

Reanalysis of the Ångström System ($B^1\Sigma^+ - A^1\Pi$) in the $^{13}\text{C}^{16}\text{O}$ Isotopic Molecule

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(Received December 20, 2011; in final form June 15, 2012)

The emission spectrum of the Ångström system ($B^1\Sigma^+ - A^1\Pi$) of $^{13}\text{C}^{16}\text{O}$ was obtained under high resolution with an accuracy estimated to be $\pm 0.002 \text{ cm}^{-1}$ as an emission spectrum using a high accuracy dispersive optical spectroscopy. The light source was a hollow-cathode lamp with two anodes built in our laboratory, with a previously deposited small quantity of ^{13}C carbon on the electrodes. The emission from the discharge was observed with a plane grating spectrograph and recorded by a photomultiplier tube. In total 195 transition wave numbers belonging to the strongest 0-1 and 0-2 bands of the $B-A$ system were precisely measured. The modern rotational reanalysis made it possible to verify the molecular information for the both combining states of the Ångström system. In particular the rovibrational constants for the $B^1\Sigma^+$ Rydberg state have been significantly improved ($B_0 = 1.8625054(65) \text{ cm}^{-1}$ and $D_0 = 6.1384(52) \times 10^{-6} \text{ cm}^{-1}$) and the obtained equilibrium rotational constants of this state are more accurate than known to date. Numerous rotational perturbations observed in the $A^1\Pi$ state were reanalysed and confronted with the previously known ones.

PACS: 33.20.Kf, 33.20.Sn, 33.15.Mt

1. Introduction

There is a considerable experimental and theoretical interest in the spectra of CO molecules, because carbon monoxide is, after H_2 , the most abundant molecule in the universe. For instance its occurrence has been documented [1-4] in the atmospheres of planets and stars, in comet tails, interstellar space, etc. A number of carbon monoxide isotopic molecules have been identified in the solar spectrum [5, 6]. CO has continued to be of interest to several areas of science, including environmental investigations, chemical physics, the technology of new materials based on connecting metals with carbon monoxide (e.g. metal carbonyls), and medicine etc.

Since the first laboratory study of the spectrum of $B^1\Sigma^+ - A^1\Pi$ band system in 1875 in CO by Ångström [7] in the $^{12}\text{C}^{16}\text{O}$ ordinary molecule, many electronic transitions have been identified in the visible region: in the ordinary molecule [8-11], as well as in various isotopologues: $^{12}\text{C}^{18}\text{O}$ [12], $^{13}\text{C}^{18}\text{O}$ [13], and $^{14}\text{C}^{16}\text{O}$ [14, 15].

The studies of the $B^1\Sigma^+ - A^1\Pi$ band system in the $^{13}\text{C}^{16}\text{O}$ molecule were initiated by McCulloh and Glockler [16] and Douglas and Møller [17] who performed, under low resolution, fragmentary observations and analyses of selected Ångström bands. Comprehensive measurements made under high resolution and a rotational analysis of the bands of this system were performed by Rytel [18]. The publication of Janjić et al. [12] appeared to be a supplement of this paper in which authors made investigations and analyses of weaker bands, that is 1-4, 1-5 and 1-6 belonging to the $1-v''$ progression of the $B^1\Sigma^+ - A^1\Pi$ system. Kępa et al. [19] obtained and analysed six bands of the Ångström system in $^{13}\text{C}^{16}\text{O}$ molecule (with an accuracy estimated to be $0.010-0.020 \text{ cm}^{-1}$), receiving very weak 1-2, 1-7, and 0-6 bands for the first time.

The analyses of the $B^1\Sigma^+$ Rydberg state in other band system in $^{13}\text{C}^{16}\text{O}$ molecule were initiated by Tilford and Vanderslice [20] on the basis of $B^1\Sigma^+ - X^1\Sigma^+$ system and next considerably extended and enriched by Eidelsberg et al. [21]. The Fourier transform record of the $C^1\Sigma^+ - B^1\Sigma^+$ (0-0) band in the four isotopomers, including $^{13}\text{C}^{16}\text{O}$ molecule, was performed by Roncin et al. [22].

Investigations of $^{13}\text{C}^{16}\text{O}$ make it possible to obtain additional information about this very important particle and to verify the data concerning this molecule as a whole and at the same time they enlarge the isotopic information about the spectrum and energetic structure of the isotopic molecule being investigated. So the major objective of this work is to determine precise values of the wave numbers of lines of the Ångström system in the $^{13}\text{C}^{16}\text{O}$ molecule on the basis of the reanalysis, with more accurate methods, of the strongest bands (0-1 and 0-2) of the $B-A$ system and on this basis to obtain more precise spectroscopic parameters especially about the $B^1\Sigma^+$ Rydberg state as well as about strongly perturbed $A^1\Pi$ state.

2. Experimental details

The experimental details were almost the same as described in our previous paper [23], so some parts of this work have been posted with the consent of Elsevier Limited (License Agreement number 2907610176408).

