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## Rotational analysis of $6\nu_3$ and $6\nu_3+\nu_2-\nu_2$ bands of $^{14}\text{N}_2$ $^{16}\text{O}$ from ICLAS spectra between 12760 and 12900 $\text{cm}^{-1}$ .

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### Research highlights

A very weak  $6\nu_3$  band of  $\text{N}_2\text{O}$  has been recorded by ICLAS between 12760 and 12900  $\text{cm}^{-1}$ .

The rotational analysis led to an improved determination of the rovibrational parameters.

The main effective dipole moment parameter has been determined from the absolute intensities values.

# Rotational analysis of $6\nu_3$ and $6\nu_3+\nu_2-\nu_2$ bands of $^{14}\text{N}_2^{16}\text{O}$ from ICLAS spectra between 12760 and 12900 $\text{cm}^{-1}$ .

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## *Abstract*

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The absorption spectrum of nitrous oxide ( $\text{N}_2\text{O}$ ) has been recorded by Intracavity Laser Absorption Spectroscopy between 12760 and 12900  $\text{cm}^{-1}$ . The rotational analysis led to an improved determination of the rovibrational parameters of the  $6\nu_3$  and  $6\nu_3+\nu_2-\nu_2$  bands of  $^{14}\text{N}_2^{16}\text{O}$ . The high  $J$  rotational levels of the  $(00^0_6)$  and  $(01^1_6)$  upper states were found perturbed by an anharmonic interaction. Line intensity values of the  $6\nu_3$  band are provided and the main effective dipole moment parameter has been determined.

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**Key words:** Nitrous oxide,  $\text{N}_2\text{O}$ , ICLAS, effective Hamiltonian

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## 1. Introduction

Fifteen years ago, we used Intracavity Laser Absorption Spectroscopy (ICLAS) to detect and analyze the high energy overtone bands of nitrous oxide between 11500 and 15000  $\text{cm}^{-1}$  [1,2]. This work extended and improved the results obtained in 1950 by Herzberg and Herzberg using absorbing path $\times$ pressure values up to 4500 m atm, corresponding to 200 transversals through a 22 m long cell [3]. To the best of our knowledge, the spectroscopy of the seven  $^{14}\text{N}_2^{16}\text{O}$  bands reported by ICLAS above 11000  $\text{cm}^{-1}$  was not revisited up to now. The present Note is devoted to an improved analysis of the  $6\nu_3$  band near 12891  $\text{cm}^{-1}$ , on the basis of higher quality ICLAS recordings. Absolute line intensities are reported allowing for the derivation of the main parameter of the effective dipole moment. Note that the same  $6\nu_3$  band of the  $^{15}\text{N}$  substituted  $\text{N}_2\text{O}$  isotopologues was very recently studied by Cavity Ring Down Spectroscopy [4].

## 2. Experimental details and line list construction

The  $\text{N}_2\text{O}$  spectra were recorded by Intracavity Laser Absorption Spectroscopy (ICLAS) between 12760 and 12900  $\text{cm}^{-1}$ . Our ICLAS spectrometer is based on a Ti:Sapphire laser and has been described in Refs. [5-7]. Each 12  $\text{cm}^{-1}$  wide portion of the spectrum was recorded with a 3754 silicon diode array placed in the focal plane of the grating spectrograph. In ICLAS, the absorption equivalent path length is determined by the generation time,  $t_g$  [8]:

$$L_{eq} = ct_g \frac{l}{L} \quad (1)$$

where  $c$  is the speed of light, and  $l$  and  $L$  the length of the absorption cell (65 cm) and of the laser cavity (155 cm), respectively. Consequently, similarly to classical absorption, ICLAS-Ti:Sa allows for quantitative measurements of absolute line intensities [2,5,8,9].

