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J.-M. Flaud, A. Anantharajah, F. Kwabia Tchana, L. Manceron, J. Orphal, et al.. High-resolution analysis of the  $12.6 \mu\text{m}$  spectral region of the nitryl chloride  $\text{ClNO}_2$  molecule. *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2019, 224, pp.217-221. 10.1016/j.jqsrt.2018.11.020 . hal-02340412

**HAL Id: hal-02340412**

**<https://hal.science/hal-02340412v1>**

Submitted on 30 Oct 2019

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# High-resolution analysis of the 12.6 $\mu\text{m}$ spectral region of the nitryl chloride $\text{ClNO}_2$ molecule

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Nb of Figures : 6

Nb of Tables : 4

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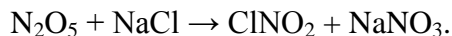
**Abstract**

The 12.6  $\mu\text{m}$  region of nitryl chloride ( $\text{ClNO}_2$ ) has been recorded at high resolution ( $0.00102\text{ cm}^{-1}$ ) using a Fourier transform spectrometer and the SOLEIL synchrotron light source.  $\text{ClNO}_2$  was found during our studies of chlorine nitrate and, after fractional distillations it was introduced into a multipass White cell made of inert materials, with an optical path length of 5.4 m. 320 scans were recorded for the range  $600\text{--}980\text{ cm}^{-1}$  at a total pressure of 0.23 hPa and a temperature of 250 K. A thorough analysis of the  $\nu_2$ ,  $2\nu_6$  and  $2\nu_3$  bands of  $^{35}\text{ClNO}_2$  and of the  $\nu_2$  band of  $^{37}\text{ClNO}_2$  falling in this region has been carried out using a Hamiltonian model which takes explicitly into account the numerous resonances affecting the ro-vibrational energy levels; especially the C-type Coriolis resonance between the  $\nu_2$  and the  $\nu_3 + \nu_6$  modes. These two modes are only separated by less than  $20\text{ cm}^{-1}$  and are thoroughly mixed. From the fittings, the following band centers were derived:  $\nu_0(\nu_2) = 792.761264(60)\text{ cm}^{-1}$ ,  $\nu_0(\nu_3 + \nu_6) = 775.8923(20)\text{ cm}^{-1}$ ,  $\nu_0(2\nu_3) = 734.183576(20)\text{ cm}^{-1}$  and  $\nu_0(2\nu_6) = 819.836727(90)\text{ cm}^{-1}$  for  $^{35}\text{ClNO}_2$  and  $\nu_0(\nu_2) = 792.258284(30)\text{ cm}^{-1}$  and  $\nu_0(\nu_3 + \nu_6) = 774.6826(30)\text{ cm}^{-1}$  for  $^{37}\text{ClNO}_2$  where the uncertainties are one standard deviation. Due to their sharp  $Q$  branches falling into an atmospheric “window”, the detection of the  $\nu_2$  bands might be an advantageous route for future attempts to quantify atmospheric  $\text{ClNO}_2$ , using infrared techniques.

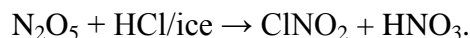
**Keywords:** nitryl chloride;  $\text{ClNO}_2$ ; high-resolution Fourier transform spectroscopy; Coriolis and Fermi resonances; line positions

## I. Introduction

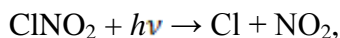
Nitryl chloride (ClNO<sub>2</sub>) is a molecule of great interest for atmospheric chemistry since it is produced in the marine troposphere, by heterogeneous reactions between NaCl sea-salt aerosols and gaseous N<sub>2</sub>O<sub>5</sub> [1,2]:



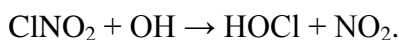
Alternatively, it is produced on polar stratospheric clouds, between N<sub>2</sub>O<sub>5</sub> and solid HCl [3,4]:



