

# Rotational analysis of the Ångström system ( $B^1\Sigma^+-A^1\Pi$ ) in the rare $^{13}\text{C}^{17}\text{O}$ isotopologue

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## ABSTRACT

Although yet unobserved in the very rare  $^{13}\text{C}^{17}\text{O}$  isotopologue, the Ångström system ( $B^1\Sigma^+-A^1\Pi$ ) was obtained under high resolution as an emission spectrum using a conventional spectroscopic technique.

The emission from the discharge was observed with a plane grating spectrograph and recorded by a photomultiplier tube. In total, 192 transition wave numbers belonging to two bands (0–1 and 0–2) were precisely measured and rotationally analyzed. This method allowed us to determine the merged rotational constants  $B_0 = 1.8131941(58) \text{ cm}^{-1}$  and  $D_0 = 5.5620(46) \times 10^{-6} \text{ cm}^{-1}$  and the individual molecular constant  $B_1 = 1.471059(47) \text{ cm}^{-1}$ ,  $D_1 = 5.315(64) \times 10^{-6} \text{ cm}^{-1}$ ,  $B_2 = 1.451762(13) \text{ cm}^{-1}$ ,  $D_2 = 7.812(16) \times 10^{-6} \text{ cm}^{-1}$  for the as yet unanalyzed  $^{13}\text{C}^{17}\text{O}$  molecule  $B^1\Sigma^+$  and  $A^1\Pi$  states, respectively. The band origins  $\sigma_{0-v''}$  of the Ångström system in the  $^{13}\text{C}^{17}\text{O}$  molecule were also calculated.

Numerous rotational perturbations observed in the  $A^1\Pi$  state in  $^{13}\text{C}^{17}\text{O}$  molecule have been identified and analyzed in detail. The suspected candidates responsible for these irregularities were indicated by means of a graph of the rovibronic levels of the neighboring states based on the estimated term value in the  $^{13}\text{C}^{17}\text{O}$  molecule. The values of these perturbations have also been defined for both the  $e$ - and  $f$ -parity of the  $A^1\Pi(v=1 \text{ and } 2)$  state. Simultaneously, the  $B^1\Sigma^+$  state was observed to be quite regular up to the observed  $J_{\text{max}}$  level.

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## 1. Introduction

The carbon monoxide molecule is, except molecular hydrogen, the most abundant molecule in the universe. It can be found in comet tails, interstellar space, planets, solar and stellar atmospheres. A number of carbon monoxide isotopologues have been identified in the solar spectrum [1,2] and in the spectra of different cosmic objects [3–6]. However, the basic information about the spectra and the energetic structure of CO isotopic molecules has been derived from laboratory investigations. Carbon monoxide is also important in other disciplines, such as environmental investigations, chemical physics, the technology of new materials based on connecting metals with carbon monoxide (e.g., metal carbonyls), and medicine. Thus, the interest in this molecule is still growing, especially in the regions of the excited electronic states that were devoted to the Rydberg states, including the first member of the Rydberg  $n\sigma$  series—the  $B^1\Sigma^+$  state. Investigations of this state can be performed by analyzing the following transitions: the Hopfield–Birge ( $B^1\Sigma^+-X^1\Sigma^+$ ) band system, the Ångström ( $B^1\Sigma^+-A^1\Pi$ ) system, the ( $B^1\Sigma^+-d^3\Delta$ ) transition, the Amiot–Rocin–Verges ( $E^1\Pi-B^1\Sigma^+$  and  $C^1\Sigma^+-B^1\Sigma^+$ ) systems, as well as transitions between

highly excited  $W^1\Pi$ ,  $K^1\Sigma^+$ ,  $L^1\Pi$  and  $n=8-10$  of the  $s$ ,  $p$ ,  $d$  and  $f$  Rydberg states and the  $B^1\Sigma^+$  as a lower state. However, the most comprehensive information about the  $B^1\Sigma^+(v=0 \text{ and } 1)$  state was derived from analyses of the Ångström bands system.

The  $B^1\Sigma^+-A^1\Pi$  bands system of CO has been the subject of numerous studies since its discovery by Ångström [7] in the principal isotopologue [8–11] as well as in minor isotopologues:  $^{12}\text{C}^{18}\text{O}$  [12];  $^{13}\text{C}^{16}\text{O}$  [12,13];  $^{13}\text{C}^{18}\text{O}$  [14]; and  $^{14}\text{C}^{16}\text{O}$  [15,16]. However, the  $B^1\Sigma^+-A^1\Pi$  system has never been observed in the rare  $^{13}\text{C}^{17}\text{O}$  isotopologue.

Here, we investigate a new isotope of the CO molecule in order to obtain additional information about this very important molecule as well as to verify pre-existing data concerning this molecule. Furthermore, our research will enlarge the body of isotopic information in regards to the spectrum and energetic structure of the isotopologue being investigated.

