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Global modeling of $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ and $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ absolute line intensities in the $1.35\ \mu\text{m}$ region

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V.I. Perevalov, S.A. Tashkun, K.F. Song, Alain Campargue. Global modeling of $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ and $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ absolute line intensities in the $1.35\ \mu\text{m}$ region. *Journal of Molecular Spectroscopy*, 2010, 263, pp.183-185. 10.1016/j.jms.2010.08.004 . hal-00563137

HAL Id: hal-00563137

<https://hal.science/hal-00563137>

Submitted on 4 Feb 2011

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NOTE

Global modeling of $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ and $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ absolute line intensities in the 1.35 μm region

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Version : 11 May 2010

Number of tables: 2

Number of figures: 2

Number of pages: 7

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Abstract

In our recent contribution, (K.F. Song, S. Kassi, S.A. Tashkun, V.I. Perevalov, A. Campargue. High sensitivity CW-Cavity Ring Down Spectroscopy of $^{12}\text{CO}_2$ near 1.35 micron (II): New observations and line intensities modeling. J. Quant. Spectrosc. Radiat. Transf. 111 (2010) 332-344), the absolute intensities of the $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ and $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ transitions detected in the high sensitivity absorption spectrum of carbon dioxide were measured. In this Note from the global fits of the obtained intensity values, we have derived the sets of effective dipole moment parameters for these isotopologues, which allow reproducing the intensities of the measured very weak lines (2×10^{-29} - 7×10^{-28} cm/molecule) with an RMS of residuals on the order of 6%.

Key words: Carbon dioxide, CO_2 , Cavity Ring Down Spectroscopy, line intensities, Global modelling, CDS

We have recently retrieved the line positions and intensities of carbon dioxide in the 7123-7917 cm^{-1} region from spectra recorded by CW-Cavity Ring Down Spectrometer (CW-CRDS) [1,2]. The very high sensitivity of the CRDS spectrometer developed in Grenoble (noise equivalent absorption $\alpha_{min} \sim 2 \times 10^{-10} \text{ cm}^{-1}$) allowed detecting lines with intensities as low as $1 \times 10^{-29} \text{ cm/molecule}$. Four isotopologues ($^{12}\text{C}^{16}\text{O}_2$, $^{13}\text{C}^{16}\text{O}_2$, $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ and $^{16}\text{O}^{12}\text{C}^{18}\text{O}$) were found to contribute to the observed spectrum. The studied spectral region is formed by $\Delta P=10$ and $\Delta P=11$ series of transitions where P is the polyad number ($P = 2V_1 + V_2 + 3V_3$, where V_i are vibrational quantum numbers [4-8]). Using the newly measured line intensities and those collected from the literature, the global modeling of the line intensities within the effective operator approach [4-8] has been performed for the $\Delta P=11$ series of transitions of the principal isotopologue and for the $\Delta P=10$ series of transitions of the $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ isotopologue [2]. The new observations include six $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ bands and two $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ bands of the $\Delta P=11$ series. This Note is devoted to the global modeling of the intensities for these $\Delta P=11$ transitions.

We followed the same effective operator approach as presented in our previous papers (see for example, Refs. [4-8]): the effective Hamiltonian globally describing the line positions is formulated with the assumption that the vibration-rotation energy levels can be separated in polyads, as a result of the approximate relations between the harmonic frequencies [4-8]

$$\omega_1 \approx 2\omega_2, \quad \omega_3 \approx 3\omega_2. \quad (1)$$

The effective Hamiltonian takes into account all resonance interactions between vibrational states belonging to the same polyad, up to the sixth order of the perturbation theory. The polyad model of the effective Hamiltonian works very well for carbon dioxide, except for asymmetric isotopologues, for which several cases of interpolyad resonance interactions have been evidenced [9-12].

The intensity of a vibration-rotation transition $P'N'J'\epsilon' \leftarrow PNJ\epsilon$ is proportional to the square of a transition dipole moment [6-8]. For the calculation of a transition dipole moment within the framework of the effective operator approach one needs the expansion coefficients ${}^J C_{PN\epsilon}^{V_1 V_2 \ell_2 V_3}$ of the eigenfunctions of upper and lower vibration-rotation states:

$$\Psi_{PNJ\epsilon}^{eff} = \sum_{\substack{2V_1+V_2+3V_3=P \\ \ell_2}} {}^J C_{PN\epsilon}^{V_1 V_2 \ell_2 V_3} |V_1 V_2 | \ell_2 | V_3 J \epsilon \rangle. \quad (2)$$

In Eq.(2), the summation runs over all states within the polyad involved. The definition of the Wang-type basis functions $|V_1 V_2 | \ell_2 | V_3 J \epsilon \rangle$ is given in Ref. [6], for example. The

equation for a transition dipole moment involves the $M_{\Delta V_1 \Delta V_2 \Delta V_3}^{|\Delta \ell_2|}$ parameters of the matrix elements of the effective dipole moment operator and Herman-Wallis type parameters [6-8]. These latter were not important in the present study.

