Precision spectroscopy and comprehensive analysis of perturbations in the $A^1\Pi$ (v = 0) state of $^{13}C^{18}O$

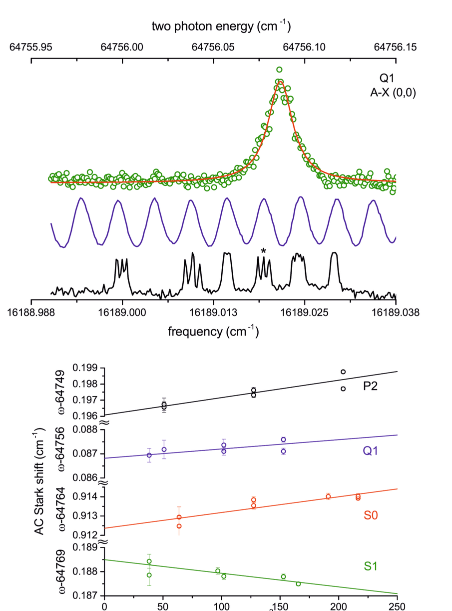
R. Hakalla[a], T. M. Trivikram[b], A. N. Heays[c,d], E. J. Salumbides[b], N. de Oliveira[e], R. W. Field[f], and W. Ubachs[b]

[a]Materials Spectroscopy Laboratory, Faculty of Mathematics and Natural Science, University of Rzeszów, Poland
[b]Department of Physics and Astronomy, and LaserLaB, Vrije Universiteit, Amsterdam, The Netherlands
[c]LERMA, Observatoire de Paris, CNRS, Sorbonne Universités, UPMC Univ. Paris 06, Meudon, France
[d]School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85281, USA
[e]Synchrotron SOLEIL, Orme de Merisiers, St. Aubin, Gif sur Yvette Cedex, France
[f]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, USA

Laser spectroscopy

LLAMS Amsterdam

Two-photon $A^1\Pi \leftarrow X^1\Sigma^+$ (0, 0) transitions of $^{13}C^{18}O$



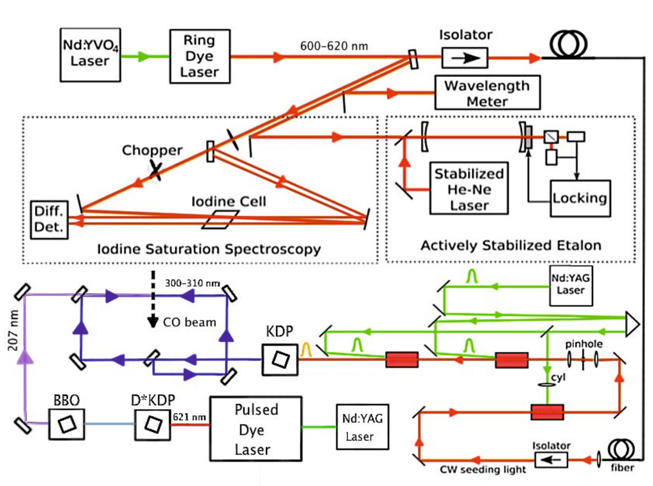
Q(1) spectral line:
- **Green points** – 2 + 1' REMPI (Doppler-free laser spectrosc.) with fitted red curve.
- **Lower black line** – saturated **iodine spectrum** used for absolute calibration
- **Middle blue line – etalon markers** from stabilized Fabry-Perot interferometer used for the interpolation and linearisation of the scan.
- Lower scale – fundamental wave number of the **cw-seed laser**
- Upper scale – **two-photon excitation energy**

(*) - a_{13} hyperfine component of the B-X (10,3) R(87) iodine line at 16,189.019 45 cm^{-1} used for calibration.

AC-Stark-plots:
- for the four A-X(0, 0) two-photon transitions.

Calibration uncertainty (1σ) : **0.001 cm^{-1}**
Accuracy of transition frequencies : **0.002 - 0.003 cm^{-1}**

VUV Doppler-free laser spectroscopy



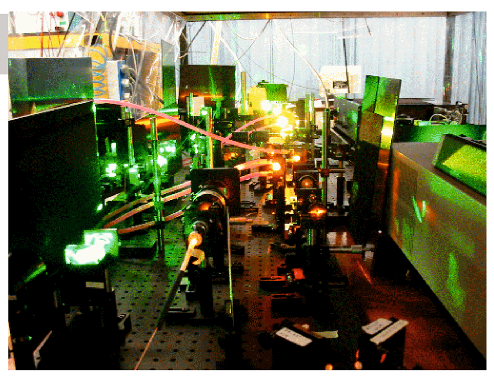
* BBO, KDP, D*KDP - crystals used for non-linear upconversion of laser radiation.