Through these reactions, ClNO<sub>2</sub>, a fairly stable molecule, is accumulated during nighttime but after sunrise, it is rapidly destroyed either by photolysis ( $\lambda > 290$  nm):



or by reaction with OH radicals [5]:



As oxidation slowly removes ClNO<sub>2</sub> [6-7], photolysis is thus contributing predominantly to the loss process of ClNO<sub>2</sub>. Moreover, by yielding active chlorine radicals and nitrogen dioxide, this reaction subsequently initiates VOCs oxidation by chlorine radicals and photolysis of NO<sub>2</sub>, both leading to the photochemical production of tropospheric ozone, as well as to stratospheric ozone depletion.

The important contribution of ClNO<sub>2</sub> in atmospheric chemistry triggered since 2006 *in situ* ground-based and aircraft measurements using chemical ionization mass spectrometry, indicating also additional continental sources of chlorine [8]. But, to the best of our knowledge, until today, there was not even a tentative detection of this atmospheric gas using infrared techniques like Fourier transform spectroscopy. In this case, the Q branch of the  $\nu_2$  band at 792.8 cm<sup>-1</sup> could be suitable for the remote sensing of ClNO<sub>2</sub> due to its strong absorption in an atmospheric “window”, similarly to the use of the 780.2 cm<sup>-1</sup> band feature for the monitoring of ClONO<sub>2</sub> in the stratosphere [9-11]. For this purpose, a complete and detailed analysis is required to provide accurate line list for atmospheric remote sensing.

ClNO<sub>2</sub> has been the subject of a number of microwave and infrared high resolution studies [12-17 and refs herein]. In this paper we present a comprehensive analysis of a very high resolution Fourier transform spectrum of nitryl chloride, taken at 0.00102 cm<sup>-1</sup> resolution (0.9/MOPD) in the 12.6  $\mu\text{m}$  spectral region using the SOLEIL synchrotron radiation. A thorough

analysis of the strongest absorbing bands  $\nu_2$  of the two isotopologues  $^{35}\text{ClNO}_2$  and  $^{37}\text{ClNO}_2$  was performed taking into account the interactions with the nearby states  $3^16^1$  and  $6^2$ . Also the very weak bands  $2\nu_3$  and  $2\nu_6$  were fully analyzed.

## II. Experimental details.

At DLR samples of bromine nitrate ( $\text{BrONO}_2$ ) were produced together with the precursor chlorine nitrate ( $\text{ClONO}_2$ ) [18]. Experimental details on the  $\text{ClONO}_2$  synthesis can be found in [19]. In the sample of  $\text{ClONO}_2$ , the original target of our work, we found a second product that showed characteristic infrared absorption features indicating a  $\text{NO}_2$  group. After fractional distillations at  $-84^\circ\text{C}$  and  $-77^\circ\text{C}$ , only  $\text{ClNO}_2$  and small traces of impurities ( $\text{NO}_2$  and  $\text{ClONO}_2$ ) were seen in the spectrum. The sample was stored at 77 K in the dark, and  $\text{ClNO}_2$  was identified by its low resolution infrared absorption spectrum [20].

A high-resolution absorption spectrum of  $\text{ClNO}_2$  was then recorded on the AILES beamline at Synchrotron SOLEIL using the synchrotron light source, coupled to the Bruker IFS125HR Fourier transform spectrometer [21, 22] and a newly developed cryogenic multipass cell suitable for corrosive products, in which the sample gas is exclusively in contact with glass, PTFE and hard alumina-coated optics and can be cooled down to 220 K [23]. The interferometer was equipped with a KBr/Ge beamsplitter. The synchrotron source was operated with 500 mA ring current and a new home-made detector developed at the AILES beamline [24] was used in conjunction with a  $600\text{--}980\text{ cm}^{-1}$  bandpass optical filter, to improve the signal-to-noise ratio (S/N). The spectrometer was evacuated to about  $5\times 10^{-3}$  Pa in order to minimize  $\text{H}_2\text{O}$  and  $\text{CO}_2$  absorptions. The diameter of the entrance aperture of the spectrometer was set to 1.5 mm to maximize the intensity of infrared radiation falling onto the detector without saturation or loss of spectral resolution. Interferograms were recorded with a 80 kHz scanner frequency and a maximum optical path difference (MOPD) of 882.35 cm. According to the Bruker definition (resolution =  $0.9/\text{MOPD}$ ), this corresponds to a resolution of  $0.00102\text{ cm}^{-1}$ .