This work presents experimental details as well as the analysis of the obtained  $B^1\Sigma^+-A^1\Pi$  bands system in the  $^{13}\text{C}^{17}\text{O}$  isotopologue for the first time.

## 2. Experimental details

The spectrum of the  $B^1\Sigma^+-A^1\Pi$  transition of rare  $^{13}\text{C}^{17}\text{O}$  isotopologue was excited in a water-cooled hollow-cathode lamp with

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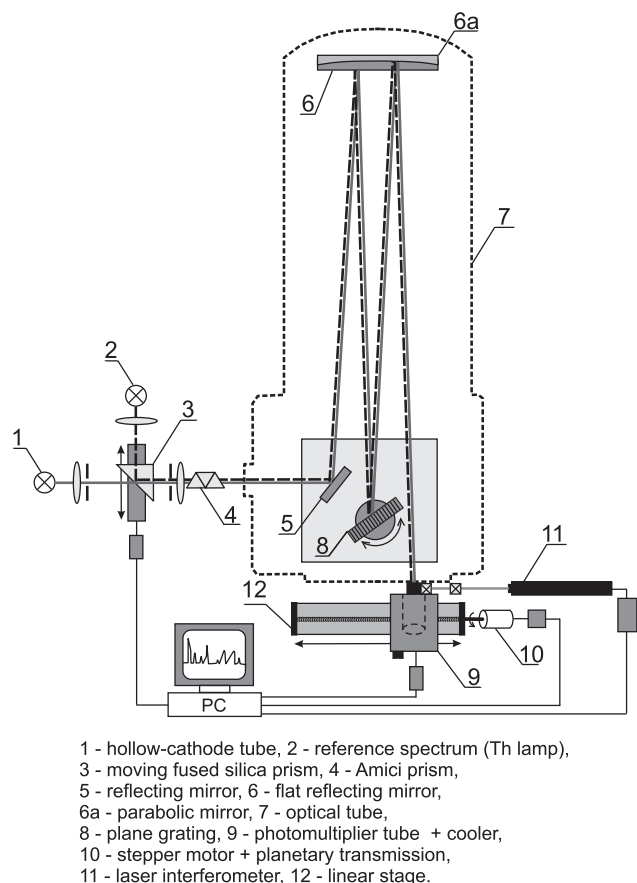


Fig. 1. Experimental setup.

two anodes described by Bacis [17]. The anodes were operated at  $2 \times 650$  V and  $2 \times 50$  mA dc as well as  $2 \times 670$  V and  $2 \times 35$  mA dc during the recording of the 0–1 and 0–2 bands, respectively.

The lamp was initially filled with a mixture of helium and acetylene  $^{13}\text{C}_2\text{D}_2$  (99% of  $^{13}\text{C}$ ) under the pressure of approximately 6 Torr of the acetylene plus 1 Torr of the helium. The electric current was passed through the mixture for about 120 h. After a small quantity of  $^{13}\text{C}$  carbon became deposited on the electrodes, the lamp was evacuated and oxygen containing 60% of the isotope  $^{17}\text{O}$  was admitted 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 equipped with a 651-grooves/mm grating with a total number of grooves of 45600, blazed at  $1.0\ \mu\text{m}$  in the 5th and 4th order for the 0–1 and 0–2 bands of the Ångström system, respectively. The reciprocal dispersion was in the range of  $0.09\text{--}0.14\ \text{nm/mm}$ , 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 widths were  $35\ \mu\text{m}$ . The line intensities were measured using a single photon counting system (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 a 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  $3\ \mu\text{m}$  (the sample step is the translation of the exit slit during the counter gate time).

This type of spectrograph is very sensitive to the 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 the physical position of the spectrum (a few microns). In order to reduce these fluctuations, 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  $0.2\ ^\circ\text{C}$  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 measurements of physical spectra positions was tested to be  $0.2\text{--}0.5\ \mu\text{m}$  according to the variations of the atmospheric pressure. The clear diagram of the experimental setup is shown in Fig. 1.

Simultaneously recorded thorium atomic lines [18], obtained from several overlapped orders of the spectrum from a water-cooled, hollow-cathode tube, were used for absolute wavenumber calibration. The physical 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 physical peak position for a single line was approximately  $0.1\text{--}0.2\ \mu\text{m}$ ). For the wavenumbers calculations, the third-order and the 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  $0.0016\ \text{cm}^{-1}$ . 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 have an accuracy of  $0.0015\ \text{cm}^{-1}$ .