Our recordings were performed with a generation time of 190  $\mu\text{s}$  which corresponds to an absorption equivalent path length of 24 km (Eq. 1). The cell was filled with  $\text{N}_2\text{O}$  at pressure values up to 75 Torr. Since the cell fills only 42% of the laser cavity, the atmospheric intracavity absorption spectrum appeared superimposed to the  $\text{N}_2\text{O}$  spectrum and in some cases atmospheric lines (oxygen A band and  $\text{H}_2\text{O}$ ) obscure  $\text{N}_2\text{O}$  lines. To suppress the atmospheric contribution, two spectra were recorded for the same spectral region. The first one contained atmospheric lines as well as  $\text{N}_2\text{O}$  lines. Then a second spectrum was recorded with the empty cell. The  $\text{N}_2\text{O}$  spectrum was obtained by division of the first spectrum by the second one.

Reference lines are needed to calibrate the frequency scale of the ICLAS spectra. In Ref. [1], very high rotational transitions of the P branch of the A band of atmospheric oxygen

centered at  $13122\text{ cm}^{-1}$ , were used to calibrate the  $6\nu_3$  band. The quality of the  $\text{O}_2$  line positions as provided in the 1992 version of the HITRAN database was uncertain as the provided values were extrapolated values. To avoid similar problems, in the present experiments we recorded for each spectral window an ICLAS spectrum of low pressure water vapor following the same procedure than for  $\text{N}_2\text{O}$ . Note that additional uncertainties were due to the fact that, in Ref.[1], the  $\text{O}_2$  atmospheric lines were pressure broadened which hampered an accurate line center determination. The  $\text{N}_2\text{O}$  lines were broadened due to the high pressure values (up to 441 Torr) used in Refs. [1,2].

The wavenumber calibration of each individual spectrum was performed in two steps: (i) correction of the non linear dispersion of the grating spectrograph by using the sharp peaks provided by an intracavity étalon and (ii) use of the  $\text{H}_2\text{O}$  reference lines to accurately calibrate the wavenumber scale. The  $\text{H}_2\text{O}$  reference lines were taken from HITRAN [10]. By comparison of the  $\text{N}_2\text{O}$  line positions retrieved from various spectra, we estimated to  $0.01\text{ cm}^{-1}$  the maximum uncertainty for the well isolated lines.

Fig. 1 shows an overview of the ICLAS absorption spectrum of the  $6\nu_3$  band of  $\text{N}_2\text{O}$  obtained by gathering 10 successive  $12\text{ cm}^{-1}$  wide spectral windows.

The line centres and line intensities were determined by using an interactive least square multi-line fitting program assuming a Voigt profile for each line (Fig. 2). The measured line width ( $\text{FWHM} = 0.055\text{ cm}^{-1}$ ) is larger than the Doppler broadening ( $\text{FWHM} = 0.022\text{ cm}^{-1}$ ). The additional contribution is a combined effect of the apparatus function and of the collisional broadening.

95 and 50 lines were measured for the  $6\nu_3$  cold band and  $6\nu_3+\nu_2-\nu_2$  hot band of the  $^{14}\text{N}_2^{16}\text{O}$  isotopologue, respectively. The corresponding values in Ref. [1] were 74 and 37 illustrating the gain in sensitivity achieved in the present recordings while lower pressure values were used (less than 75 Torr compared to 441 Torr in Ref. [1]). The position and strength values of the lines are given as Supplementary Material.

### 3. Rotational assignments and spectroscopic parameters

The rotational analysis was carried out using the combination difference method, using literature constants for the ground and  $(01^10)$  state [11]. The standard expression of the vibration–rotation energy levels was used for the fit of the spectroscopic parameters:

$$F_\nu(J) = G_\nu + B_\nu J(J+1) - D_\nu J^2(J+1)^2 + H_\nu J^3(J+1)^3 \quad (2)$$

Where  $G_v$  is the vibrational term value,  $B_v$  is the rotational constant,  $D_v$  and  $H_v$  are centrifugal distortion constants.

The spectroscopic parameters of the upper state were fitted directly to the observed line positions, the lower state rotational constants being constrained to their literature values [11]. The hot band involves  $e$  and  $f$  rotational levels but the  $ee$  and  $ff$  sub bands were not resolved. Hence, the two subbands were fitted independently with the same input data of line positions.