The cell optical set-up is based on a 0.67 m base length and, in this experiment, an optical path of 5.4 m was used. The spectrum was recorded at a temperature of 250 K. The following procedure was used for measurements: first a background spectrum was recorded at the same temperature of 250 K while the cell was being continuously evacuated; next the infrared gas cell

was filled and passivated with ClNO<sub>2</sub> vapour and, for the final measurement, a sample pressure of 0.23 hPa was used. The sample pressure in the cell was measured using a home made PTFE-coated capacitive pressure sensor [23] calibrated against a MKS Baratron gauge (10 hPa full scale). The spectrum was ratioed against a background spectrum of the empty cell which was recorded at a resolution of 0.01 cm<sup>-1</sup> in order to ensure the best possible S/N in the ratioed spectrum. For the Fourier transform, a Mertz-phase correction with a 2 cm<sup>-1</sup> phase resolution, a zero-filling factor of 4 and no apodization (boxcar option) were applied to the averaged interferograms (320 scans). The spectrum was calibrated by matching the measured positions of about 30 lines of residual CO<sub>2</sub> observed therein to reference wavenumbers available in HITRAN [25] with a root mean square (RMS) deviation of 0.00006 cm<sup>-1</sup>.

Fig. 1 gives an overview of the ClNO<sub>2</sub> spectrum around 12.6 μm showing the high S/N ratio which was obtained. The distinctive shape of the A-type ν<sub>2</sub> band with its narrow Q-branch is clearly visible. Also the very weak bands 2ν<sub>6</sub> and 2ν<sub>3</sub> are visible.

### III. Analysis and results

ClNO<sub>2</sub> is belonging to C<sub>2v</sub> symmetry and Fig. 2 provides the corresponding C<sub>2v</sub> point group together with the symmetry types of the 6 vibrational modes as well as the components of an axial and a polar vector and the symmetry types and statistical weights of the rotational levels. Indeed, because there are two identical oxygen nuclei with zero nuclear spin, the overall wavefunction of the molecule should obey the Bose-Einstein statistics. Accordingly, all vibration-rotation wavefunctions must have even parity with respect to the axis of the molecule. As a consequence, only rotational levels with K<sub>a</sub> even exist for states of A<sub>1</sub> or A<sub>2</sub> symmetry (the ground, 2<sup>1</sup>, 3<sup>2</sup>, and 6<sup>2</sup> states of the molecule in the present case). On the contrary, only rotational levels with K<sub>a</sub> odd exist for states of B<sub>1</sub> or B<sub>2</sub> symmetry (3<sup>1</sup>6<sup>1</sup> vibrational state).

The ν<sub>2</sub> band of <sup>35</sup>ClNO<sub>2</sub> has been previously studied in ref. [15, 16] where the authors noted an interaction between the rotational levels of 2<sup>1</sup> and the rotational levels of 3<sup>1</sup>6<sup>1</sup> but did not take it into account. In addition, their spectrum was recorded at medium resolution (0.005 cm<sup>-1</sup>), with a pressure of 10 Torr, resulting in a rotational structure that was not fully resolved. The analysis was started using the upper state rotational constants of the 2<sup>1</sup> vibrational state given in ref. [16]. In this way it was possible to assign levels not or weakly perturbed. However, it appeared rapidly that such a model was not suitable to fit the upper state levels to within the

