

HIGH SENSITIVITY INTRACAVITY ABSORPTION SPECTROSCOPY OF JET COOLED MOLECULES : THE VISIBLE SPECTRUM OF NO₂ AND (O₂)₂

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We have combined the high sensitivity of the Intracavity Laser Absorption Spectroscopy (ICLAS) with the rotational cooling of a jet expansion. By inserting a 24 cm long slit jet expansion in a dye or Ti:Sapphire laser cavity, an equivalent absorption pathlength of more than 5 km through molecules rotationally cooled at about 15°K has been achieved. By this method, the thermally congested molecular spectra are drastically simplified and analysis becomes possible. We will present the results obtained with this set up on NO₂ and oxygen dimer (O₂)₂.

NO₂

Due to a conical intersection between the X²A₁ state and the first excited state A²B₂ located at about 10000 cm⁻¹, the near infrared and visible absorption spectrum corresponds to the superposition of many vibronic bands which strongly resists rotational and vibrational analysis at room temperature. We have recorded the rotationally cooled absorption spectrum of NO₂ from 11200 to 16150 cm⁻¹ which corresponds to the intermediate range between the regular range (up to 10000 cm⁻¹) and the chaotic range (above 17000 cm⁻¹) which shows clearly a chaotic character. 249²B₂ vibronic bands have been observed among which 175 are cold bands and 74 hot bands. They correspond to 65 % of the total number of levels calculated in the studied range. The correlation properties of this set of levels have been analysed by calculating the power spectrum of the absorption stick spectrum and the Next Neighbor Spacing Distribution.

(O₂)₂

The open-shell (triplet) character of the O₂ molecule makes the (O₂)₂ dimer one of the most interesting Van der Waals molecules. The (O₂)₂ dimer is also an important minor atmospheric compound whose structure is not clearly understood. Two unresolved broad absorption bands have been previously reported : the ¹Δ_g (v = 0) + ¹Δ_g (v = 0) ← ³Σ_g⁻ (v = 0) centered at 629 nm and the ¹Δ_g (v = 0) + ¹Δ_g (v = 1) ← ³Σ_g⁻ (v = 0) centered at 578 nm (only a vibrational analysis has been proposed for this band twenty years ago [1]). We have recorded the corresponding absorption spectrum of the rotationally cooled (O₂)₂ formed in our slit jet expansion. A rotationally resolved structure is observed for both bands and its simulation using spectroscopic constants derived from ab initio calculations is in progress. These two bands seem to arise from electric dipole allowed transitions between the electronic states of the dimer. Indeed two electronic states may be involved and the related well depths were calculated to be about 150 cm⁻¹ in the ground level and 120 cm⁻¹ in the excited one.

RECENT RESULTS IN THE 3.2 μm 4.2 μm and 6.2 μm
BANDS OF NITROGEN DIOXIDE

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The 6.2 μm band of nitrogen dioxide is the strongest infrared band of this molecule. Then it is important, for atmospheric purposes, to get high quality parameters not only for the (main) ν_3 band¹, but also for the hot bands namely the $\{3\nu_2, \nu_2 + \nu_3\} - \nu_2$ and the $\{2\nu_2 + \nu_3, 4\nu_2, 2\nu_3\} - \{\nu_1, 2\nu_2, \nu_3\}$ bands which appears clearly in the low frequency range of the 6.2 μm band.

Using new Fourier transform spectra recorded at Brussels and at Paris, it has been possible to perform a new analysis of the $\{3\nu_2, \nu_2 + \nu_3\}$, $\{2\nu_2 + \nu_3, 4\nu_2, 2\nu_3\}$ and $\{3\nu_2, \nu_2 + \nu_3\} - \nu_2$ bands of $^{14}\text{N}^{16}\text{O}_2$, located at 4.2 μm , 3.2 μm and 6.2 μm respectively. From the spin-rotation levels of the upper vibrational states obtained from these analyses, a set of molecular parameters (vibrational band centers, rotational, spin-rotation and coupling constants) for the $\{(030), (011)\}$ and $\{(002), (021), (040)\}$ interacting states has been determined using a Hamiltonian matrix which takes explicitly into account both the $(\nu_1, \nu_2 \pm 2, \nu_3 \mp 1) \leftrightarrow (\nu_1, \nu_2, \nu_3)$ Coriolis type interactions and the spin-rotation resonances. Finally, synthetic spectra were generated for NO_2 at 6.2 μm , including in the linelist the contribution from the hot bands.

Financial support from the European Community under contract EV5V-CT92-0076 is gratefully acknowledged.

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Mol. Spectrosc. 154 391-406 (1992).

INFRARED HIGH RESOLUTION SPECTRA OF OZONE
 IN THE 4.3 - 3.8 μ .
 LINE POSITIONS AND INTENSITIES OF $\nu_1+2\nu_2$ AND $\nu_3+2\nu_2$
 $3\nu_3-\nu_2$ AND $\nu_1+2\nu_3-\nu_2$ BANDS

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The spectra of ozone in the range 2300-2600 cm^{-1} have been recorded with the high resolution Fourier Transform Spectrometer of Reims. A White cell with a length of 36 m and pressure of 50 Torr has been used. This region correspond mainly to the weak bands $\nu_1+2\nu_2$ and $2\nu_2+\nu_3$, which were previously analysed with much lower amount of ozone. Then high values of J and K_a have been observed up to 55 and 11 respectively. The final fit on the 615 energy levels is very satisfactorily : $0.39 \cdot 10^{-3} \text{ cm}^{-1}$, equal to experimental accuracy. Good agreement is also obtained for line intensities.

Furthermore the two hot bands $3\nu_3-\nu_2$ and $\nu_1+2\nu_3-\nu_1$ have been observed for the first time and transition moment constants are given.

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