Note

The $v_1 + 3v_2 + 3v_3$ and $4v_1 + v_2 + v_3$ bands of ozone by CW-cavity ring down spectroscopy between 5900 and 5960 cm^{-1}

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Abstract

The absorption spectrum of ozone, $^{16}O_3$, has been recorded in the 5903–5960 cm^{-1} region by high sensitivity CW-cavity ring down spectroscopy ($\alpha_{min} \sim 5 \times 10^{-10}$ cm^{-1}). The $v_1 + 3v_2 + 3v_3$ and $4v_1 + v_2 + v_3$ A-type bands centred at 5919.15 and 5947.07 cm^{-1} were newly observed. A set of 173 and 168 energy levels could be experimentally determined for the (1 3 3) and (4 1 1) states, respectively. Except for a few $K_a = 5$ levels of the (4 1 1) state, the rotational structure of the two states was found mostly unperturbed. The spectroscopic parameters were determined from a fit of the corresponding line positions by considering the (1 3 3) and (4 1 1) states as isolated. The determined effective Hamiltonian and transition moment operators were used to generate a list of 785 transitions given as Supplementary Material.
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1. Introduction

This work continues our study of the infrared rovibrational bands of ozone approaching the dissociation energy at about 8000 cm^{-1}. The CW-CRDS spectrometer developed in Grenoble, has allowed for the new observations of a number of very weak bands of $^{16}O_3$ between 5980 and 6830 cm^{-1} [1–4]. The present paper is devoted to the 5903.4–5960.0 cm^{-1} spectral region corresponding to the lower energy range accessible with this set-up.

2. Experiment

The experimental set-up has been described in details in Refs. [1,3]. The studied spectrum between 5903.4 and 5960.0 cm^{-1} corresponds to the spectral acquisition with two newly purchased DFB laser diodes, each of them having a typical tuning range of 7 nm (~30 cm^{-1}). H_2O line

positions [5] present in the ozone sample were used for the checking and refinement of the absolute wavenumber calibration. The typical wavenumber accuracy is estimated to be 1×10^{-3} cm^{-1}, in agreement with the rms deviations obtained for the values of the energy levels determined from wavenumbers of different transitions reaching the same upper energy level (see below). Experimental line positions 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, we estimate the absolute accuracy on the line intensity values to be about 15%, while the relative precision is significantly better. The overview of the analysed spectrum is displayed in Fig. 1. It shows two A-type bands with their characteristic R branch head around 5930 and 5957 cm^{-1}.

3. Assignment and modelling of the $v_1 + 3v_2 + 3v_3$ and $4v_1 + v_2 + v_3$ bands

The ambiguities of the normal mode labelling of the observed upper states have been previously discussed

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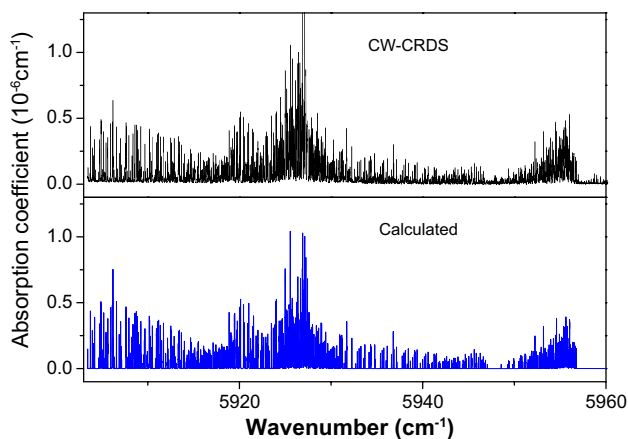*E-mail address:* Alain.Campargue@ujf-grenoble.fr (A. Campargue).

Fig. 1. Overview of the absorption spectrum of ozone between 5903.4 and 5960.0 cm^{-1}. *Upper panel*: Experimental spectrum recorded by CW-CRDS with a pressure of about 15 Torr of $^{16}O_3$. *Lower panel*: Spectrum simulated by using the effective Hamiltonian (Table 3) and transition moment operators (Table 4) determined in this work.