The spectrum of the $B^1\Sigma^+ - A^1\Pi$ transition of $^{13}\text{C}^{16}\text{O}$ isotopic molecule was excited in a water-cooled hollow-cathode lamp with two anodes [24]. The anodes were operated at $2 \times 650 \text{ V}$ and $2 \times 50 \text{ mA}$ dc as well as $2 \times 670 \text{ V}$ and $2 \times 35 \text{ mA}$ dc in order to register the strongest 0-1 and 0-2 bands of the Ångström system, respectively. The lamp was initially filled with a mixture

of helium and acetylene $^{13}\text{C}_2\text{D}_2$ (99 at.% of ^{13}C) under a pressure of approximately 6 Torr of the acetylene plus 1 Torr of the helium. The electric current was passed through it for a long period of time (about 100 h). Afterwards a small quantity of ^{13}C carbon became deposited on the electrodes. The $^{13}\text{C}^{16}\text{O}$ spectrum was obtained during the first investigation of the Ångström band system in the very rare $^{13}\text{C}^{17}\text{O}$ isotope molecule performed recently by Hakalla and Zachwieja [23]. For this reason the lamp was evacuated and oxygen containing 60% of the isotope ^{17}O was let in as the non-flowing gas under pressure at approximately 2 Torr. These conditions were found to be optimal for the production of a relatively strong spectrum.

The emission from the discharge was observed with the 2 m Ebert plane grating PGS-2 spectrograph in the 5th and 4th order for the 0–1 and 0–2 bands of the Ångström system, respectively. The reciprocal dispersion was about 0.09–0.14 nm/mm and the theoretical resolving power was approximately 228 000 for the 0–1 band and approximately 182 400 for the 0–2 band.

The spectrum of CO was recorded by translating on a linear stage (HIWIN KK5002) an exit slit and photomultiplier tube (HAMAMATSU R943–02) along the focal curve of the spectrograph. The entrance and exit slit width was 35 μm .

The line intensities were measured by a single photon counting (HAMAMATSU C3866 photon counting unit and M8784 photon counting board) with a counter gate time of 200 ms (no dead time between the gates). The positions of the exit slit were measured using a He–Ne laser interferometer (LASER-TEX) synchronized with the photon counting board (during the counter gate time, the position is measured 64 times and a mean value with the number of counts are transmitted to PC as a measurement point). The total number of the measurement points was approximately 73 000, for one 21 cm long scan with the sample step of 3 μm (the sample step is the translation of the exit slit during the counter gate time).

This type of spectrograph is very sensitive to mechanical and thermal deformation of its solid, optical tube. Variations of the atmospheric pressure and optical alignments of the spectroscopic lamps have a comparable effect on a line position (a few μm). In order to reduce the fluctuations of the line positions, the apparatus is thermally insulated and mounted on the main wall with a channel iron and a 6 cm thick granite plate, whereas the temperature in the laboratory room is stabilized with an air conditioner with 0.2 degree centigrade accuracy. Moreover, the optical alignments of the CO and reference lamps were corrected to get the same light distribution along the exit slit. The repeatability of the line position measurements was tested to be 0.2–0.5 μm according to the variations of the atmospheric pressure. The clear diagram of the experimental setup is presented in Fig. 1. This high accuracy dispersive optical spectroscopy measurement system has been assembled and calibrated in

our laboratory for the couple of last years. Apart from examining the carbon monoxide molecule [23] it has also been used to analyse the very little known AlH molecule [25–27] and AlH $^+$ ionic molecule [28] as well as CD radical molecule [29].

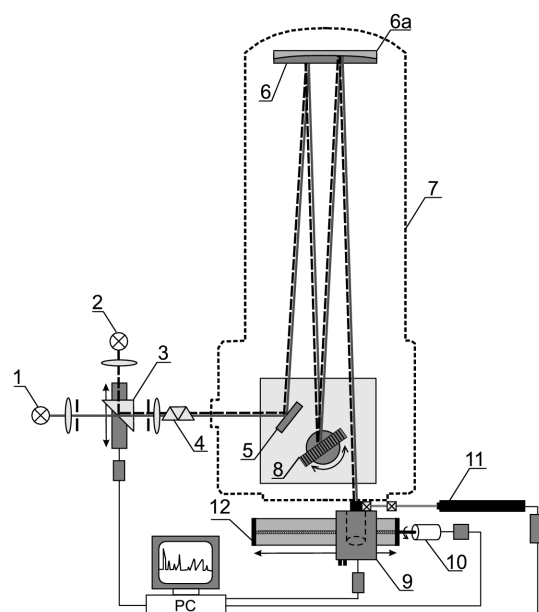


Fig. 1. Experimental setup: 1 — hollow-cathode tube, 2 — reference spectrum (Th lamp), 3 — moving fused silica prism, 4 — Amici prism, 5 — reflecting mirror, 6 — flat reflecting mirror, 6a — parabolic mirror, 7 — optical tube, 8 — plane grating, 9 — photomultiplier tube + cooler, 10 — stepper motor + planetary transmission, 11 — laser interferometer, 12 — linear stage (from Hakalla et al. [23] with permission of Elsevier Limited — License Agreement number 2907601072560).

Simultaneously recorded thorium atomic lines [30], obtained from several overlapped orders of the spectrum from a water-cooled, hollow-cathode tube were used for absolute wave number calibration. The peak positions of the spectral lines were calculated by using the least-squares method and assuming a Gaussian line-shape for each spectral contour (30 points per line, the uncertainty of the peak position for a single line was approximately 0.1–0.2 μm). For the wave numbers calculations third-order and sixth-order interpolation polynomials for the 0–1 and 0–2 bands, respectively, were used. The typical standard deviation of the least-squares fit for the 30–40 calibration lines was approximately 0.0016 cm^{-1} . The calibration procedure was tested (with two lamps simultaneously — one as an examination light source and the second one to provide the reference spectrum) to be 0.0015 cm^{-1} .