The values of the expansion coefficients ${}^J C_{PN\mathcal{E}}^{V_1 V_2 \ell_2 V_3}$ of the eigenfunctions have been obtained from the global fit of the effective Hamiltonian parameters to the observed line positions. The initial sets of effective Hamiltonian parameters which were used for the generation of CDSDB databank [13] were slightly refined using new observations [1, 2]. The partition functions $Q(T)$ and nuclear statistical weights were taken from Ref. [14].

The effective dipole moment parameters of the $\Delta P=11$ series of transitions of ${}^{16}\text{O}^{12}\text{C}^{17}\text{O}$ and ${}^{16}\text{O}^{12}\text{C}^{18}\text{O}$ were derived from a least-squares fit of the intensity values derived in Ref. [2]. The derivation of absolute intensity values for ${}^{16}\text{O}^{12}\text{C}^{17}\text{O}$ and ${}^{16}\text{O}^{12}\text{C}^{18}\text{O}$ from measurements performed with carbon dioxide in “natural” isotopic abundance [1,2] relies on the assumption that the isotopic abundances in our CO_2 sample was close to the standard values adopted in HITRAN. This assumption may add some uncertainty on the experimental intensity values but the isotopic fractionation of oxygen is known to be very limited. It is worth emphasizing that no other measurements of line intensities are available for these isotopologues in the 1.35 μm region.

The standard procedure of the least-squares fitting minimizes the dimensionless weighted standard deviation χ , defined according to the usual formula

$$\chi = \sqrt{\frac{\sum_{i=1}^N \left(\frac{S_i^{obs} - S_i^{calc}}{\delta_i} \right)^2}{(N - n)}}, \quad (4)$$

where S_i^{obs} and S_i^{calc} are, respectively, observed and calculated values of the intensity for the i -th line; $\delta_i = \frac{S_i^{obs} \sigma_i}{100\%}$, where σ_i is the measurement error of the i -th line in %, N is the number of fitted line intensities, and n is the number of adjusted parameters. For both isotopologues we used the same weighting. Relative uncertainties values of 3 % and 6% were assumed for the intensity values larger and smaller than 1×10^{-28} cm/molecule, respectively. The summary of the line intensity fits is presented in Table 1 which provides the weighted standard deviation χ together with the root mean squares of the residuals

$$RMS = \sqrt{\frac{\sum_{i=1}^N (S_i^{obs} - S_i^{calc})^2}{\sum_{i=1}^N S_i^{obs}}} \times 100\%. \quad (5)$$

The sets of the effective dipole moment parameters for both isotopologue are presented in Table 2. It is interesting to note that the two principal effective dipole moment parameters for these isotopologues are very close each to other. This fact could be considered as a confirmation of the above assumption concerning the “natural” isotopic abundance of the used CO₂ sample. The residuals between observed and calculated values of the line intensities are displayed in Fig. 1 and Fig. 2 for ¹⁶O¹²C¹⁷O and ¹⁶O¹²C¹⁸O, respectively. A similar quality of data reproduction is achieved for both isotopologues. The achieved RMS value on the order of 6% is satisfactory considering the weakness of the modeled transitions. To reach these results, some blended and very weak lines were excluded from the fit: 16 from 96 observations for ¹⁶O¹²C¹⁷O and 59 from 293 for ¹⁶O¹²C¹⁸O.

The results presented in this Note will allow to include the $\Delta P=11$ series of transitions of ¹⁶O¹²C¹⁷O and ¹⁶O¹²C¹⁸O in the new version of the CDSD databank.

Acknowledgments

This work is jointly supported by CNRS (France), RFBR (Russia, grant N 09-05-93105) and CAS (China) in the frame of Groupement de Recherche International SAMIA (Spectroscopy of Molecules of Atmospheric Interest).

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Table 1. Summary of the line intensity fits.