experimental uncertainty. We then set up and used a Hamiltonian model taking into account the C-type Coriolis interaction between the rotational levels of  $2^1$  and the rotational levels of  $3^16^1$ . In this way it was possible to assign a rather large number of lines by iterating between calculation and observation: more precisely new assignments allow one to improve the upper state Hamiltonian constants, which are then used to provide better predictions. However it turned out that such a Hamiltonian model was still not fully suitable and that one has also to take into account the Fermi-type interaction between the rotational levels of  $2^1$  and the rotational levels of  $6^2$ . The final Hamiltonian matrix used to fit the  $2^1$  and  $6^2$  rotational levels is given in Table 1. At this stage it is indeed worth noticing that we had to assign in parallel the very weak  $2\nu_6$  band which appears on the experimental spectrum (see Fig. 1). Table 2 gives the range of quantum numbers for the observed upper state energy levels obtained by adding the observed line positions to the calculated ground state levels as well as the statistical analysis of the results of the energy level calculations, whereas the upper state Hamiltonian constants derived from the final fit are given in Table 3.

The analysis of the  $\nu_2$  band of  $^{37}\text{ClNO}_2$  was started by using the same Hamiltonian model as for the  $\nu_2$  band of  $^{35}\text{ClNO}_2$  and upper state Hamiltonian constants derived from the corresponding upper state constants of  $^{35}\text{ClNO}_2$ . In this way, it was possible to locate lines with medium J and  $K_a$  values. These lines were used to improve the upper state constants, providing then better predictions and hence allowing new assignments. The process was repeated until no new assignment was possible.

Table 2 gives the range of quantum numbers for the observed upper state energy levels as well as the statistical analysis of the results of the energy level calculations, whereas the upper state Hamiltonian constants derived from the final fit are given in Table 4. It is worth noticing that given the range of observed energy levels it was not necessary to account for the interaction with the  $6^2$  levels. The assignment of the  $2\nu_3$  band was done by using, for the  $3^2$  state, Hamiltonian constants extrapolated from the ground and  $3^1$  states [16]. In fact, the assignments started by improving the modeling of the Q-branch. The upper state levels were reproduced using a Watson type Hamiltonian [27] since no interaction was detected. The range of quantum numbers for the observed upper state energy levels, as well as the statistical analysis of the results of the energy level calculations, are given in Table 2 whereas the upper state Hamiltonian constants derived from the final fit are given in Table 3. It should be underlined that the upper state Hamiltonian

parameters determined in the fits are effective and have some empirical character, since the values of these parameters depend on the set and the accuracy of the observed energy levels, as well as on the number of terms in the expansions of the interacting terms.

#### IV. Simulation of the experimental spectrum.

To emphasize the quality of the calculations, we have compared the observed and calculated spectra in a few spectral regions. Fig. 3 shows that the entire region of the  $\nu_2$  bands of the 2 isotopologues  $^{35}\text{ClNO}_2$  and  $^{37}\text{ClNO}_2$  is adequately simulated. In Figs. 4-6 we present a comparison between observation and calculation for the Q-branches of the  $\nu_2$  band of  $^{37}\text{ClNO}_2$  and of the  $2\nu_6$  and  $2\nu_3$  bands of  $^{35}\text{ClNO}_2$ . Indeed, modeling properly such Q branches is the most difficult part of the work, given the piling of lines and the high J lines involved. It is also interesting to notice the very different shapes of these Q-branches. In all cases excellent agreement between the observed and calculated spectrum is achieved.

#### VI. Conclusion.

A high-resolution Fourier transform spectrum of the 12.6  $\mu\text{m}$  absorption bands of the nitril chloride  $\text{ClNO}_2$  molecule has been thoroughly analyzed. The energy levels belonging to the interacting upper states  $\{2^1, 3^16^1, 6^2\}$  of  $^{35}\text{ClNO}_2$  were fitted using a Hamiltonian matrix accounting for the C-type Coriolis interaction between the  $2^1$  and  $3^16^1$  levels and the Fermi-type interaction between the  $2^1$  and  $6^2$  levels. For  $^{37}\text{ClNO}_2$  it was sufficient to fit properly the  $2^1$  rotational levels to take into account the C-type Coriolis interaction between the  $2^1$  and  $3^16^1$  levels. Finally it was possible to model properly the rotational levels of the  $3^2$  state using a single Watson type Hamiltonian. The synthetic line list obtained in this study is potentially interesting for future measurements of  $\text{ClNO}_2$  in the atmosphere.



