states have a clearly defined major contribution. For the upper state at 6356 cm$^{-1}$, the major contribution corresponding to the (501) normal mode wave function is 73.4% while for three other upper states, the maximum fraction ranges between 43% and 48%. On the contrary, the upper states at 6344 and 6387 cm$^{-1}$ are strong mixtures of normal mode wave function and the normal mode assignment is ambiguous. For instance, the $(124)_0$ normal mode is the first contribution of the state at 6344 cm$^{-1}$ with $P_1 = 25.9\%$, but also, of a recently reported level at 6155 cm$^{-1}$ [4] ($P_1 = 31.9\%$). In the same manner, the fraction relative to $(223)_0$ appears as the first contribution of the state at 6387 cm$^{-1}$ ($P_1 = 28.0\%$), and also in that of the state at 6125 cm$^{-1}$ ($P_1 = 44\%$) [4].

Table 1
Comparison of the experimental band centres with theoretical predictions and corresponding normal mode assignments

| Band centre (cm$^{-1}$) | | | Three major normal mode contributions [a] | | | | | |
|---|---|---|---|---|---|---|---|---|
| Calc-1 [b] | Calc-2 [c] | Exp.[d] | $P_1$ (%) | $W_1$ | $P_2$ (%) | $W_2$ | $P_3$ (%) | $W_3$ |
| 6305.8 | 6306.7 | 6305.047 | 46.3 | $(025)_0$ | 14.3 | $(313)_0$ | 12.2 | $(115)_0$ |
| 6320.9 | 6321.2 | 6320.248 (d) | 43.1 | $(152)_0$ | 34.0 | $(260)_0$ | 10.7 | $(044)_0$ |
| 6344.1 | 6344.8 | 6343.983 | 25.9 | $(124)_0$ | 25.7 | $(430)_0$ | 24.2 | $(214)_0$ |
| 6355.9 | 6355.6 | 6355.722 | 73.4 | $(501)_0$ | 22.6 | $(303)_0$ | 3.3 | $(105)_0$ |
| 6366.6 | 6366.4 | 6365.264 | 48.3 | $(430)_0$ | 17.4 | $(214)_0$ | 8.8 | $(322)_0$ |
| 6387.9 | 6387.3 | 6386.997 | 28.0 | $(223)_0$ | 20.4 | $(313)_0$ | 18.8 | $(115)_0$ |

[a] Columns $P_n$'s indicate the mixing coefficients (in%) of $\Psi^{\text{eff}}$ in the harmonic normal mode basis. Columns $W_n$'s indicate the corresponding vibration normal mode quantum numbers $(v_1v_2v_3)_0$. *n* is the order of the contribution. The subscript "0" of $(v_1v_2v_3)_0$ means that contributions correspond to zero-order normal mode basis.

[b] Global variational predictions from the potential function $V^M$ of Ref. [7] in internal coordinates ($r_1$, $r_2\theta$).

[c] Non-empirical effective Hamiltonian predictions derived from the potential function of Ref. [8] in normal coordinates $q_1$, $q_2$, $q_3$ using 10-th order Contact Transformations [9].

[d] Our values resulting from experimental data reduction; (d) means energy value of a dark state determined from the perturbations of the observed bands (see Table 2).