- **2+1' REMPI process**
- **Narrow-band pulsed dye amplifier (PDA)** laser system [3]
  - pulsed output is frequency doubled
  - then employed in a two-photon experiment
    - with counter-propagating beams aligned in the **geometry of a Sagnac interferometer** [3] to avoid a residual Doppler shift.
- **Cw ring dye laser** (at 618 nm)
  - for seeding PDA
- **Nd:YAG laser** (rep. rate of 10 Hz)
- **Detector: Multichannel plate**
- **Second pulse-time-delayed laser** (at 202 nm) for ionising $A^1\Pi$ excited state population.
  - **delayed by around 10 ns** from the probe laser **to minimise the AC-Stark effects**.

$^{13}C^{18}O$ measurements

9 high accuracy absorption lines

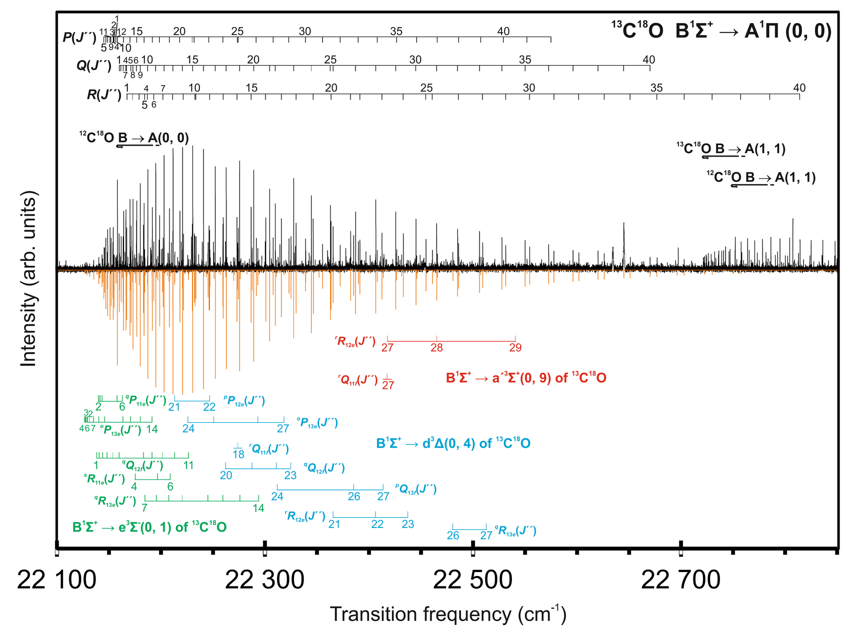
- **Laser resolution: 0.0067 cm^{-1}**
- Maximum **SNR**: **20 : 1**
- The lines were measured, calibrated, and corrected for chirp and AC-Stark effects
  - leading to **44 ± 8 MHz correction**
- **FWHM** = **0.0067 cm^{-1}** for best CO lines



Fourier - transform spectroscopy

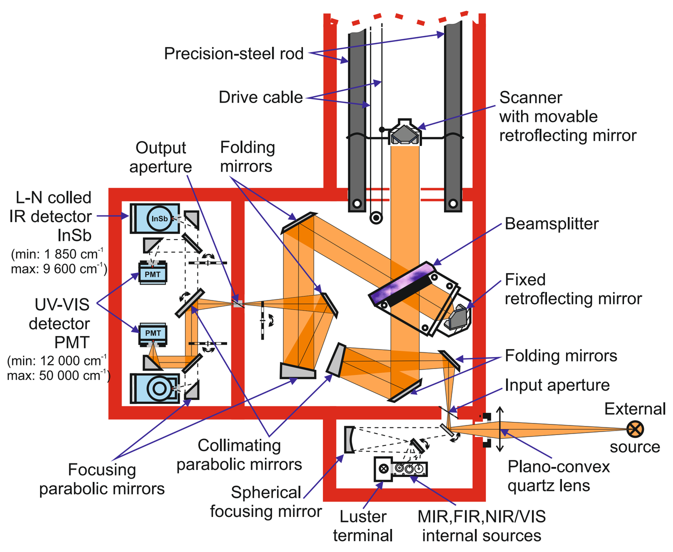
LSM Rzeszów

One-photon $B^1\Sigma^+ \rightarrow A^1\Pi$ (0, 0) transitions of $^{13}C^{18}O$



Calibration uncertainty (1σ) : **0.003 cm^{-1}**
Accuracy of transition frequencies : **0.003 - 0.03 cm^{-1}**