In a first step, we tried to include the largest amount of line positions in the fit of the  $6\nu_3$  band. It led to an unrealistic (effective) value of the  $H_v$  distortion term (fit 2). In order to provide more meaningful parameters, we give in Table 1 the results of the fit (fit 1) obtained excluding the higher rotational quantum number  $J$  values and using only the first distortion term in the expression of the energy levels (Eq. 2).

The observed and calculated line positions of the cold and hot bands are given as Supplementary Material. In Table 1, the observed band origins and the rotational constants  $B_v$ ,  $D_v$  and  $H_v$  are listed together with the corresponding  $rms$  value. The comparison with the parameter values of Ref. [1] included in this Table shows (i) an important difference of about  $0.07\text{ cm}^{-1}$  on the band centers for both the cold and hot bands (but with opposite sign) indicating some calibration problem on the position values of Ref. [1], (ii) a gain of more than a factor of 3 on the  $rms$  values of the fit.

**Table 1. Rovibrational parameters of the  $6\nu_3$  and  $6\nu_3+\nu_2-\nu_2$  bands of  $^{14}\text{N}_2^{16}\text{O}$ .**

Band	$G_v^a$	$B_v$	$D_v \times 10^7$	$H_v \times 10^{13}$	Lines <sup>b</sup>	$J_{incl}/J_{max}^c$	$rms \times 10^3$
$6\nu_3$ (fit 1 without $H$ )	12891.0869(18)	0.398417(62)	1.748(38)	-	81(95)	41(48)	8.5
$6\nu_3$ (fit 2 with $H$ )	12891.0766(12)	0.3985044(32)	3.446(16)	693.5(76)	90(95)	48(48)	5.7
$6\nu_3$ [1]	12891.153(4)	0.398379(10)	1.57(5)	-	73(74)		16
$6\nu_3+\nu_2-\nu_2 e$	12806.9283(28)	0.399566(22)	0.27(28)	-	37(50)	30(30)	9.1
$6\nu_3+\nu_2-\nu_2 f$	12806.9285(29)	0.399647(22)	0.23(29)	-	39(50)	30(30)	9.6
$6\nu_3+\nu_2-\nu_2$ [1]	12806.854(5)	0.399480(30)	3.65(18)	-	35(37)		30

<sup>a</sup> Difference of the vibrational term values of the upper and lower states.

<sup>b</sup> The number of fitted lines is indicated, as well as, between parenthesis, the total number of assigned lines.

<sup>c</sup> The maximum value of  $J$  included in the fit is indicated as well as the maximum assigned  $J$  value.

Notes: The constants for the ground and ( $01^10$ ) state were taken from Ref. [11].

The uncertainties are given in parenthesis in the unit of the last quoted digit.

The upper panel of Fig. 3 shows the deviation between the observed positions and the corresponding values calculated from the ( $00^06$ ) parameters (fit 1 in Table 1). The large deviation observed for high  $J$  values reveals the occurrence of a perturbation (see below).

#### 4. Discussion

Perevalov *et al* have developed a global effective Hamiltonian model reproducing the rovibrational energy levels of  $^{14}\text{N}_2^{16}\text{O}$  [12,13]. The effective Hamiltonian describing all vibrational-rotational energy levels and absorption line intensities in the electronic ground state of nitrous oxide ( $^{14}\text{N}_2^{16}\text{O}$ ) is based on the normal mode polyad approach.

The lower panel of Fig. 3 shows the (*Obs.-Pred.*) deviations of the line positions of the (00<sup>0</sup>6) state. The differences increase linearly from -0.06 to +0.06  $\text{cm}^{-1}$  for  $J$  values ranging from 0 to 48. The predictive ability of the effective Hamiltonian (EH) model is then satisfactory but the present measurements will be useful to improve the effective Hamiltonian parameters. In the case of the (01<sup>1</sup>6) state observed through the hot band, the measured line positions are systematically higher by about 0.15  $\text{cm}^{-1}$ , the shift being nearly constant over the 0-30 range of observed  $J$  values.

On the basis of the predictions of the EH model [12,13], the perturbation responsible of the large deviations observed for high  $J$  values (Fig. 3) was identified as due to a resonance anharmonic interaction between 00<sup>0</sup>6 and 04<sup>0</sup>5 vibrational states at  $J=65$  (overcrossing). In addition, the 00<sup>0</sup>6 vibrational state is perturbed by the 04<sup>2</sup>5 vibrational state (anharmonic +  $l$ -type interaction). The energy level crossing is predicted at  $J=53$ .

