High sensitivity Cavity Ring Down spectroscopy of NO_2 between 7760 and 7917 cm^{-1}

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The very weak absorption spectrum of the main isotopologue of nitrogen dioxide, $^{14}N^{16}O_2$, is investigated for the first time between 7760 and 7917 cm^{-1}. The studied region corresponds to the highest energy range of the vibrational spectra of $^{14}N^{16}O_2$ investigated so far at high spectral resolution. The absorption spectra were recorded by very high sensitivity Continuous Wave-Cavity Ring Down Spectroscopy with a noise equivalent absorption of $\alpha_{min} \approx 5\times10^{-11}$ cm^{-1}. The spectrum results from the superposition of the rovibrational transitions of the $2\nu_1+5\nu_2+\nu_3$, $2\nu_1+\nu_2+3\nu_3$ and $5\nu_1+\nu_3$ bands at 7790.9, 7888.2 and 7904.3 cm^{-1}, respectively. The spectrum assignment and modeling were performed using the effective Hamiltonian approach, which involves, during the upper energy-level calculation, altogether three bright -(2,5,1), (2,1,3) and (5,0,1)- and three dark -(2,7,0), (2,3,2) and (5,2,0)- states. As a result, 3020 rovibrational transitions were assigned including 51 extra lines of the $2\nu_1+3\nu_2+2\nu_3$ and $5\nu_1+2\nu_2$ bands. In this way, the overall set of 1494 spin-rotation energy levels were reproduced with an *rms* of 4.9×10^{-3} cm^{-1} for the (obs.-calc) deviations, leading to the determination of 66 fitted parameters. The effective Hamiltonian for the {(5,2,0), (2,3,2), (2,7,0), (2,5,1), (2,1,3), (5,0,1)} interacting states takes into account both the spin-rotation interactions within each vibrational state and C-type Coriolis and anharmonic resonances between different vibrational states, according to symmetry considerations. Indeed for NO_2 the $(v_1, v_2 \pm 2, v_3 \mp 1) \leftrightarrow (v_1, v_2, v_3)$ spin rotation energy levels are usually coupled through C-type Coriolis resonances, and accordingly the (2,7,0) ↔ (2,5,1) ↔ (2,3,2) ↔ (2,1,3) and (5,2,0) ↔ (5,0,1) interactions were included in the effective Hamiltonian model. Furthermore, these two blocks of interacting states are coupled by additional C-type Coriolis and anharmonic resonances. Using the fitted values of the Hamiltonian parameters and the values of the $2\nu_1+5\nu_2+\nu_3$, $2\nu_1+\nu_2+3\nu_3$ and $5\nu_1+\nu_3$ bands transition dipole moment operators determined from a fit of a selected set of experimental line intensities, a synthetic spectrum was generated for the entire investigated region.

This work is supported by the Laboratoire International Associé SAMIA between CNRS (France) and RFBR (Russia).