The CO lines have spectral widths of approximately  $0.15\ \text{cm}^{-1}$  and appear with a maximum signal-to-noise ratio of approximately 100:1 and 130:1 for the 0–1 and 0–2 band, respectively. The most intense lines produced a count rate of approximately 50 000 photons/s for the 0–1 and approximately 80 000 photons/s for the 0–2 band. Consequently, the positions for strong and isolated lines were determined with an accuracy better than  $\pm 0.002\ \text{cm}^{-1}$ . However, some weaker and blended lines were measured with a lesser accuracy of  $\pm 0.005\ \text{cm}^{-1}$ . The statistical information for the analyzed bands is shown in Table 1. In total, 192 lines belonging to 0–1 and 0–2 bands of the  $B^1\Sigma^+ \text{--} A^1\Pi$  system in the  $^{13}\text{C}^{17}\text{O}$  isotopologue have been measured, and their wavenumbers are presented in Tables 2 and 3.

The bands belonging to the  $B^1\Sigma^+ \text{--} A^1\Pi$  transition of  $^{13}\text{C}^{17}\text{O}$  isotopologue were observed in the  $19\,300\text{--}21\,200\ \text{cm}^{-1}$  spectral region at  $20\,726.1104(74)\ \text{cm}^{-1}$  and  $19\,328.6558(16)\ \text{cm}^{-1}$  for the (0–1) and (0–2) band, respectively. The parts of their high quality spectrum, especially in the range of their band heads, are shown in Figs. 2 and 3, where clearly resolved lines of the R and P and Q branches are rotationally assigned.

Table 1

Summary of observations and analyses of the Ångström system ( $B^1\Sigma^+ \text{--} A^1\Pi$ ) in the  $^{13}\text{C}^{17}\text{O}$  isotopologue.

Band	Band head ( $\text{cm}^{-1}$ )	Total number of lines	Number of lines actually employed in the fits	$J_{\text{max}}$	$\sigma^a \times 10^3$ ( $\text{cm}^{-1}$ )
0–1	20 719.481	94	82	34	2.90
0–2	19 322.830	98	95	35	1.28

<sup>a</sup> Standard deviation of the fit for the individual band analysis.

**Table 2**Wavenumbers (in  $\text{cm}^{-1}$ ) and their rotational assignments for the 0–1 band of the  $B^1\Sigma^+-A^1\Pi$  system in the  $^{13}\text{C}^{17}\text{O}$  isotopologue.<sup>a</sup>

$J$	$P_{11ee}(J)$		$Q_{11fe}(J)$		$R_{11ee}(J)$	
1	20724.0572	*	20727.5842	(0)	20734.9369	(0)
2	20721.8769	(24)	20728.9351	(0)	20740.0032	(–24)
3	20720.3831	(0)	20730.9991	(0)	20745.7752	(96)
4	20719.6044	(–10)	20733.8270	(0)	20752.2395	(10)
5	20719.4806	(–5)	20737.3654	(0)	20759.3642	(6)
6	20720.0854	(–11)	20741.6148	(0)	20767.2181	(12)
7	20721.2353	(0)	20746.5201	(0)	20775.6219	*
8	20723.1486	*	20752.0387	(0)	20784.7560	(0)
9	20725.7089	(30)	20758.2600	(0)	20794.5654	(–31)
10	20728.9351	(–37)	20765.1446	(0)	20805.0445	(38)
11	20732.8691	(10)	20772.6932	(0)	20816.2055	(–10)
12	20737.4682	(6)	20780.9195	(0)	20828.0390	(–6)
13	20742.7483	(5)	20789.8263	(0)	20840.5494	(–5)
14	20748.7130	(–41)	20799.4072	(0)	20853.7498	(41)
15	20755.3584	*	20809.7099	(0)	20867.6228	(0)
16	20762.7031	*	20820.6175	(0)	20882.1614	(0)
17	20770.7135	(17)	20832.2416	(0)	20897.3939	(–18)
18	20779.4124	(24)	20844.5506	(0)	20913.3011	(–23)
19	20788.8047	(0)	20857.5426	(0)	20929.8818	*
20	20798.8864	*	20871.2082	(0)	20947.1390	(0)
21	20809.6564	*	20885.5786	(0)	20965.1024	(0)
22	20821.0789	*	20900.6215	(0)	20983.7289	(0)
23	20833.2262	*	20916.3587	(0)	21003.0507	(0)
24	20846.0404	(0)	20932.7616	(0)	21023.0555	*
25	20859.5761	(–8)	20949.8930	(0)	21043.7838	(7)
26	20873.8063	(–8)	20967.7292	(0)	21065.1765	(8)
27	20888.8046	(16)	20984.1368	(0)	21087.3253	(–16)
28	20904.7103	(–9)	21004.4734	(0)	21110.3840	(8)
29	20920.1324	(0)	21024.8608	(0)	21132.9447	(–1)
30	20937.7423	(0)	21045.5279	(0)		
31	20954.6518	(0)	21066.7696	(0)		
32			21088.7795	(0)		
33			21111.3716	(0)		
34			21134.2721	(0)		

\* Denotes less accurate lines not used in the evaluation of molecular constants of the  $B^1\Sigma^+$ .✓ Denotes the selected band lines with negligible effect of the perturbation used to the calculation of the effective individual rotational constants of the  $A^1\Pi$  state as well as the bands origins  $\sigma_{(0-v'')}$ .<sup>a</sup> Figures in parentheses denote observed minus calculated values in units of  $10^{-4} \text{ cm}^{-1}$ .