UV-VIS 1.71-m spectrometer (Bruker IFS 125HR)



- **Spectral range:**
  12 000 – 25 000 cm^{-1}
  (360 – 750 THz)
  (830 – 400 nm)
- Optical Path Diffeerence:
  $(OPD)_{max}$ = 258 cm
- **Calibration:**
  - **He-Ne** atomic line: **632.9912383 nm**
  - stability (over 1 h): **±2 × 10^{-9}**
  - **FWHM** : **0.002 cm^{-1}**

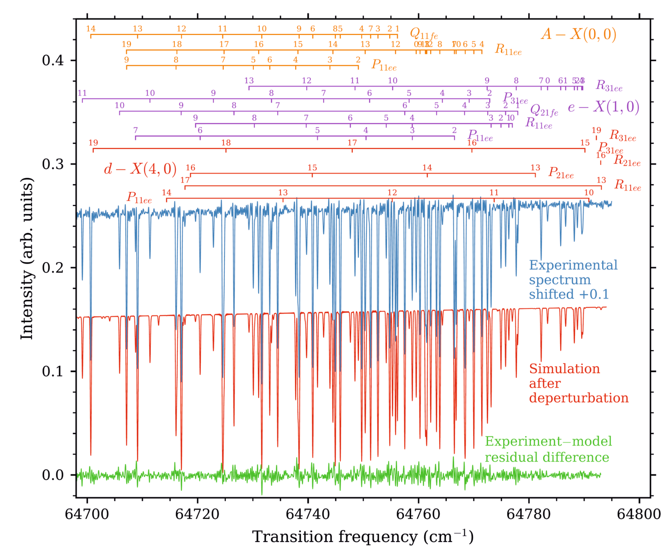
$^{13}C^{18}O$ measurements

185 emission lines

- **Spectral resolution:** **$(\Delta\upsilon)$ = 0.018 cm^{-1}**
- **Hollow-cathode discharge lamp** (air-cooled; 950 V, 80 mA dc)
- **Mixture of He** and **$^{13}C_2D_2$**
- Sedimentation of **^{13}C (99,98 % purity)**
- Admitted: **$^{18}O_2$(98.1%)** with **$^{16}O_2$ (1.9%)**
- **T** (of the $^{13}C^{18}O$ plasma) ≈ **900 K**
- Maximum **SNR 60 : 1**
- **FWHM = 0.1 cm^{-1}** for best CO lines

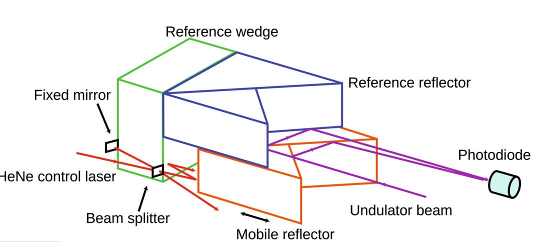
SOLEIL St. Aubin

One-photon $A^1\Pi \leftarrow X^1\Sigma^+$(0, 0), $a^3\Pi \leftarrow X^1\Sigma^+$(11, 0), $e^3\Sigma^- \leftarrow X^1\Sigma^+$(1, 0), $d^3\Delta \leftarrow X^1\Sigma^+$(4, 0), $a'^3\Sigma^+ \leftarrow X^1\Sigma^+$(9, 0), and $B^1\Sigma^+ \leftarrow X^1\Sigma^+$(0, 0) transitions of $^{13}C^{18}O$

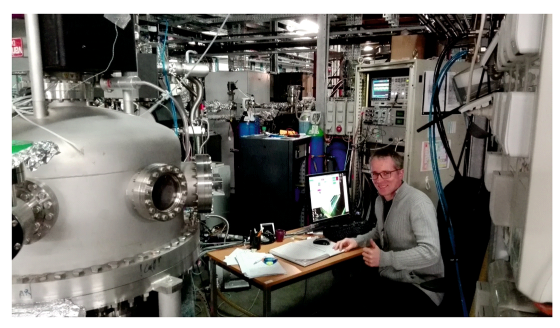


Calibration uncertainty (1σ) : **0.01 cm^{-1}**
Accuracy of transition frequencies : **0.01 - 0.05 cm^{-1}**