The CO lines have spectral widths of approximately 0.15 cm^{-1} and appear with a maximum signal-to-noise ratio of about 70:1 and approximately 100:1 for the 0–1 and 0–2 band, respectively. The most intense lines produced a count rate of approximately 25 000 photons/s

TABLE I
Summary of observations and reanalyses of the Ångström system ($B^1\Sigma^+ - A^1\Pi$) of the $^{13}\text{C}^{16}\text{O}$ isotopic molecule.

Band	Band head [cm ⁻¹]	Total number of lines	J_{max}	$\sigma^a \times 10^3$ [cm ⁻¹]
0-1	20704.464	96	34	1.01
0-2	19289.558	99	35	1.24

^a Standard deviation of the fit for the individual band analysis.

for the 0-1 and approximately 50 000 photons/s for the 0-2 band. Consequently, the positions for strong and isolated lines were determined with an accuracy better than ± 0.002 cm⁻¹. However, some weaker and blended lines were measured with a lesser accuracy of ± 0.005 cm⁻¹. The statistical information for the analysed bands is shown in Table I. In total, 195 lines belonging to 0-1 and 0-2 bands of the $B^1\Sigma^+ - A^1\Pi$ system in the $^{13}\text{C}^{16}\text{O}$ isotopic molecule have been measured, and their wave numbers are provided in Tables II and III.

TABLE II
Wavenumbers (cm⁻¹) of the rotational structure of the $B^1\Sigma^+ - A^1\Pi$ (0-1) band in the $^{13}\text{C}^{16}\text{O}$ isotopic molecule ^a.

J	$P_{11ee}(J)$		$Q_{11ef}(J)$		$R_{11ee}(J)$	
1	20709.4536	*	20713.1792	(0)	20720.6285	(0)
2	20707.1545	(-1)	20714.5945	(0)	20725.7788	(0)
3	20705.5243	(-1)	20716.7186	(0)	20731.5973	(1)
4	20704.6479	(-3)	20719.5498	(0)	20738.1689	(3)
5	20704.4561	(-3)	20723.0871	(0)	20745.4236	(4)
6	20704.9650	(-5)	20727.3304	(0)	20753.3775	(6)
7	20706.1938	(8)	20732.2782	(0)	20762.0464	(-8)
8	20708.1115	(0)	20737.9173	(0)	20771.4022	*
9	20710.7562	*	20744.2749	(0)	20781.4866	(0)
10	20714.0997	(-2)	20751.3483	(0)	20792.2680	(2)
11	20718.1518	(0)	20759.1450	(0)	20803.7456	*
12	20722.9501	(-5)	20767.7328	(0)	20815.9801	(6)
13	20728.4190	(-7)	20773.4837	(0)	20828.8745	(8)
14	20734.7283	(4)	20786.0610	(0)	20842.6026	(-4)
15	20742.1755	(-3)	20796.8381	(0)	20857.4680	(3)
16	20747.4611	(4)	20808.1794	(0)	20870.1645	(-4)
17	20756.4825	*	20820.2236	(0)	20886.5871	(0)
18	20765.6181	(-4)	20833.0952	(0)	20903.1326	(3)
19	20775.3502	(21)	20844.9295	(0)	20920.2564	(-22)
20	20785.7362	(-7)	20859.8967	(0)	20938.0391	(6)
21	20796.8381	*	20874.7891	(0)	20956.5135	(0)
22	20808.6192	(5)	20890.3068	(0)	20975.6834	(-6)
23	20821.1298	*	20906.4697	(0)	20995.5562	*
24	20834.3220	(-8)	20923.3923	(0)	21016.1259	(7)
25	20848.2941	(-4)	20941.0358	(0)	21037.4552	(4)
26	20862.9896	(-7)	20959.4552	(0)	21059.5018	(8)
27	20876.7799	(8)	20976.8963	(0)	21080.6317	(-7)
28	20893.9290	(-2)	20997.7421	(0)	21105.1172	(2)
29	20910.7376	(-7)	21018.2812	(0)	21129.2529	(7)
30	20928.2411	(0)	21039.3938	(0)		
31	20946.4108	(0)	21061.2830	(0)		
32	20965.3023	(0)	21083.8756	(0)		
33	20984.8986	(0)	21107.2168	(0)		
34			21131.4441	(0)		

^aValues in parentheses denote observed minus calculated values in units of the last quoted digit. *Denotes the less accurate lines and not used in the evaluation of molecular constants.

The bands belonging to the $B^1\Sigma^+ - A^1\Pi$ transition of $^{13}\text{C}^{16}\text{O}$ isotopologue were observed in the 19200–21200 cm⁻¹ spectral region. The parts of their high

quality spectrum in the range of their band heads are shown in Figs. 2 and 3, where clearly resolved lines of the P , Q , and R branches are rotationally interpreted.

TABLE III

Wavenumbers (cm^{-1}) of the rotational structure of the $B^1\Sigma^+ - A^1\Pi$ (0-2) band in the $^{13}\text{C}^{16}\text{O}$ isotopic molecule^a.