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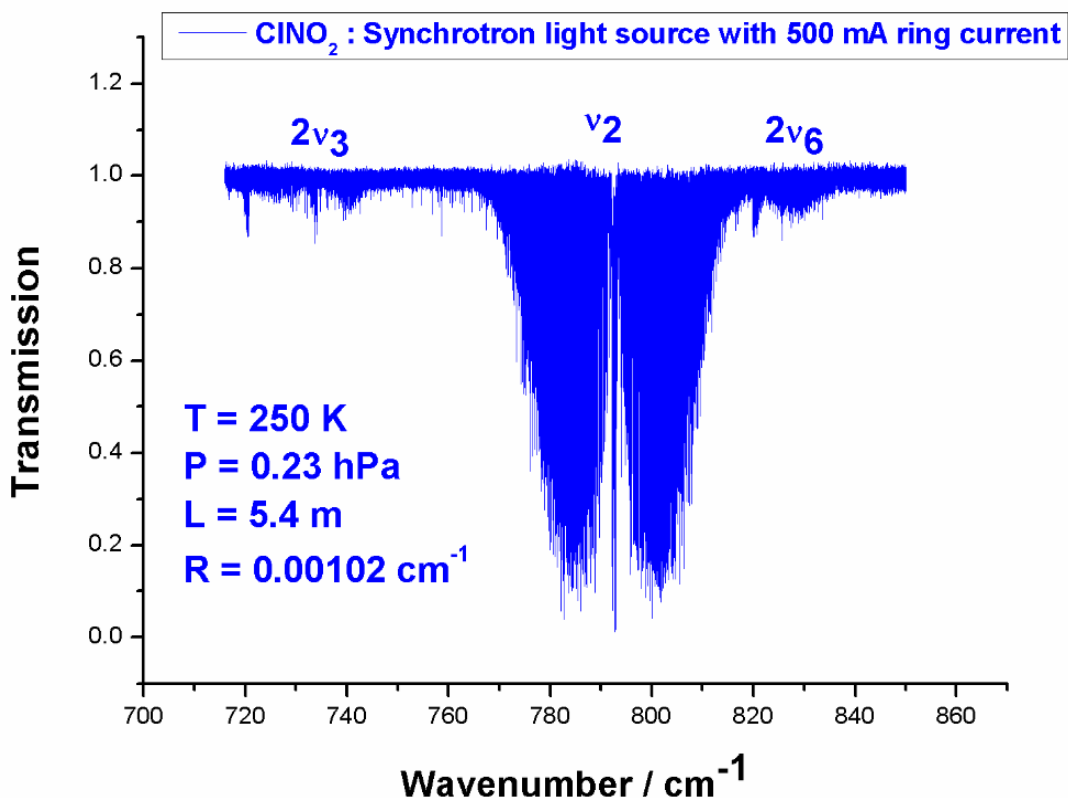
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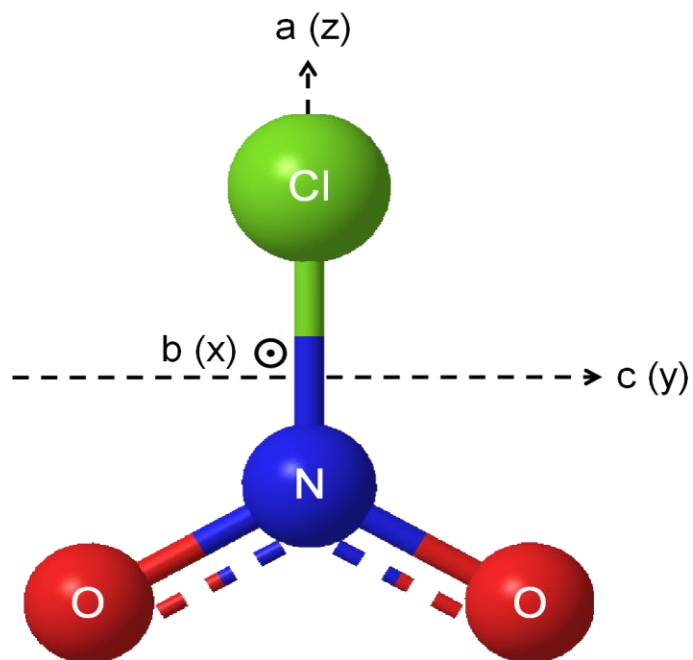
### Figures:

**Fig. 1.** Overview of the observed  $\text{ClNO}_2$  spectrum in the  $12.6 \mu\text{m}$  spectral region.

The distinctive shape of the A-type  $\nu_2$  band of  $^{35}\text{ClNO}_2$  with its narrow Q-branch is clearly recognizable. The spectrum is recorded with a resolution of  $0.00102 \text{ cm}^{-1}$ , an optical path length of  $5.4 \text{ m}$ , a nitryl chloride pressure of  $0.23 \text{ hPa}$  and a temperature of  $250 \text{ K}$ .



**Fig. 2.** Structure and symmetry properties of the nitryl chloride (ClNO<sub>2</sub>) molecule

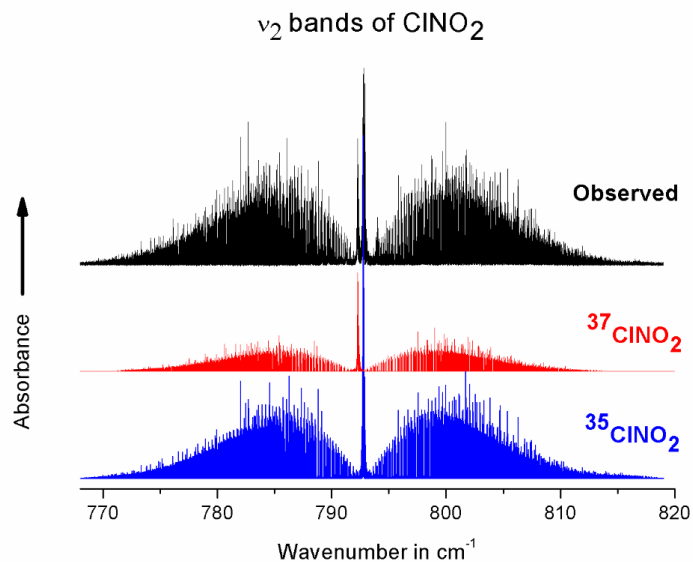


$C_{2v}$  group character table

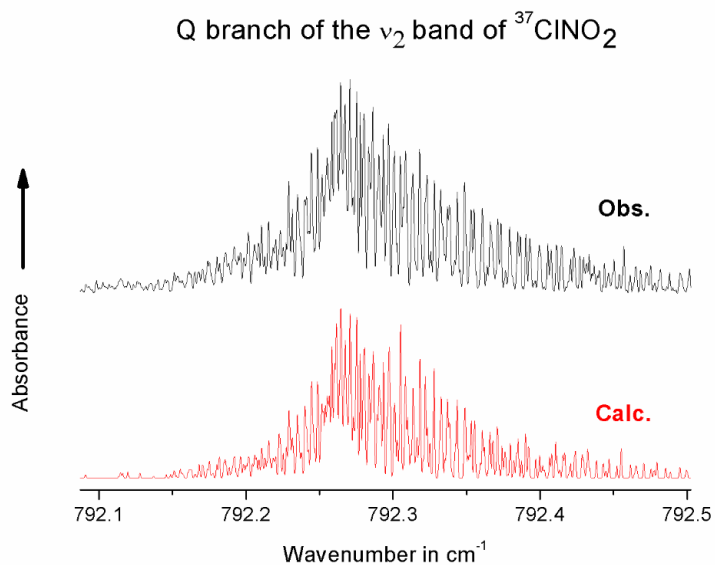
	I	$C_{2z}$	$\sigma_{xz}$	$\sigma_{yz}$	Polar vector	Axial vector	Vibrations	Levels
$A_1$	1	1	1	1	$T_z$		$\nu_1, \nu_2, \nu_3$	Even $K_a$
$A_2$	1	1	-1	-1		$R_z$		Even $K_a$
$B_1$	1	-1	1	-1	$T_x$	$R_y$	$\nu_4$	Odd $K_a$
$B_2$	1	-1	-1	1	$T_y$	$R_x$	$\nu_5, \nu_6$	Odd $K_a$