### 3. Analysis and results

The vibrational identification of the initial recording for the  $B^1\Sigma^+-A^1\Pi$  transition in the  $^{13}\text{C}^{17}\text{O}$  isotopologue and a preliminary  $J$ -numbering of the rotational lines belonging to the 0–1 and 0–2 bands was conducted based on the information about the  $B^1\Sigma^+$  and  $A^1\Pi$  states in the  $^{13}\text{C}^{16}\text{O}$  contained in the work of Keça et al. [13] by means of Dunham's isotopic relationship. The appropriate formulas were given by Dunham [19] and Brown et al. [20]. The final analysis of the bands and reduction of the spectrum to molecular constants have been performed in several stages by means of a few methods and using 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 [11,13,16] that  $\Lambda$ -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.

The analysis of perturbations (described in detail in Section 4 of this paper) convinced us that the  $\nu=0$  level of the  $B^1\Sigma^+$  state in  $^{13}\text{C}^{17}\text{O}$  is regular, whereas the  $A^1\Pi$  state is very strongly perturbed as in other known isotopologues of CO.

Due to those perturbations, in the first stage of the calculations, the method of an individual band-by-band analysis using the linear least-squares method suggested by Curl and Dane [21] and Watson

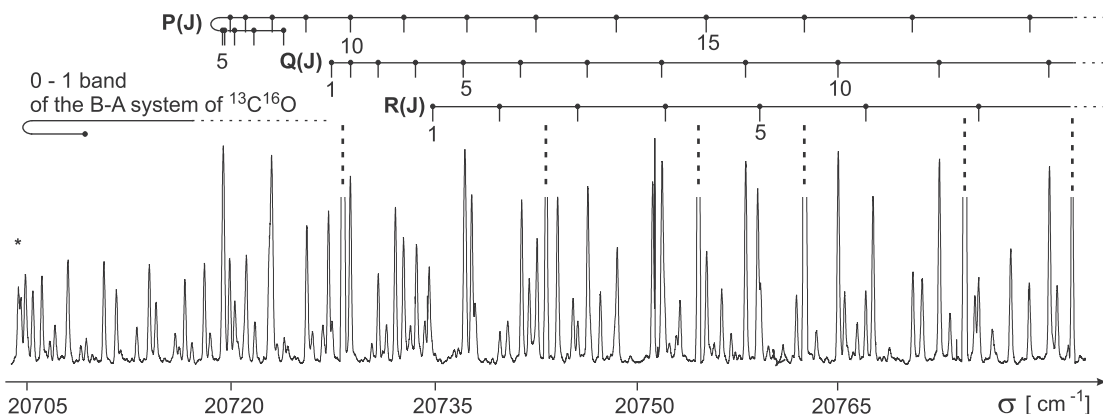
[22] was implemented. This method enabled us to separate molecular information about the  $B^1\Sigma^+$  regular state from that concerning the irregular  $A^1\Pi$  state and to determine the individual rotational constants for the  $\nu=0$  level of the  $B^1\Sigma^+$  state and the real (perturbed)  $T(\nu, J)_{\text{obs}}$  term values of the  $A^1\Pi(\nu=1, 2)$  state derived relative to the upper  $B(\nu=0)$  level (the perturbed lines have been included in the fit).

The final constant values for the  $B^1\Sigma^+$  state were conducted using the least squares merge fittings implemented for the 0–1 and 0–2 bands of the  $B^1\Sigma^+-A^1\Pi$  transition in the  $^{13}\text{C}^{17}\text{O}$  isotopologue as described by Albritton et al. [23] and Coxon [24]. The estimated variance of the merging and the number of degrees of freedom were  $\sigma_M^2 = 0.27$  and  $f_M = 2$ , respectively. The results are presented in Table 4.

The calculation of the effective individual rotational constants of the  $A^1\Pi$  state as well as the bands origins  $\sigma_{(0-v'')}$  were determined in connection with its very strong and complicated perturbations. In this case, both states considered were represented by Hamiltonians given by Eqs. (1) and (2). Only the carefully selected band lines with negligible effect of the perturbational interactions (indicated by checkmarks in the Tables 2 and 3) as well as the well-determined values of molecular constants of the regular  $B^1\Sigma^+$  upper state have been considered in the least-squares procedure using a computer program described previously [25]. The constants of the  $B$  state were fixed in these fits. The results are highlighted in Tables 5 and 6 for the rotational constants and for the band origins, respectively. In the frame of the body of this fit, the calculated (un-perturbed)  $T(\nu, J)_{\text{calc}}$  rotational term values of the  $A^1\Pi \nu=1$  and 2 state were derived.