VUV beamsplitter-less FTS (DESIRS beamline)



Dichroïsme Et Spectroscopie par Interaction avec le Rayonnement Synchrotron



- **Installed on the 2.75 GeV storage ring SOLEIL synchrotron**
- **Spectral range:**
  40 000 – 250 000 cm^{-1}
  (1 200 – 7 500 THz)
  (250 – 40 nm !!!)
- Optical Path Diffeerence: **$(OPD)_{max}$ = 10 cm**
- The reference-mobile reflector gap: **100 µm**

$^{13}C^{18}O$ measurements

712 absorption lines

T [K]	Cell	Resolution [cm^{-1}]	Doppler broadening [cm^{-1}]
90	liquid nitrogen colled	0.07	0.08
300	room conditions	0.07	0.14
900	heated	0.27	0.25

- **Spectral resolution:** **$(\Delta\upsilon)_{max}$ = 0.21 - 0.32 cm^{-1}**
- Column density: **2×10^{-15}** to **6×10^{-13}cm^{-2}**
- Pressure shift: **-2×10^{-5} [cm^{-1}/mbar]**
- Purified gas sample: **$^{12}C^{16}O$: $^{12}C^{18}O$: $^{12}C^{17}O$ = 1 : 0.85 : 0.20**

Summary

We have reinvestigated the $A^1\Pi(v = 0)$ level of $^{13}C^{18}O$ using new high-resolution spectra obtained via multi-photon laser excitation as well as with synchrotron-based Fourier-transform absorption spectroscopy of the $A^1\Pi \leftarrow X^1\Sigma^+$(0, 0), $a^3\Pi \leftarrow X^1\Sigma^+$(11, 0), $e^3\Sigma^- \leftarrow X^1\Sigma^+$(1, 0), $d^3\Delta \leftarrow X^1\Sigma^+$(4, 0), $a'^3\Sigma^+ \leftarrow X^1\Sigma^+$ (9, 0), and $B^1\Sigma^+ \leftarrow X^1\Sigma^+$(0, 0). In addition, Fourier-transform emission spectroscopy in the visible range is performed on the $B^1\Sigma^+ \rightarrow A^1\Pi$ (0, 0) band.

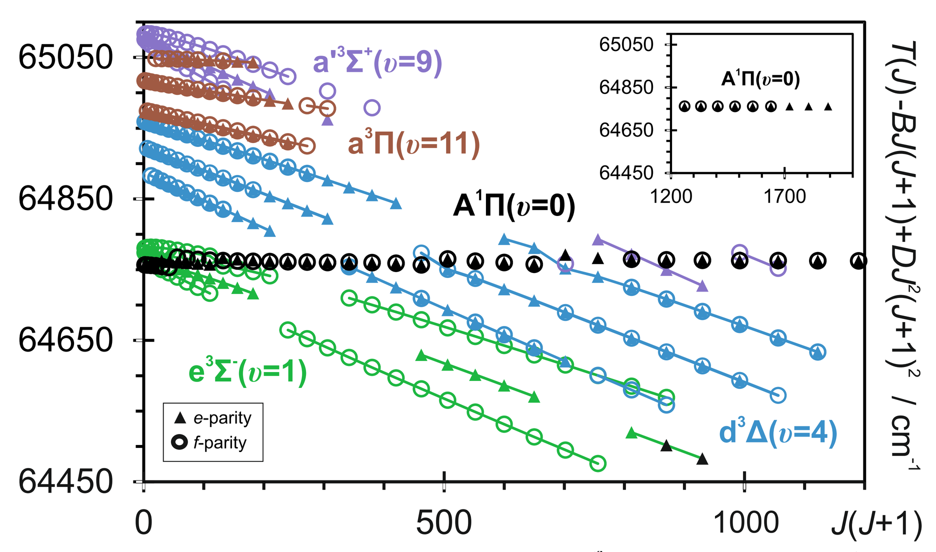
All information, in total over 900 spectral lines, was included in an efective-Hamiltonian analysis of the **$A^1\Pi$(v = 0, J)** levels that are **directly perturbed** by the $e^3\Sigma^-$(v = 1), $d^3\Delta_i$(v = 4), $a'^3\Sigma^+$(v = 9), $D^1\Delta$(v = 0), and $I^1\Sigma^-$(v = 0, 1) close-lying levels and the $e^3\Sigma^-$(v = 0, 2), $d^3\Delta_i$(v = 3, 5), $a'^3\Sigma^+$(v = 8, 10) remote levels, as well being **indirectly influenced by the $a^3\Pi$(v = 10, 11) state.** The influence of six further perturber states and their interactions was investigated and are not signicant for reproducing the present experimental data.