Isotopologue	Number of lines	Number of bands	J_{\max}	$S_{\min}^a)$	$S_{\max}^a)$	χ	RMS (%)	$n^b)$
$^{16}\text{O}^{12}\text{C}^{17}\text{O}$	80	2	39	3.04×10^{-29}	1.61×10^{-28}	1.5	6.0	2
$^{16}\text{O}^{12}\text{C}^{18}\text{O}$	234	6	53	1.83×10^{-29}	6.87×10^{-28}	1.5	6.1	3

^{a)} S_{\min} and S_{\max} (in cm/molecule) are the minimum and maximum values of line intensity included into the fit.

^{b)} n is the number of adjusted parameters.

Table 2. Effective dipole moment parameters for $\Delta P=11$ series of transitions in $^{16}\text{O}^{12}\text{C}^{17}\text{O}$ and $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ isotopologues of carbon dioxide molecule.

Parameter ^{a)} $M_{\Delta V_1 \Delta V_2 \Delta V_3}^{ \Delta \ell_2 }$				Value	Order
ΔV_1	ΔV_2	ΔV_3	$\Delta \ell_2$		
4	0	1	0	$0.16738(62)^b)$	10^{-4}
3	2	1	0	-0.151(11)	10^{-5}
4	0	1	0	0.16594(28)	10^{-4}
3	2	1	0	-0.149(27)	10^{-5}
2	4	1	0	0.63(12)	10^{-7}

^{a)} The parameters are given in *Debye*. Only relative signs of the M parameters within a given series of transitions are determined.

^{b)} The numbers in parentheses correspond to one standard deviation in units of the last quoted digit.

List of Tables

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Figure captions

Figure 1. Residuals between observed and calculated values of the line intensities for $\Delta P=11$ series of transitions in $^{16}\text{O}^{12}\text{C}^{17}\text{O}$.

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Fig.1.

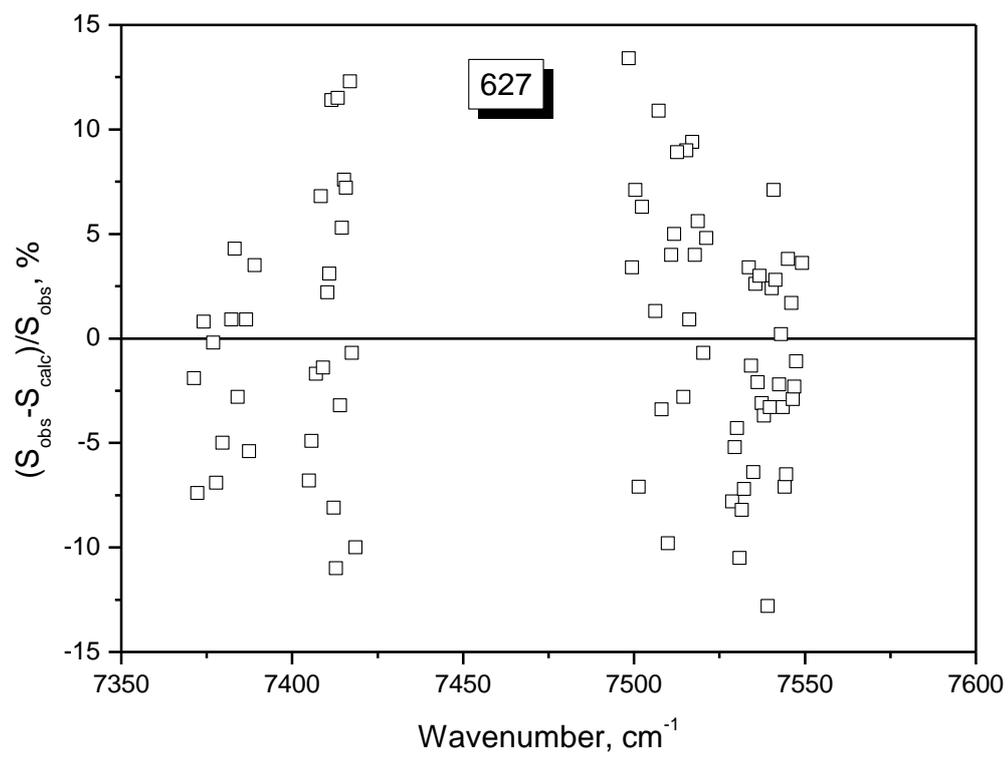


Fig. 2.