The same resonance interactions take place for the hot band. The 01<sup>1</sup>6 vibrational state is perturbed by the 05<sup>3</sup>5 vibrational state (anharmonic +  $l$ -type interaction). The energy level crossings are predicted at  $J=33$  and  $J=35$  for  $e$  and  $f$  sublevels, respectively.

Using the eigenfunctions of the 00<sup>0</sup>6 state provided by the effective Hamiltonian model [12,13], the effective dipole moment parameter  $M_{006}$  has been fitted (see Refs. [14,15] for the definition of this parameter). Two fits were performed. In the first one, all 91 measured intensity values of the  $6\nu_3$  band were used. We have obtained the value  $M_{006}=0.2238(46)\times 10^{-6}$  Debye. In the second fit, 27 very badly reproduced line intensities were removed. A RMS value of 11% was achieved in this second fit leading to  $M_{006}=0.2458(17)\times 10^{-6}$  Debye. This RMS value is close to the estimated uncertainty of our experimental intensity values. The line intensities calculated using this last  $M_{006}$  value lead to a band intensity of  $1.87(2)\times 10^{-25}$   $\text{cm}/\text{molecule}$  which is in a very good agreement with the value  $1.9(2)\times 10^{-25}$   $\text{cm}/\text{molecule}$  reported in Ref.[2]. The calculated line intensities are included in the Supplementary Material. The vibrational transition dipole moment squared obtained using this effective dipole moment parameter is presented in Table 1 together with those of the  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ ,  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  and  $^{15}\text{N}_2^{16}\text{O}$  isotopologues [4]. It is interesting to note that

the values obtained for the homogeneous isotopic species,  $^{15}\text{N}_2^{16}\text{O}$  and  $^{14}\text{N}_2^{16}\text{O}$ , are close but differ significantly from those of the non homogeneous isotopologues  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ ,  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ .

**Table 2. Comparison of vibrational transition dipole moments squared for  $6\nu_3$  band of different isotopologues of nitrous oxide**

ISO <sup>a)</sup>	Band center (in $\text{cm}^{-1}$ )	$ R_0 ^2$ (in $10^{-10} \text{ D}^2$ )	Reference
446	12 891.07	1.658(11)	This work
556	12 507.55	1.567(09)	[4]
456	12 636.21	2.615(15)	[4]
546	12 766.20	2.505(17)	[4]

## 5. Conclusion

New experimental information about the  $6\nu_3+\nu_2-\nu_2$  and the  $6\nu_3$  bands of  $^{14}\text{N}_2^{16}\text{O}$  has been obtained from ICLAS spectra. A perturbation affecting the high rotational states was evidenced and explained in the frame of the effective Hamiltonian approach. The main dipole moment parameter of the  $6\nu_3$  band has been determined from the measured absolute line intensities. The obtained results will be applied to improve the effective Hamiltonian parameters of  $^{14}\text{N}_2^{16}\text{O}$ .

## Acknowledgments

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## Figure Captions

**Fig. 1.**

Overview of the ICLAS absorption spectrum of N<sub>2</sub>O between 12800 and 12900 cm<sup>-1</sup>.

**Fig. 2.**

Line profile fitting of the P(12) line of the 6v<sub>3</sub> band of <sup>14</sup>N<sub>2</sub><sup>16</sup>O.

**Fig. 3.**

Variation of the differences between the measured and calculated values energy levels of the (00<sup>0</sup>6) state of <sup>14</sup>N<sub>2</sub><sup>16</sup>O, versus the upper state *J* values. Crosses and circles correspond to the levels calculated from *P* and *R* transitions, respectively.

*Upper panel:* the calculated values were computed with the spectroscopic parameters of Table 1 (fit 1)

*Lower panel:* the calculated values were predicted by the effective Hamiltonian model [12,13].