**Table 3**Wavenumbers (in  $\text{cm}^{-1}$ ) and their rotational assignments for the 0–2 band of the  $B^1\Sigma^+ - A^1\Pi$  system in the  $^{13}\text{C}^{17}\text{O}$  isotopologue.<sup>a</sup>

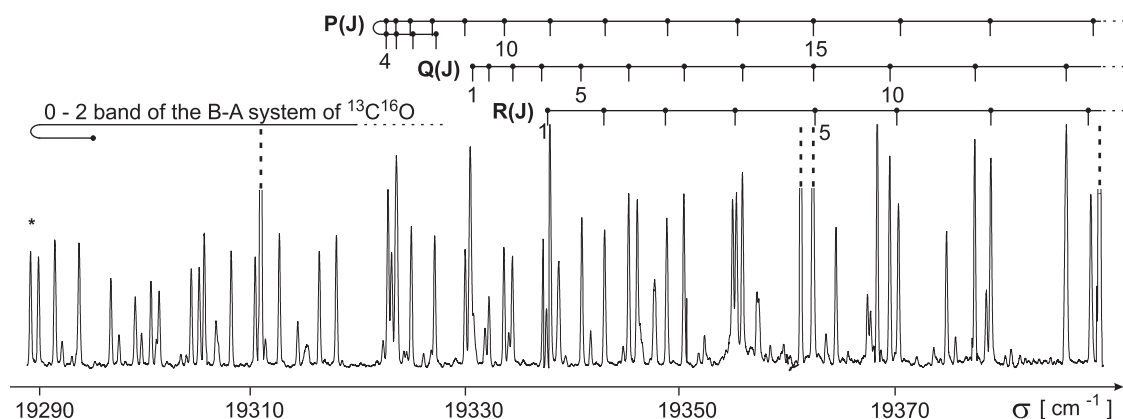
$J$	$P_{11ee}(J)$	$Q_{11fe}(J)$	$R_{11ee}(J)$
1	19327.2088 *	19330.8170 (0)	19338.0877 (0)
2	19325.0191 (–1)	19332.2655 (0)	19343.1506 (2)
3	19323.5720 (2)	19334.4386 (0)	19348.9543 (–2)
4	19322.8299 (5)	19337.3297 (0)	19355.4622 (–5)
5	19322.8299 (–13)	19340.9522 (0)	19362.7153 (14)
6	19323.5358 (4)	19345.3216 (0)	19370.6657 (–3)
7	19324.9890 (–5)	19350.4903 (0)	19379.3670 (6)
8	19327.1419 (4)	19355.9822 (0)	19388.7622 (–4)
9	19330.0394 (–2)	19362.6535 (0)	19398.9027 (2)
10	19333.6522 (1)	19369.8487 (0)	19409.7543 (–1)
11	19337.9987 (0)	19377.8294 (0)	19421.3377 (1)
12	19343.0763 (–3)	19386.5091 (0)	19433.6492 (2)
13	19348.8704 (–2)	19395.9283 (0)	19446.6735 (3)
14	19355.3972 (–2)	19406.0698 (0)	19460.4268 (2)
15	19362.6535 (–3)	19416.9433 (0)	19474.9060 (3)
16	19370.6386 (2)	19428.5330 (0)	19490.1086 (–2)
17	19379.3670 (–4)	19440.8637 (0)	19506.0523 (3)
18	19388.8249 (–4)	19453.9171 (0)	19522.7198 (4)
19	19399.0292 (15)	19467.7095 (0)	19540.1249 (–14)
20	19409.9920 *	19482.2308 (0)	19558.2863 *
21	19421.7113 (–5)	19497.5055 (0)	19577.2041 (4)
22	19434.2684 (–4)	19513.5280 (0)	19596.9492 (4)
23	19447.8381 (–5)	19530.3160 (0)	19617.7012 (5)
24	19463.7688 (6)	19547.8862 (0)	19640.8055 (–6)
25	19473.2003 (8)	19566.3454 (0)	19657.4058 (–9)
26	19489.5472 (22)	19586.0166 (0)	19680.9126 (–22)
27	19505.7147 (–11)	19607.7714 (0)	19704.2421 (11)
28	19523.6485 (–14)	19619.5884 (0)	19729.3244 (13)
29	19541.6238 (19)	19645.6570 (0)	19754.4338 (–19)
30	19560.3684 (–16)	19668.5565 (0)	19780.3181 (17)
31	19580.0276 (0)	19691.9317 (0)	
32	19595.0452 (0)	19715.6738 (0)	
33	19617.7012 (0)	19740.8158 (0)	
34		19753.4135 (0)	
35		19789.4558 (0)	

\* Denotes less accurate lines not used in the evaluation of molecular constants of the  $B^1\Sigma^+$ .✓ Denotes the selected band lines with negligible effect of the perturbation used to the calculation of the effective individual rotational constants of the  $A^1\Pi$  state as well as the bands origins ( $\sigma_{(0-2^0)}$ ).<sup>a</sup> Figures in parentheses denote observed minus calculated values in units of  $10^{-4} \text{ cm}^{-1}$ .**Fig. 2.** An expanded view of the 0–1 band of the  $B^1\Sigma^+ - A^1\Pi$  transition in the rare  $^{13}\text{C}^{17}\text{O}$  isotopologue. The less intense 0–1 band of the Ångström system in the  $^{13}\text{C}^{16}\text{O}$  molecule (its band head is marked with asterisk) is regarded here as an isotopic contaminant. The dotted lines indicate the tips of the relatively very strong calibration lines.

