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High sensitivity cavity ring down spectroscopy of N₂O near 1.22 μm: (II) ¹⁴N₂¹⁶O line intensity modeling and global fit of ¹⁴N₂¹⁸O line positions

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ABSTRACT

In a recent work (Karlovets et al., 2016 [1]), we reported the measurement and rovibrational assignments of more than 3300 transitions belonging to 64 bands of five nitrous oxide isotopologues (¹⁴N₂¹⁶O, ¹⁴N¹⁵N¹⁶O, ¹⁵N¹⁴N¹⁶O, ¹⁴N₂¹⁸O and ¹⁴N₂¹⁷O) in the high sensitivity CRDS spectrum recorded in the 7915–8334 cm⁻¹ spectral range. The assignments were performed by comparison with predictions of the effective Hamiltonian models developed for each isotopologue. In the present paper, the large amount of measurements from our previous work mentioned above and literature are gathered to refine the modeling of the nitrous oxide spectrum in two ways: (i) improvement of the intensity modeling for the principal isotopologue, ¹⁴N₂¹⁶O, near 8000 cm⁻¹ from a new fit of the relevant effective dipole moment parameters, (ii) global modeling of ¹⁴N₂¹⁸O line positions from a new fit of the parameters of the global effective Hamiltonian using an exhaustive input dataset collected in the literature in the 12–8231 cm⁻¹ region. The fitted set of 81 parameters allowed reproducing near 5800 measured line positions with an RMS deviation of 0.0016 cm⁻¹. The dimensionless weighted standard deviation of the fit is 1.22. As an illustration of the improvement of the predictive capabilities of the obtained effective Hamiltonian, two new ¹⁴N₂¹⁸O bands could be assigned in the CRDS spectrum in the 7915–8334 cm⁻¹ spectral range. A line list at 296 K has been generated in the 0–10,700 cm⁻¹ range for ¹⁴N₂¹⁸O in natural abundance with a 10⁻³⁰ cm/molecule intensity cutoff.

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1. Introduction

This contribution follows a recent work devoted to the measurement and rovibrational assignments of the high sensitivity absorption spectrum of nitrous oxide recorded

by Cavity Ring Down Spectroscopy (CRDS) between 7915 and 8334 cm⁻¹ [1]. The high sensitivity of the recordings (typical noise equivalent absorption of the spectra on the order of $\alpha_{min} \sim 2 \times 10^{-11}$ cm⁻¹) allowed for the detection of lines with intensities on the order of 5×10^{-29} cm/molecule. The rovibrational assignments of the resulting large number of new observations were performed on the basis of the predictions of the effective Hamiltonian (H^{eff})

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models developed for each isotopologue. Overall, more than 3300 transitions belonging to 64 bands of five isotopologues ($^{14}\text{N}_2^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}_2^{18}\text{O}$ and $^{14}\text{N}_2^{17}\text{O}$) could be assigned.

In the case of the principal isotopologue, $^{14}\text{N}_2^{16}\text{O}$, 41 new bands belonging to the $\Delta P=13$ and $\Delta P=14$ series of transitions were identified (the pseudo quantum number, P , is given by $P=2V_1+V_2+4V_3$ where V_1 , V_2 , and V_3 denote the normal mode vibrational quantum numbers). The comparison of their measured line intensities to the corresponding values predicted with existing sets of the effective dipole moment (D^{eff}) parameters [2] showed important deviations indicating that the $\Delta P=13$ and $\Delta P=14$ D^{eff} parameters have to be improved. In the present paper, we have performed new fittings of the line intensities for the $\Delta P=13$ and $\Delta P=14$ series of transitions using the CRDS line intensities of Ref. [1] and those collected from the literature [2–4].

A second issue evidenced from our analysis of the CRDS spectrum near 8000 cm^{-1} concerns the insufficient quality of the line positions of the $^{14}\text{N}_2^{18}\text{O}$ isotopologue obtained using the available H^{eff} parameters from Ref. [5]. Due to the lack of experimental data, some important parameters were not determined and some predicted line positions deviated by more than 1 cm^{-1} from the CRDS values of Ref. [1]. The inclusion of the line positions of two newly measured $^{14}\text{N}_2^{18}\text{O}$ bands is expected to improve significantly the set of the H^{eff} parameters of this isotopologue. In the present work, we have performed a new fit of the H^{eff} parameters of $^{14}\text{N}_2^{18}\text{O}$ to the line positions collected from the literature including the line positions of these two new bands. The new set of parameters has allowed us to assign two additional $^{14}\text{N}_2^{18}\text{O}$ bands in the CRDS spectrum of Ref. [1]. In the final fit, all four bands assigned in the CRDS spectrum in the $7915\text{--}8334\text{ cm}^{-1}$ spectral range have been involved.