J	$P_{11ee}(J)$		$Q_{11ef}(J)$		$R_{11ee}(J)$	
1	19294.0075	*	19297.7745	(0)	19305.1831	(0)
2	19291.7667	(0)	19299.2827	(0)	19310.3908	(-1)
3	19290.2852	(-6)	19301.4978	(0)	19316.3593	(7)
4	19289.5318	(-22)	19304.4832	(0)	19323.0565	(21)
5	19289.5528	*	19308.2111	(0)	19330.5123	(0)
6	19290.2852	(-13)	19312.6967	(0)	19338.6992	(13)
7	19291.7892	(-3)	19318.0050	(0)	19347.6439	(3)
8	19294.0294	(25)	19323.6667	(0)	19357.3191	(-25)
9	19297.0185	(-3)	19330.4920	(0)	19367.7520	(4)
10	19300.7462	(0)	19337.9213	(0)	19378.9194	*
11	19305.2167	(-5)	19346.1253	(0)	19390.8178	(5)
12	19310.4779	(2)	19355.0615	(0)	19403.5064	(-2)
13	19316.4202	(-1)	19364.7851	(0)	19416.8745	(2)
14	19323.1329	(-8)	19375.1750	(0)	19431.0096	(8)
15	19330.6116	(7)	19386.3597	(0)	19445.9022	(-6)
16	19338.8385	(10)	19398.2928	(0)	19461.5406	(-11)
17	19347.8132	*	19410.9704	(0)	19477.9211	*
18	19357.5409	(4)	19424.4040	(0)	19495.0537	(-5)
19	19368.0341	(0)	19438.5822	(0)	19512.9419	*
20	19379.3138	(0)	19453.5150	(0)	19531.6155	(0)
21	19391.3577	(-2)	19469.2180	(0)	19551.0447	(1)
22	19404.2065	(1)	19485.6815	(0)	19571.2716	(-1)
23	19417.9774	(-1)	19502.8761	(0)	19592.4148	(0)
24	19433.1931	(-2)	19520.9179	(0)	19614.9958	(1)
25	19443.2415	*	19539.8543	(0)	19632.4032	(0)
26	19461.0326	(3)	19559.7406	(0)	19657.5427	(-3)
27	19477.9574	(1)	19581.2722	(0)	19681.8105	(-1)
28	19495.4987	(2)	19592.8685	(0)	19706.6862	(-1)
29	19513.7748	(0)	19618.5600	(0)	19732.2858	*
30	19532.9590	(8)	19642.0456	(0)	19758.7886	(-8)
31	19553.9251	*	19665.5951	(0)	19787.0612	(0)
32	19569.5232	(0)	19689.7091	(0)		
33	19592.1967	(0)	19714.9310	(0)		
34			19740.0143	(0)		
35			19766.4360	(0)		

^a and * — the same as in Tab. II.

3. Analysis and results

The obtained molecular constants for the $B^1\Sigma^+$ ($v = 0$) and $A^1\Pi$ ($v = 1, 2$) levels will be presented and discussed in this section.

3.1. Identification of the spectra

The vibrational-rotational identification of the recorded $B^1\Sigma^+ - A^1\Pi$ transition in the $^{13}\text{C}^{16}\text{O}$ isotopic molecule was started by determining the upper and the lower vibrational level and a preliminary quantum number J -numbering of the lines belonging to the 0-1 and 0-2 bands of the system under consideration as well as assembling all the lines into P , Q , and R branches. It was executed on the basis of the results obtained by Кепа et al. [19].

3.2. Perturbations of the $A^1\Pi$ state

The $A^1\Pi$ electronic state of the CO molecule is the most extensively and intensively perturbed among all states of the diatomic molecules. One can actually observe the perturbations of the rotational structure in each vibrational level. In the region of $66\,000\text{ cm}^{-1}$, in addition to the $A^1\Pi$ state, six other electronic states are located, namely: $I^1\Sigma^-$, $D^1\Delta$, $e^3\Sigma^-$, $a'^3\Sigma^+$, $a^3\Pi_r$, and $d^3\Delta_i$. Therefore there are perturbations of the rotational structure observed in each vibrational level of the A state. They were very often a subject of the analysis during the studies of different band systems involving the $A^1\Pi$ state, like $A^1\Pi - X^1\Sigma^+$ (the fourth-positive band system) [14, 31–32], $C^1\Sigma^+ - A^1\Pi$ (the Herzberg

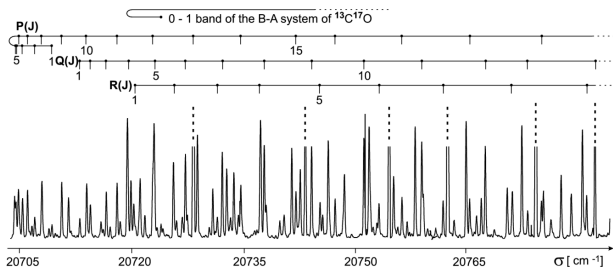


Fig. 2. An expanded view of high resolution spectrum of the 0–1 band of $B^1\Sigma^+ - A^1\Pi$ system in $^{13}\text{C}^{16}\text{O}$ isotopic molecule recorded while receiving the Ångström band system in the very rare $^{13}\text{C}^{17}\text{O}$ isotopologue [23]. The dotted lines indicate the tips of the relatively very strong calibration lines.

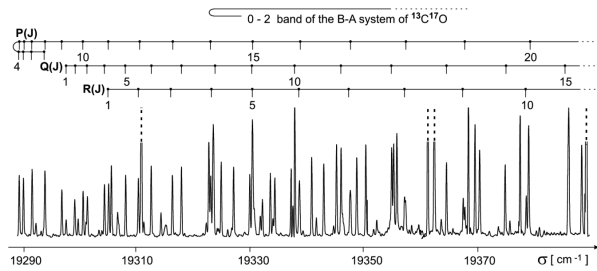


Fig. 3. As in Fig. 2, but for 0–2 band.