**Fig. 3.** Overview of the observed and calculated spectrum of  $\text{ClNO}_2$  in the  $12.6 \mu\text{m}$  spectral region.

Upper trace: observed spectrum with the same experimental conditions as in Fig. 1. Lower traces: synthetic spectra, calculated at the same experimental conditions using the line lists generated in this work. The observed and synthetic spectra are in absorbance ( $-\ln(I/I_0)$ ) and shifted vertically for clarity.

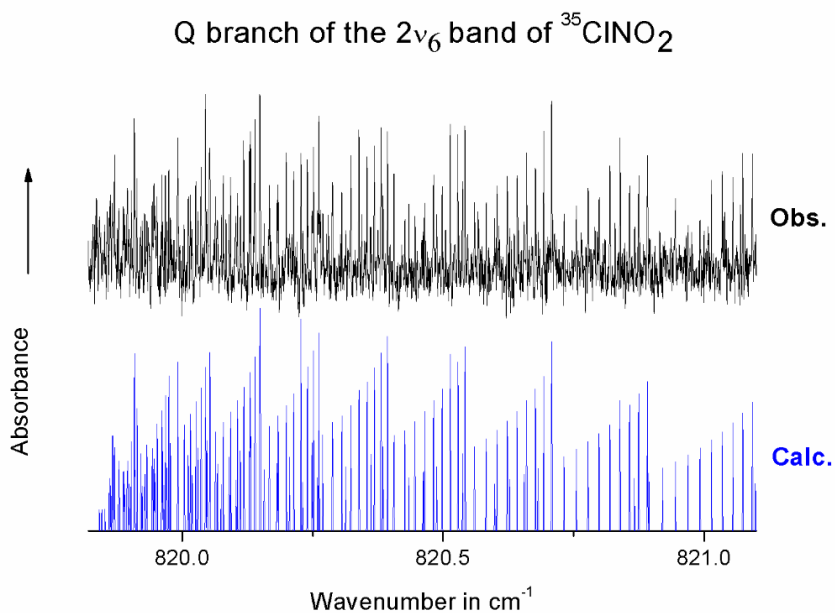


**Fig. 4.** Portion of the observed and calculated spectra of  $^{37}\text{ClNO}_2$ , showing the region of the  $Q$  branch of the  $\nu_2$  fundamental band. Upper trace: observed spectrum with the same experimental conditions as in Fig. 1. Lower trace: synthetic spectrum calculated as in Fig. 3.



**Fig. 5.** Portion of the observed and calculated spectra of  $^{35}\text{ClNO}_2$ , showing the region of the  $Q$  branch of the  $2\nu_6$  overtone band.

Upper trace: observed spectrum with the same experimental conditions as in Fig. 1. Lower trace: synthetic spectrum calculated as in Fig. 3.



**Fig. 6.** Portion of the observed and calculated spectra of  $^{35}\text{ClNO}_2$ , showing the region of the  $Q$  branch of the  $2\nu_3$  overtone band. Upper trace: observed spectrum with the same experimental conditions as in Fig. 1. Lower trace: synthetic spectrum calculated as in Fig. 3.