#### 4. Perturbations of the $A^1\Pi$ state

It is known that the  $A^1\Pi$  state of the CO molecule belongs to the most extensively and most intensively perturbed states among diatomic molecules. Six other electronic states are located in the region of  $66000 \text{ cm}^{-1}$  in addition to the  $A^1\Pi$  state, 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.

The numerous and extensive perturbations of the  $A^1\Pi$  state in the  $^{12}\text{C}^{16}\text{O}$  molecule have already been repeatedly described and analyzed [11,26–29]. The most comprehensive analysis and deperturbation calculation on the basis on the data obtained up to 1971 were performed by Field [26] and Field et al. [29]. Le Floch et al. [30] conducted an extensive study of the  $A^1\Pi$  ( $v=0$ ) state perturbation. Le Floch [31] performed perturbation calculations for the  $A^1\Pi$  ( $v=0-4$ ) state. Finally, Le Floch [32] collected the exact term values for  $A^1\Pi$  ( $v=0-8$ ) state of  $^{12}\text{C}^{16}\text{O}$ .



**Fig. 3.** An expanded view of the 0–2 band of the  $B^1\Sigma^+ - A^1\Pi$  transition in the rare  $^{13}\text{C}^{17}\text{O}$  isotopologue. The less intense 0–2 band of the Ångström system in the  $^{13}\text{C}^{16}\text{O}$  molecule (its band head is marked with asterisk) is regarded here as an isotopic contaminant. The dotted lines indicate the tips of the relatively very strong calibration lines.

**Table 4**

Rotational constants (in  $\text{cm}^{-1}$ ) of the  $B^1\Sigma^+$  in the  $^{13}\text{C}^{17}\text{O}$  molecule.<sup>a</sup>

Constant	Individual		Merged constant
	From 0–1 band	From 0–2 band	
$B_0$	1.813186(35)	1.813195(12)	1.8131941(58)
$D_0 \times 10^6$	5.563(27)	5.5617(92)	5.5620(46)

<sup>a</sup> Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

**Table 5**

Effective individual rotational constants (in  $\text{cm}^{-1}$ ) of the  $A^1\Pi$  in the  $^{13}\text{C}^{17}\text{O}$  molecule.<sup>a</sup>

Level	$B_v$	$D_v \times 10^6$
$v = 1$	1.471059(47)	5.315(64)
$v = 2$	1.451762(13)	7.812(16)

<sup>a</sup> Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

**Table 6**

Bands origins (in  $\text{cm}^{-1}$ ) for the Ångström system ( $B^1\Sigma^+ - A^1\Pi$ ) of the  $^{13}\text{C}^{17}\text{O}$  molecule.<sup>a</sup>

Band	Band origin
0–1	20726.1104(74)
0–2	19328.6558(16)

<sup>a</sup> Uncertainties in parentheses represent one standard deviation in units of the last quoted digit.

Much less information is available for other isotopologues. However, there is currently no information concerning the perturbations for the A state in the rare  $^{13}\text{C}^{17}\text{O}$  isotopologue. The analyses of perturbations in minor isotopologues can be the source of additional information about the nearby electronic states interacting with the A state as well as simultaneously verifying the already known perturbations and the quality of the molecular constants of all interacting states in the CO molecule.

Thus, the present analysis of the perturbation in the  $A^1\Pi$  state of the  $^{13}\text{C}^{17}\text{O}$  has been performed by means of comparisons of the observed perturbations with those predicted theoretically. The identification and classification of irregularities were carried out by means of the appropriate functions  $f_x(J)$  and  $g_x(J)$  (where  $x = Q, PR$ , and  $\overline{PR}$ ), as introduced by Gerö [33] and Kovács [34]:

$$f_Q(J) = [Q(J) - Q(J-1)]/2J \quad (3)$$

$$f_{PR}(J) = [P(J+1) - P(J) + R(J-1) - R(J-2)]/4J \quad (4)$$

$$f_{\overline{PR}}(J) = [P(J) - P(J-1) + R(J) - R(J-1)]/4J \quad (5)$$

$$g_Q(J) = [(J+1)Q(J-1) - (J-1)Q(J)]/2 \quad (6)$$

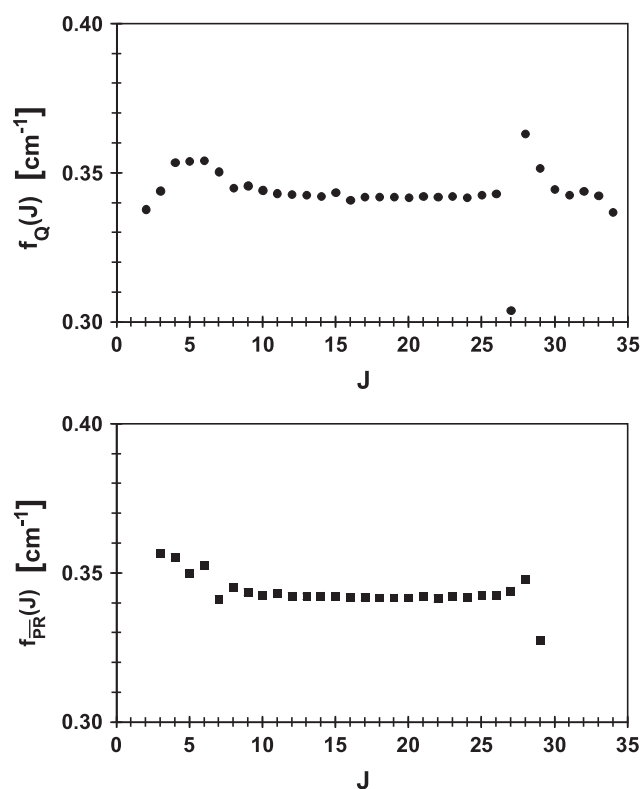
$$g_{PR}(J) = (J+1)[P(J) + R(J-2)] - (J-1)[P(J+1) + R(J-1)]/4 \quad (7)$$

$$g_{\overline{PR}}(J) = (J+1)[P(J-1) + R(J-1)] - (J-1)[P(J) + R(J)]/4 \quad (8)$$

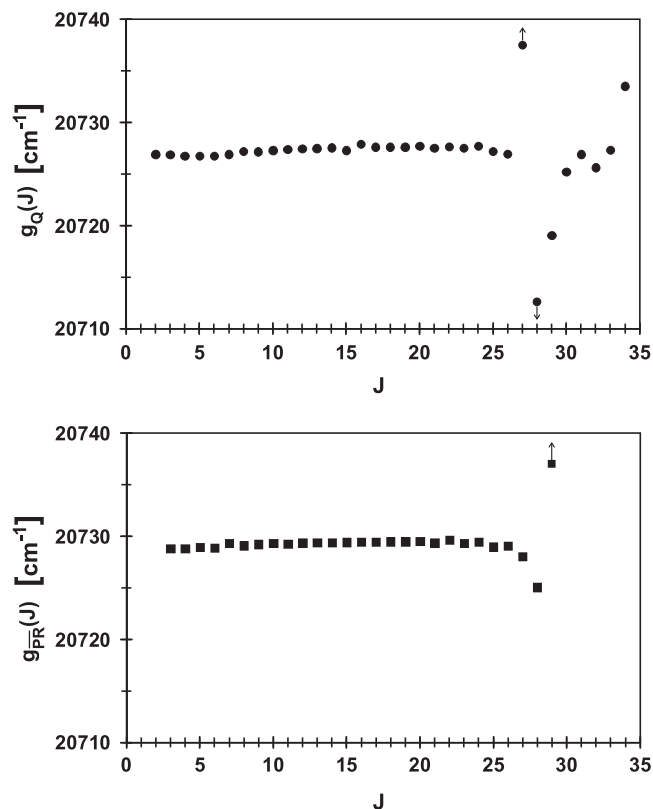
The most important area of applying these functions is the discovery and identification of rotational perturbations. If irregularities appear in the Q branch, formulae (3) and (6) should be applied, irrespective of whether this perturbation affects an upper or lower state of the system discussed. If irregularities appear in the P or R branches, then formulae (4) and (7) or (5) and (8) should be examined, depending on whether the perturbation is observed in an upper or lower state, respectively. Graphs  $f_x(J)$  in  $J^2$  and  $g_x(J)$  in  $J^2(J^2 - 1)$  functions, linear and regular in the unperturbed intervals, will either rise or fall in the neighborhood of points of perturbation passing over into regular lines, depending on whether the rotational constants of the perturbing term is greater or smaller than that of the perturbed term. These deviations from the linear course of the graphs make fixing of the rotational constants of the perturbing term possible. In the present case, there is a negligible difference between the centrifugal distortion constants  $D'$  and  $D''$  such 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 selected charts for the 0–1 and 0–2 bands of the Ångström system in the  $^{13}\text{C}^{17}\text{O}$  isotopologue are shown in the Figs. 4 and 5 as well as in the Figs. 6 and 7, respectively.