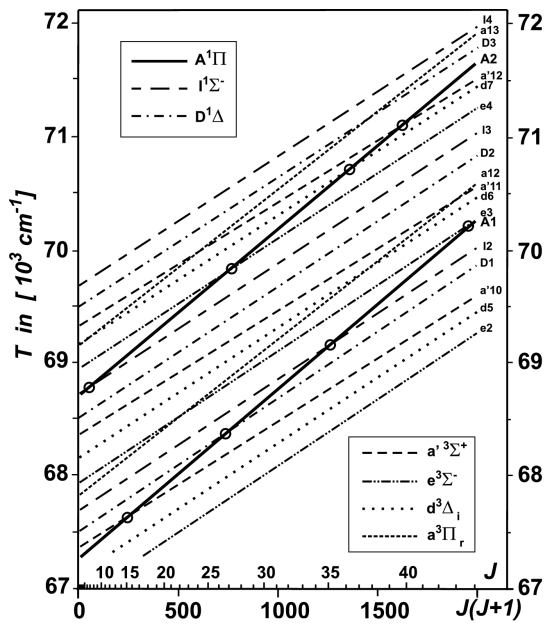


Fig. 4. Values of rovibronic terms of the perturbed $A^1\Pi$, $v = 1$ and 2 levels together with perturbing $I^1\Sigma^-(v = 2-4)$, $D^1\Delta(v = 1-3)$, $e^3\Sigma^-(v = 2-4)$, $a^3\Sigma^+(v = 10-12)$, $d^3\Delta_i(v = 5-7)$, and $a^3\Pi_r(v = 12-13)$ levels of $^{13}\text{C}^{16}\text{O}$ versus $J(J+1)$. The origin is the minimum of the ground state. Points of crossing (marked by circles) show the positions of expected perturbations (compare Table IV) [19].

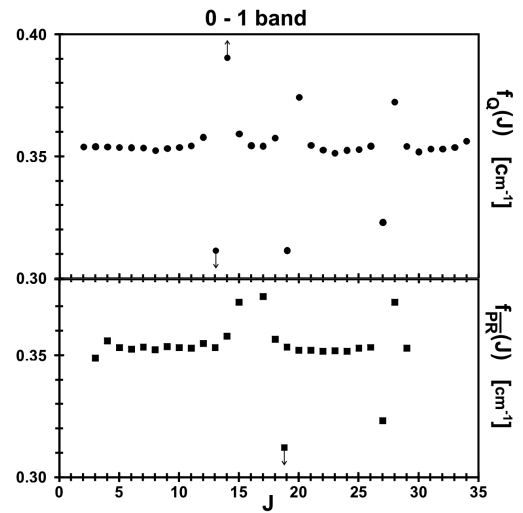


Fig. 5. The $f_x(J)$ functions of Kovács [45], where $x = Q$ or $\overline{P}\overline{R}$, for the 0–1 band of the $B^1\Sigma^+ - A^1\Pi$ system in the $^{13}\text{C}^{16}\text{O}$ isotopic molecule. The ordinate values of the points indicated by arrows go beyond the range established for the charts.

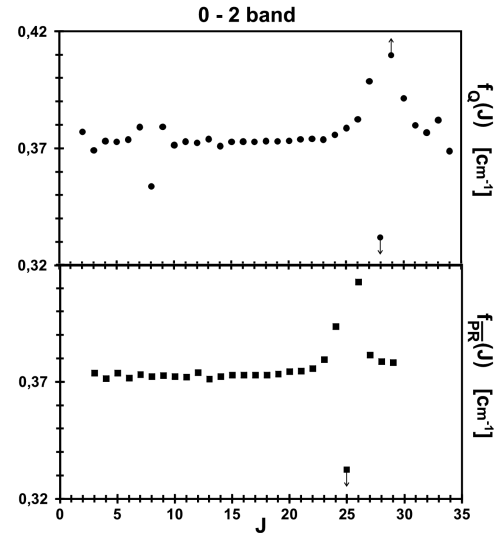


Fig. 6. As in Fig. 5, but for 0–2 band.

band system) [33], $E^1\Pi - A^1\Pi$ (the Keça-Rytel band system) [34].

For the $^{12}\text{C}^{16}\text{O}$ ordinary molecule many perturbations of the $A^1\Pi$ state have been reported [11, 35–38]. A systematic classification of the $A^1\Pi$ state perturbation observed up to 1966 year was carried out by Krupenie [39] and completed by Simmons et al. [37]. The most comprehensive analysis and deperturbation calculation on the basis of the data obtained up to 1971 was performed by Field [35] and Field et al. [38]. Le Floch et al. [40] conducted an extensive study of the $A^1\Pi$ ($v = 0$) state perturbation. Le Floch [41] performed perturbation calculations for the $A^1\Pi$ ($v = 0-4$) state. Finally, Le Floch [42] collected the exact term values for $A^1\Pi$ ($v = 0-8$) state of $^{12}\text{C}^{16}\text{O}$.