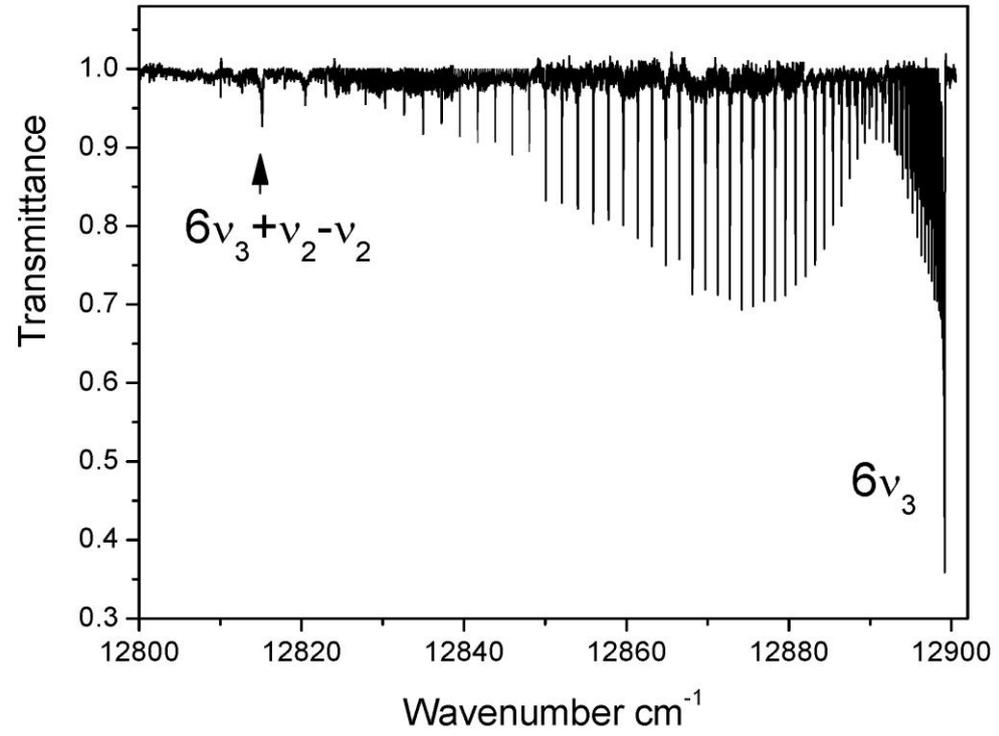


Fig. 1. Overview of the ICLAS absorption spectrum of  $\text{N}_2\text{O}$  between 12800 and 12900  $\text{cm}^{-1}$ .