[2–4]. On the basis of theoretical calculations using the $^{16}O_3$ molecular potential energy surface (PES) of Refs. [7,8], the upper vibrational state of the two bands centred around 5919 and 5947 cm^{-1} were found to have a dominant character of the (133) and (411) state in the zero-order normal mode basis, respectively. The fractions i.e. the square of the corresponding coefficient in the eigenvector expansion are 49.1% and 72.5%, respectively [9].

The calculations of the rovibrational energy levels and transitions were performed using the GIP (General Inverse Problem solver) code [7]. As the two considered A-type bands could be treated as unperturbed bands, only the diagonal part of the effective Hamiltonian was used. The corresponding matrix element expanded in powers of the elementary rotational operators was used in its usual Watson form [10]. The experimental intensities were modelled by fitting the parameters involved in the transition moment operators expanded in powers of the elementary rotational operators as expressed in Refs. [11,12].

Rotational assignments were based on Ground State Combination Differences relations, using transition series following branches and sub-branches. The ASSIGN code [13] was used to perform the first assignments corresponding to $K_a = 0$, 1 values with J values between about 8 and 15. Then, further assignments were possible by following series with smooth variations of the (obs. − calc.) values. As a result, 173 and 168 energy levels have been experimentally determined for the (133) and (411) states, respectively. Their values are listed in Table 1 together with their assignments, the statistical errors when determined as upper level of several transitions and the deviations between the experimental and calculated values.

Contrary to most of our analysis of the $^{16}O_3$ bands observed above 6000 cm^{-1} [1–4], the rotational structure

of the two upper vibrational states under consideration was found mostly unperturbed. Except for the $K_a = 5$ series of the (411) state which is perturbed, the determined energy levels could be reproduced as those of an isolated state. The calculation statistics are given in Table 2, while the parameter values are listed in Table 3.

The rms deviations of the (obs. − calc.) values achieved for the two states are, however, about five times larger than the experimental uncertainty, indicating that the considered states are probably weakly interacting with nearby dark states. Considering the weakness of these interactions and the lack of additional experimental information concerning the interacting states, we did not try to further improve the rms of the residuals by elaborating a more sophisticated effective Hamiltonian model. The most probable perturbers are the (340) and (034) states predicted [9] near 5890 and 5971 cm^{-1}, respectively. Similar perturbation was indeed evidenced for the (401) and (123) states which differ by one bending excitation from the presently studied (133) and (411) states and which were found perturbed by the (330) and (024) states [15].

Ninety-two and 135 transitions of well isolated lines of the $v_1 + 3v_2 + 3v_3$ and $4v_1 + v_2 + v_3$ bands were measured by using the MultiFit code [6]. The values of the transition moment parameters listed in Table 4 together with the statistics were obtained from a fit of these intensity values. We note that the experimental line intensities are reproduced with an rms value of 15% which is satisfactory but significantly larger than the relative precision on the experimental line intensities. As mentioned above, the absolute uncertainty due to the uncertainty on the ozone concentration, may reach a value of 15% for the integrated band strengths.

As a result of the small but significant deviations between the calculated and measured line positions, we adopted the same procedure as described in Ref. [4] to construct the line list provided as Supplementary Material: the wavenumber values were corrected by replacing calculated upper state energies by their experimentally determined value (Table 1) while the line intensities values were calculated with the transition momentum parameters (Table 4). As illustrated in Figs. 2 and 3, the corrections on the line positions are significant for a few transitions. This procedure allows accounting for transitions which were not observed, as for instance, very weak lines corresponding to high J values in the Q branches, blended lines in the R branch or lines obscured by impurity lines. Note that the present line list is then limited to transitions reaching experimentally determined levels and then no intensity cut off was applied.

Let us finally mention that a number of weak lines remain unassigned (see Figs. 2 and 3). They may be due to transitions of the two bands in consideration, involving higher rotational quantum numbers or transitions of very weak B-type bands.