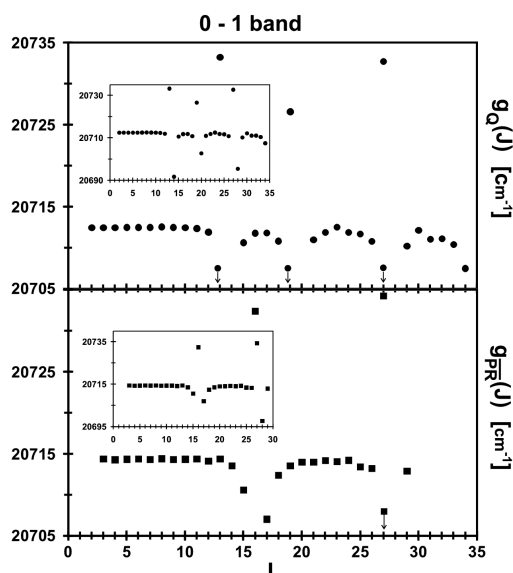


Fig. 7. The $g_x(J)$ functions of Kovács [45], where $x = Q$ or \overline{PR} , for the 0-1 band of the $B^1\Sigma^+ - A^1\Pi$ system in the $^{13}\text{C}^{16}\text{O}$ isotopic molecule. The ordinate values of the points indicated by arrows go beyond the range established for the charts. The small graphs are a compressed view of all the values of these functions in the regions under consideration.

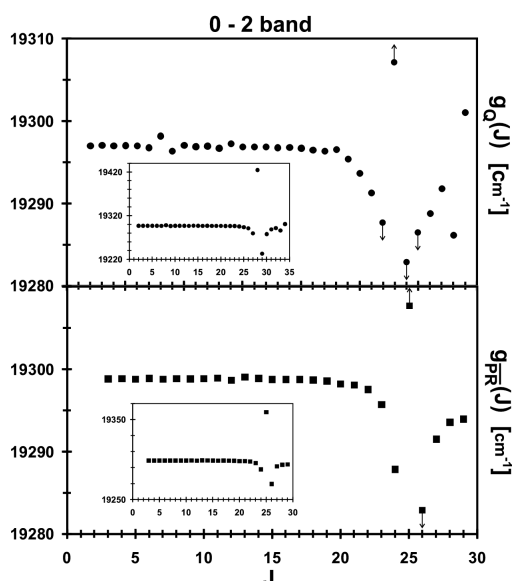


Fig. 8. As in Fig. 7, but for 0-2 band.

There have been comparatively few explorations of the $A^1\Pi$ perturbations in $^{13}\text{C}^{16}\text{O}$ isotopologue. However there is only one paper elaborated by Kępa et al. [19] in which the perturbation analysis results of the A state are presented on the basis of the investigations of extremely favorable to the spectroscopic analysis — the Ångström band system. However, their work does not include an up-to-date analysis of the differences between the observed and calculated term values

$[T(v, J)_{\text{obs}} - T(v, J)_{\text{calc}}]$ of the $A^1\Pi$ state. This analysis has been performed recently by Kępa et al. [32] on the basis of the fourth-positive ($A^1\Pi - X^1\Sigma^+$) band system, but for higher vibrational levels ($v \geq 7$) of the $A^1\Pi$ state.

The predicted perturbations of the $A^1\Pi$ and nearby $I^1\Sigma^-$, $D^1\Delta$, $e^3\Sigma^-$, $a'^3\Sigma^+$, $a^3\Pi_r$, and $d^3\Delta_i$ electronic states in the $^{13}\text{C}^{16}\text{O}$ molecule in the studied range of 19200–21200 cm^{-1} have been recalculated by means of the rovibronic term crossing diagrams. The respective recalculations were performed by making use of the rovibronic structure constants for the $A^1\Pi$ in the range of $v = 1$ and 2 and $J = 1-35$ levels for the A , I , e , a' , a , and d states calculated by Field [35] and by means of the constants for the D state calculated by Kittrell and Garetz [43] for the $^{12}\text{C}^{16}\text{O}$ molecule and recalculated for the $^{13}\text{C}^{16}\text{O}$ isotopologue by means of standard isotope relations. Results are shown in Fig. 4.

Next, the places of occurrence of the observed perturbations in the $A^1\Pi$ state of the $^{13}\text{C}^{16}\text{O}$ were verified again following a course of the $f_x(J)$ and $g_x(J)$ functions, where $x = Q$ and \overline{PR} , as introduced by Gerö [44] and Kovács [45]. In the present case, there is a negligible difference between the centrifugal distortion constants D' and D'' so that $f_x(J)$ and $g_x(J)$ can be displayed simply as functions of J . In the absence of perturbations, such plots become horizontal lines corresponding to the values of $B' - B''$ and $\sigma_{v'-v''}$ for the $f_x(J)$ and $g_x(J)$ functions, respectively. The deviations from the regularity of these functions course indicated the appearance of some specific perturbation interactions and enabled the localization of the observed perturbation. The results were presented in Figs. 5 and 6 for the 0-1 band as well as in Figs. 7 and 8 for the 0-2 band of the $^{13}\text{C}^{16}\text{O}$ molecule.

The perturbation occurrence in the rotational structure of the observed bands can also be directly exhibited by a plot of the deviations $[T(v, J)_{\text{obs}} - T(v, J)_{\text{calc}}]$ versus the rotational quantum number J . The observed (perturbed) $T(v, J)_{\text{obs}}$ rotational term values were obtained by means of the Curl-Dane-Watson method [46, 47] which used all the lines of demanded accuracy, whereas the calculated (unperturbed) $T(v, J)_{\text{calc}}$ rotational term values were calculated on the basis of molecular constants of the $A^1\Pi$ ($v = 1$ and 2) state estimated from rotational lines which were recognized as unperturbed ones (see descriptions in Sect. 3.3). Such plots for the $A^1\Pi$, $v = 1$ and 2 levels of $^{13}\text{C}^{16}\text{O}$ are shown in Fig. 9. As one can see, more or less strong discontinuities occur at different J values for each vibrational $A^1\Pi$ state levels. These are characteristic of the observed perturbations.