This analysis leads to a much improved description in terms of molecular constants and interaction parameters, compared to previous studies of the same energy region for other CO isotopologues.

Spectroscopy of Exoplanets
Cumberland Lodge
Windsor Great Park
8 - 11 July 2018

DEPERTURBATION of $A^1\Pi$(v = 0) in $^{13}C^{18}O$

Experimental reduced term values



$$(\eta+\xi)_{A-d} = \langle a^3\Pi_{1,1}, v_a | H^{SO}+H^{RE} | d^3\Delta_{1,2}, v_d \rangle = -\sqrt{12}\left(\tfrac{1}{4}a_{a-d}\langle v_a|v_d\rangle - b_{a-d}\langle v_a|B(R)|v_d\rangle\right)$$

$$\xi_{a-d} = \langle a^3\Pi_{1,2}, v_a | H^{RE} | d^3\Delta_{1,2}, v_d \rangle = b_{a-d}\langle v_a|B(R)|v_d\rangle$$

$$(\eta+\xi)_{a-a'} = \langle a^3\Pi_{0,1}, v_a | H^{SO}+H^{RE} | a'^3\Sigma^+_{0,1}, v_{a'} \rangle = -\sqrt{6}\left(\tfrac{1}{4}a_{a-a'}\langle v_a|v_{a'}\rangle - b_{a-a'}\langle v_a|B(R)|v_{a'}\rangle\right)$$

$$\xi_{a-a'} = \langle a^3\Pi_{1,1}, v_a | H^{RE} | a'^3\Sigma^+_{0,1}, v_{a'} \rangle = \tfrac{1}{\sqrt{2}} b_{a-a'}\langle v_a|B(R)|v_{a'}\rangle$$

$$(\eta+\xi)_{a-e} = \langle a^3\Pi_{0,1}, v_a | H^{SO}+H^{RE} | e^3\Sigma^-_{0,1}, v_e \rangle = \sqrt{6}\left(\tfrac{1}{4}a_{a-e}\langle v_a|v_e\rangle - b_{a-e}\langle v_a|B(R)|v_e\rangle\right)$$

$$\xi_{a-e} = \langle a^3\Pi_{1,2}, v_a | H^{RE} | e^3\Sigma^-_{1,1}, v_e \rangle = \tfrac{1}{\sqrt{2}} b_{a-e}\langle v_a|B(R)|v_e\rangle$$

$$\eta_{a-I} = \langle a^3\Pi_0, v_a | H^{SO} | I^1\Sigma^-_0, v_I \rangle = \sqrt{3}\left(\tfrac{1}{4}a_{a-I}\langle v_a|v_I\rangle\right)$$

$$\eta_{a-D} = \langle a^3\Pi_1, v_a | H^{SO} | D^1\Delta_2, v_D \rangle = -\sqrt{6}\left(\tfrac{1}{4}a_{a-D}\langle v_a|v_D\rangle\right)$$

	$A^1\Pi$ (v = 0)	$B^1\Sigma^+$ (v = 0)	$I^1\Sigma^-$ (v = 0)	$I^1\Sigma^-$ (v = 1)	$D^1\Delta$ (v = 0)
T_v	64762.7339(6)	86917.3603(9)	64571.871 c	65593.173 c	65448.421k
B	1.4574220(41)	1.7697646(30)	1.14543c	1.13021 c	1.1339 k
D x 10^6	6.0841(28)	5.5388(15)	5.65 l	5.67 l	1.1339 k
H x 10^{12}	-12.8 f		2.25 l	2.25 l	-0.22 l
q x 10^5	2.53(18)				
$\xi(\sim A, v=0)$			-0.032 m	0.057 m	0.019 m
$\eta(\sim a, v=11)$				-2.409 n	-0.339 n