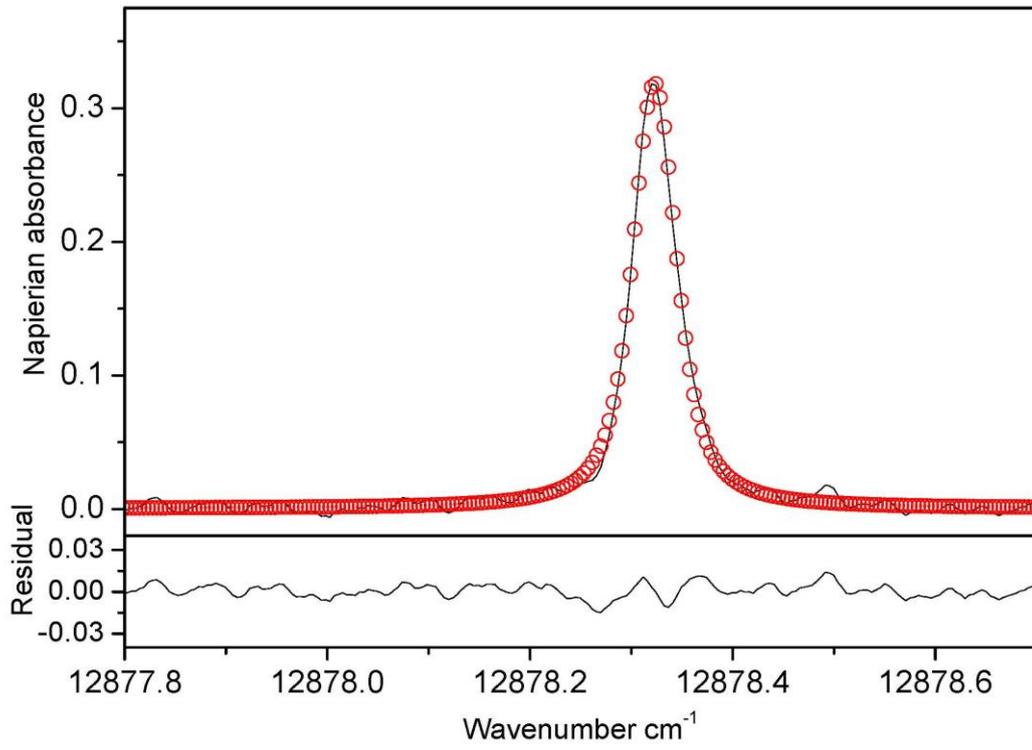
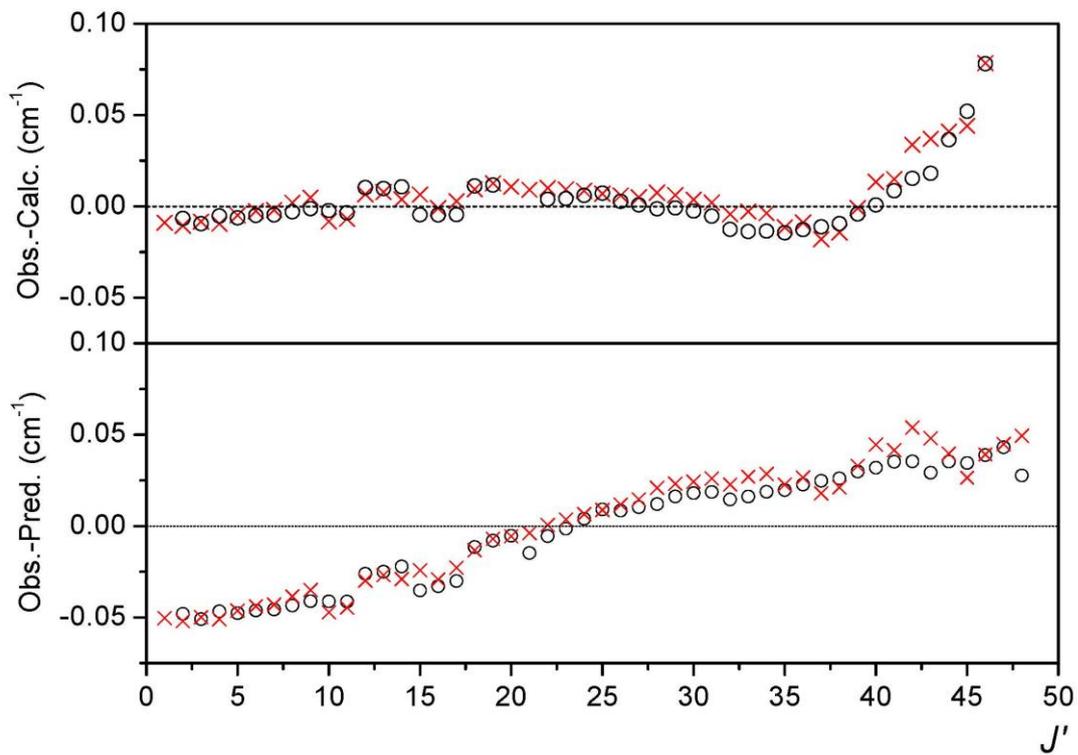


Fig. 2. Line profile fitting of the P(12) line of the  $6\nu_3$  band of  $^{14}\text{N}_2^{16}\text{O}$ .



**Fig. 3.**

Variation of the differences between the measured and calculated values energy levels of the  $(00^0_6)$  state of  $^{14}\text{N}_2^{16}\text{O}$ , versus the upper state  $J$  values. Crosses and circles correspond to the levels calculated from  $P$  and  $R$  transitions, respectively.

*Upper panel:* the calculated values were computed with the spectroscopic parameters of Table 1 (fit 1)

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