Observed and predicted perturbations of the $A^1\Pi$ state in the $^{13}\text{C}^{16}\text{O}$ isotopologue were summarized in Table IV. Hereby, the results presented by Kępa et al. [19] (Table V) were made more precise.

3.3. Molecular parameters

The further analyses of the bands as well as their reduction to the molecular parameters run thanks to a well-known theoretical model, in which both states participating in the explored transition are represented by the

well-known Hamiltonians for both states involved in this transition: for the upper $B^1\Sigma^+$ state

$$\langle H \rangle = T_v + B_v J(J+1) - D_v J^2(J+1)^2 + \dots, \quad (1)$$

and for the lower $A^1\Pi$ state (having the knowledge from the previous works [11, 15, 19] that A -doubling in this state is negligibly small for unperturbed levels):

$$\langle H \rangle = T_v + B_v[J(J+1) - 1] - D_v[J(J+1) - 1]^2 + \dots, \quad (2)$$

where T_v is rotationless energy calculated with respect to the lowest rovibrational level in the $X^1\Sigma^+$ ground state.

TABLE IV

Observed and predicted perturbations of the $A^1\Pi$ state in the $^{13}\text{C}^{16}\text{O}$ isotopologue ^a.

$A^1\Pi(v)$	Maximum of perturbation [J] of the A -doubling component				Perturbing state	
	f -parity		e -parity		triplet component	vibrational level
	obs.	calc.	obs.	calc.		
1	13–14	12–13			$F(1)$	$a'^3\Sigma^+(v=10)$
			16–17	15–16	$F(2)$	
	19–20	18–19			$F(3)$	
	27–28	26–27 ^b	27–28	26–27 ^b		$D^1\Delta(v=1)$
	*	35 ^b				$I^1\Sigma^-(v=2)$
2			*	40–41	$F(1)$	$e^3\Sigma^-(v=3)$
	*	43–44	*	46–47	$F(2)$	
			*		$F(3)$	
	7–8	7 ^b				$I^1\Sigma^-(v=3)$
	28–29	28 ^b	25–26	25 ^b	$F(1)$	$e^3\Sigma^-(v=4)$
		31–32	31 ^b	$F(2)$		
				$F(3)$		
2	33–34	32–33 ^b	*	32–33 ^b	$F(3)$	$d^3\Delta_i(v=7)$
	*	36–37 ^b	*	36–37 ^b	$F(2)$	
	*	40–41 ^b	*	40–41 ^b	$F(1)$	
	*	36–37	*	39–40	$F(1)$	$a'^3\Sigma^+(v=12)$
	*	42–43			$F(2)$	
				$F(3)$		

^a The spaces marked by asterisks indicate the regions experimentally unverified.

^b The improved values in comparison to the values given by Keřpa et al. [19].

It is a well-known fact that the $A^1\Pi$ state is widely and intensively perturbed, whereas the $v=0$ level of the $B^1\Sigma^+$ state is quite regular. That is why the calculations of the molecular constants were performed in stages and by means of several methods.

At the first stage of the calculations, the reduction of wave numbers to rovibronic parameters was calculated within the framework of an individual band-by-band analysis using the linear least-squares method suggested by Curl and Dane [46] and Watson [47]. This method enables us to separate molecular information about the regular $B^1\Sigma^+$ from that concerning irregular $A^1\Pi$ state and determine the individual rotational constants for the $v=0$ level of the $B^1\Sigma^+$ state and the observed (perturbed) $T(v, J)_{\text{obs}}$ rotational term values of the $A^1\Pi$ ($v=1, 2$) derived relative to the upper $B(v=0)$ level of the $^{13}\text{C}^{16}\text{O}$ isotopologue.

At the second stage of the molecular parameters, calculations of the effective B_v and D_v rotational constants of the lower $A^1\Pi$ state levels as well as band origins of the $B^1\Sigma^+ - A^1\Pi$ transition were obtained. In this case both states under consideration were represented by Hamilto-

TABLE V

Effective individual rotational constants (in cm^{-1}) of the $A^1\Pi$ in the $^{13}\text{C}^{16}\text{O}$ molecule ^a.

Constant	This work	Keřpa et al. [19]
B_1	1.511 553(16)	1.511 540(49)
$D_1 \times 10^6$	6.623 ^b	6.623(35)
B_2	1.489 822(22)	1.489 876(54)
$D_2 \times 10^6$	6.133(28)	6.125(51)

^a Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

^b In order to determine the rotational constants with greater precision the value was constrained to the one given by Keřpa et al. [19].

nians given in Eqs. (1) and (2). As for the $A^1\Pi$ state, this model was simplified to the version in which additional perturbing matrix elements were disregarded. Only the carefully selected band lines with negligible effect of the perturbational interactions as well as the well-determined values of molecular constants of the regular $B^1\Sigma^+(v=0)$ upper state have been considered in the least-squares fits.