Using this new set of H^{eff} parameters of $^{14}\text{N}_2^{18}\text{O}$, the D^{eff} parameters of this isotopologue were fitted to the measured line intensities for several series of transitions with ΔP up to 14. Finally, the H^{eff} and D^{eff} parameters have been used for the generation of a room temperature line list of the $^{14}\text{N}_2^{18}\text{O}$ isotopologue up to $10,700\text{ cm}^{-1}$.

2. Effective operators approach

The polyad model of H^{eff} has been used for the global modeling of the line positions and intensities of the different isotopologues of the nitrous oxide molecule. The N_2O polyad model was suggested by Pliva [6] and developed by Teffo and Chedin [7]. A reduced model of this Hamiltonian was elaborated by Teffo et al. [8] and extended up to the sixth-order terms by Perevalov et al. [9]. The polyad model of H^{eff} is based on the polyad structure of the N_2O vibrational states resulting from the approximate relations between harmonic frequencies

$$\omega_1 \approx 2\omega_2 \text{ and } \omega_3 \approx 4\omega_2. \quad (1)$$

As a result, the vibrational states are grouped into vibrational polyads corresponding to different pseudo quantum numbers $P=2V_1+V_2+4V_3$. The H^{eff} matrix

elements are calculated in the basis of harmonic oscillator and rigid symmetric top rotor eigenfunctions

$$|V_1V_2l_2V_3J\rangle = |V_1V_2l_2V_3\rangle |JK=l_2\rangle, \quad (2)$$

where J is the total angular momentum quantum number, K is quantum number of the projection of the total angular momentum on the molecular-fixed z -axis, and l_2 is the vibrational angular momentum quantum number. In order to reduce the size of the effective Hamiltonian matrix, Wang-type basis functions are generally used:

$$|V_1V_2l_2V_3J\varepsilon\rangle = \frac{1}{\sqrt{2}} (|V_1V_2l_2V_3\rangle |JK=l_2\rangle + \varepsilon |V_1V_2-l_2V_3\rangle |JK=-l_2\rangle) \quad (l_2 \neq 0), \quad (3a)$$

$$|V_1V_20V_3J\varepsilon=1\rangle = |V_1V_20V_3\rangle |JK=0\rangle \quad (l_2=0), \quad (3b)$$

where $\varepsilon=1$ and -1 correspond to the so-called e and f levels, respectively. In this basis, H^{eff} matrix splits into independent blocks, each block being defined by three labels: P , the Wang parity, $C=\{e, f\}$, and J . Thus, the eigenvalues of H^{eff} can be unambiguously labeled by four labels (P, C, J, i), where i is the ranking index of the eigenvalues in a (P, C, J) block. These labels are called the generalized nomenclature of an energy level.

Our model takes into account explicitly all intrapolyad resonance anharmonic and anharmonic- l -type interactions up to the sixth order of perturbation theory. All Coriolis interactions are interpolyad interactions within the framework of this model. They are assumed to be accounted for by the effective values of the H^{eff} parameters. The detailed presentation of the used effective Hamiltonian together with its matrix elements and notations for the parameters are given in Ref. [9].

In the process of the least-squares fits of $^{14}\text{N}_2^{16}\text{O}$ data [9] and analysis of the experimental spectra [1,3,10–20], several interpolyad resonance Coriolis and anharmonic perturbations were evidenced. An analysis of these interactions showed that they become pronounced for high-excited vibrational states and affect rather weak bands. Perturbed lines affected by these interactions were removed from the input data file. The polyad model was found to be accurate for the majority of non-weak measured $^{14}\text{N}_2^{16}\text{O}$ bands in the $0\text{--}9700\text{ cm}^{-1}$ range [9], i.e. for the bands with line intensities larger than $10^{-26}\text{ cm/molecule}$ at 296 K . Line intensities can be calculated using the eigenfunctions of the effective Hamiltonian but, for this purpose, it is necessary to use an effective dipole moment operator instead of a dipole moment operator. The former is obtained from the dipole moment operator by the same unitary transformation as the effective Hamiltonian from the vibration-rotation Hamiltonian. This approach is presented in Refs. [21,22]. Within the framework of polyad model, all vibrational bands are distributed among different series of transitions, each series corresponding to a different variation of the polyad number, $\Delta P=P'-P''$, where P' and P'' are the polyad numbers of upper and lower states, respectively. Consequently, for each ΔP series, a set of effective dipole moment parameters has to be determined from a fit of the available experimental line intensities.

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