	$e^3\Sigma^-$ (v = 0)	$e^3\Sigma^-$ (v = 1)	$e^3\Sigma^-$ (v = 2)	$a'^3\Sigma^+$ (v = 9)	$a'^3\Sigma^+$ (v = 10)
T_v	63729.173 c	64774.9627(5)	65802.444 c	65078.4975(41)	66066.949 c
B	1.15849 c	1.142611(12)	1.12738 c	1.079761(32)	1.06557 c
D x 10^6	5.67 c	5.571(18)	5.58 c	5.188(34)	5.17c
H x 10^{12}	-1.50 l	-1.50l	-1.50 l	-0.30 l	-0.30 l
λ	0.52 c	0.5363(15)	0.54 c	-1.1445(44)	-1.09 c
γ x 10^3		-2.401(88)		-7.02(25)	-5.14 c
$\eta(\sim A, v=0)$	-8.480 m	14.4001(13) 14.143 m	-17.544 m	2.739(17) 2.8137 m	-1.8865 m
$\eta(\sim a, v=11)$ o		2.516 n,o		3.450(61) 13.195 n	
$\xi(\sim a, v=11)$		-0.056 n		-0.0018(10) -0.035 n	

	$d^3\Delta$ (v = 3)	$d^3\Delta$ (v = 4)	$d^3\Delta$ (v = 5)	$a^3\Pi$ (v = 10)	$a^3\Pi$ (v = 11)
T_v	63886.481 c	64928.6973(8)	65953.987 c	63642.313 c	65012.3093(45)
B	1.13829 c	1.122937(10)	1.10873 c	1.35899 c	1.341838(54)
D x 10^6	5.361 c	5.153(12)	5.327 c	5.59 c	5.51(17)
H x 10^{12}	-0.60 l	-0.60 l			
A	-15.649 c	-16.5817(19)	-0.60 l	37.50 c	39.2809(55)
A_D x 10^5	-0.92 c	-0.92 c	-15.909 c	-2.29 c	-2.17 c
λ	0.67 c	1.1242(23)	-0.92 c	-0.0012 s	-0.0121(36)
γ x 10^3	-4.95 c	-4.35(18)	0.85 c	3.71 c	3.53 c
o			-6.28 c	0.67 c	0.9098(33)
p x 10^3				2.91 s	1.43(52)
q x 10^5				3.27 c	3.106 c
$\eta(\sim A, v=0)$	27.748(42) 25.7037 m	-22.1336(39) -23.391 m	19.764 m		
$\eta(\sim a', v=10)$ q		-32.405 n			
$\xi(\sim a, v=10)$		0.073 n			
$\eta(\sim a, v=11)$ o		-34.503(24) -25.770 n	-33.533 n		
$\xi(\sim a, v=11)$		0.0598(17) 0.054 n	0.074 n		
$\epsilon(\sim a', v=9)$ p		0.196(37)			

a All values are in cm^{-1}. c Calculated from Ref. [3] based on mass-scaling, where the spin-spin constant λ = −1.5 × C, the Λ-doubling constants o = C, and q = 2 × B_v. The $^{13}C^{18}O$ $X^1\Sigma^+$ G(0) was taken from [6] to obtain the $T_{v=0}$. f After Ref. [9]. i After Ref. [10]. k Calculated from Ref. [7] based on mass-scaling. l On the basis of the isotopically recalculated values given in Refs. [1] for the $B^1\Sigma^+$ as well as using constants determined in Ref. [6] for the $X^1\Sigma^+$ state. m After Ref. [11]. n After Ref. [12]. o After Ref. [13]. p From Ref. [14] based on mass-scaling. q From Ref. [5] based on mass-scaling. r The theoretical **spin-orbit η** and **rotational-electronic ξ** interaction parameter values were calculated on the basis of the a_v and b_v **isotopically invariants** given by Hakalla et al. [1] and the appropriate vibrational overlap integrals for $^{13}C^{18}O$. s The value was deduced using elements of an effective Hamiltonian matrix by Field [15], electronic perturbation matrix elements from Ref. [18] and compare them with the symmetrized matrix elements implemented in the current fit. t Determined on the assumption that **ξ << η for the ($H^{SO}+H^{RE}$) interactions**, which condition is very well fulfilled in the present case. u The **spin-orbit off-diagonal interaction**. v Calculated from Ref. [3] based on mass-scaling, where A_v = 2 × A_v [17]. w Obtained and isotopically recalculated from Ref. [16], where the spin-spin constant λ = 1.5 × ε and the Λ-doubling constant p = 2 × p_v.

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hakalla@ur.edu.pl