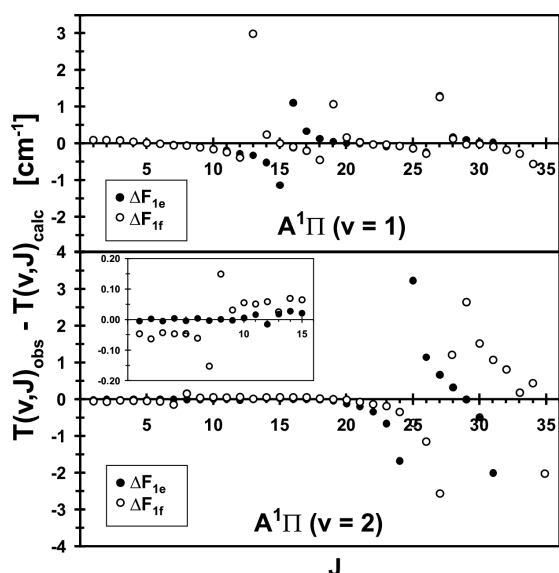


Fig. 9. Differences between the observed and calculated term values [$T(v, J)_{\text{obs}} - T(v, J)_{\text{calc}}$] of the $A^1\Pi$ ($v = 1$ and 2) rovibrational levels versus J in $^{13}\text{C}^{16}\text{O}$. The small graph was zooming the selected region of perturbations.

The constants of the $B(v = 0)$ state were fixed in these fits. The results are highlighted in Tables V and VI for

the rotational constants and for the band origins, respectively. In the frame of the body of this fit the calculated (unperturbed) $T(v, J)_{\text{calc}}$ rotational term values of the $A^1\Pi$ $v = 1$ and 2 state were derived.

TABLE VI

Band origins (in cm^{-1}) for the Ångström system ($B^1\Sigma^+ - A^1\Pi$) of the $^{13}\text{C}^{16}\text{O}$ isotopologue^a.

Band	Band origin		
	this work	Keřa et al. [19]	Rytel [18] ^b
0–1	20711.0586(98)	20711.067(12)	20712.48(2)
0–2	19295.4936(24)	19295.516(11)	19297.02(2)

^a Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

^b Values calculated with included $B_v A^2$ terms of the A state.

The final values of the rotational structure parameters of the studied $B^1\Sigma^+$ state were achieved at the third stage of the calculations, as a result of the least squares merge fittings of all bands analysed in this work, according to the procedure proposed by Albritton et al. [48] and Coxon [49]. In this method, the fitted bands have to have the common upper vibrational level. The estimated variance of the merging was $\sigma_M^2 = 0.62$. The rotational parameter values derived for the explored $v = 0$ level of the $B^1\Sigma^+$ state are gathered in Table VII.

TABLE VII

Rotational constants (in cm^{-1}) of the $B^1\Sigma^+$ in the $^{13}\text{C}^{16}\text{O}$ molecule^{a,b}.

Constant	This work	Keřa et al. [19]	Eidelsberg et al. [21]	Rytel [18]	Tilford et al. [20]
B_0	1.862 505 4(65)	1.862 517(55)	1.862 58(14)	1.862 5(1)	1.862 4
$D_0 \times 10^6$	6.138 4(52)	6.142(28)	6.178(48)	6.20(7)	6.3
B_e	1.874 641(27)	1.874 659(74)	1.874 ₉		
$\alpha_e \times 10^2$	2.427 1(50)	2.428 3(86)	2.4 ₅		
$D_e \times 10^6$	5.834(35)	5.839(54)	6.0 ₀		
$\beta_e \times 10^7$	6.10(68)	6.06(73)			

^a Uncertainties in parentheses represent one standard deviation excluding Eidelsberg et al. [21] data (3σ), in units of the last quoted digit.

^b The equilibrium molecular parameters for the $B^1\Sigma^+$ Rydberg state were calculated on the basis of the obtained in this work B_0 and D_0 values of the rovibronic constants as well as B_1 and D_1 constants derived by Keřa et al. [19].

On the basis of the obtained in this work B_0 and D_0 values of the rovibronic constants as well as B_1 and D_1 derived by Keřa et al. [19], the equilibrium molecular parameters for the $B^1\Sigma^+$ Rydberg state were calculated from a fit of the data in which the number of data equals the number of determined parameters. The standard deviations of equilibrium parameters determined were calculated by means of the Gauss error propagation method. The results were added to Table VII.

4. Discussion and conclusions

This paper presents new observations and modern reanalysis of the high resolution spectrum of the Ångström

($B^1\Sigma^+ - A^1\Pi$) band system of the $^{13}\text{C}^{16}\text{O}$ isotopologue. For this reason, there was a high accuracy dispersive optical spectroscopy used with much better accuracy than the previous ones used for this system so far in the isotope under consideration.

The applied great precision of the measurements for the strongest 0–1 and 0–2 bands of this band system, consisting of 195 emission lines, allowed us to obtain the significantly more precise information, especially regarding the high lying $B^1\Sigma^+$ Rydberg state in the $^{13}\text{C}^{16}\text{O}$ isotopic molecule, which considerably makes our knowledge about the Rydberg states in the carbon monoxide molecule more detailed. To compare, the accuracy

of our investigations was about $(0.002\text{--}0.005)\text{ cm}^{-1}$, towards the best one so far in $^{13}\text{C}^{16}\text{O}$ with this state, which equalled $(0.010\text{--}0.020)\text{ cm}^{-1}$ [19].

Additionally, the experimental data obtained for the extensive perturbed $A^1\Pi$ state in the $^{13}\text{C}^{16}\text{O}$ molecule could be used for a more precise characterization of this state.

In conclusion, we believe that the present results significantly improved the spectroscopic data for the Ångström ($B^1\Sigma^+ - A^1\Pi$) system in the $^{13}\text{C}^{16}\text{O}$ isotopologue and for the CO molecule as a whole.

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