The analysis of the course of these functions calculated from the lines of the respective branches and bands allows us to localize  $(J)$  and identify the perturbing state. The predicted perturbations of the  $A^1\Pi$  and nearby lying  $I^1\Sigma^+$ ,  $D^1\Delta$ ,  $e^3\Sigma^-$ ,  $a^3\Sigma^+$ ,  $a^3\Pi_r$ , and  $d^3\Delta_i$  electronic states in the  $^{13}\text{C}^{17}\text{O}$  molecule have been calculated by means of the rovibronic term crossing diagrams shown in the Fig. 8. The respective calculations were performed by making use of the rovibronic structure constants for the  $A^1\Pi$  in the range of  $v = 1$  and  $J = 1-35$  levels for the A, I, e,  $a'$ , a and d states calculated by Field [26] and by means of the constants for the D state calculated by Kittrell and Garetz [35] for the  $^{12}\text{C}^{16}\text{O}$  molecule and recalculated for the  $^{13}\text{C}^{17}\text{O}$  molecule by means of standard isotope relations. Table 7 presents the comparison of the perturbations observed and predicted for both  $\Lambda$ -doubling components of the  $A^1\Pi$  state in the  $^{13}\text{C}^{17}\text{O}$  molecule.

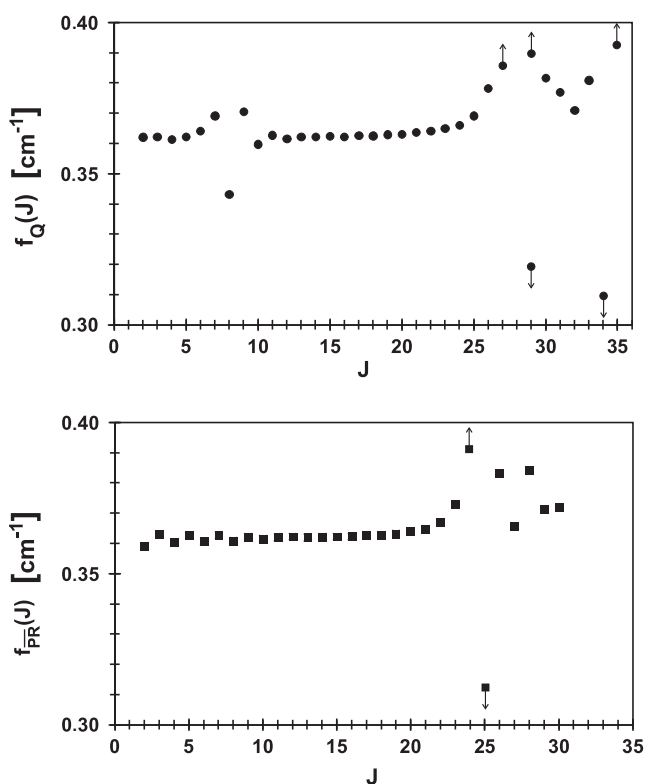




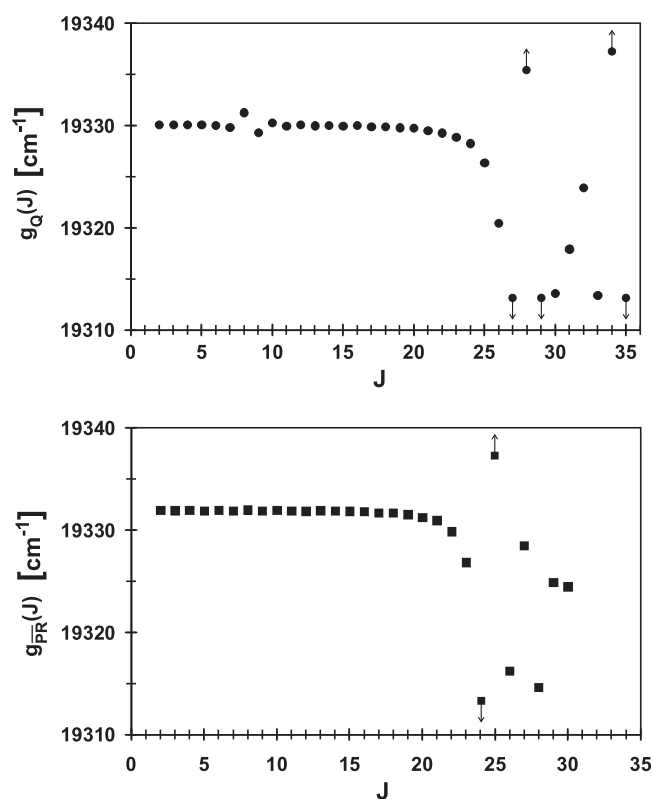
**Fig. 4.** The  $f_x(J)$  functions for the 0–1 band of the  $B^1\Sigma^+-A^1\Pi$  system in the  $^{13}\text{C}^{17}\text{O}$  molecule. The functions were introduced by Kovács [34], where  $x = Q$  or  $\overline{PR}$ .



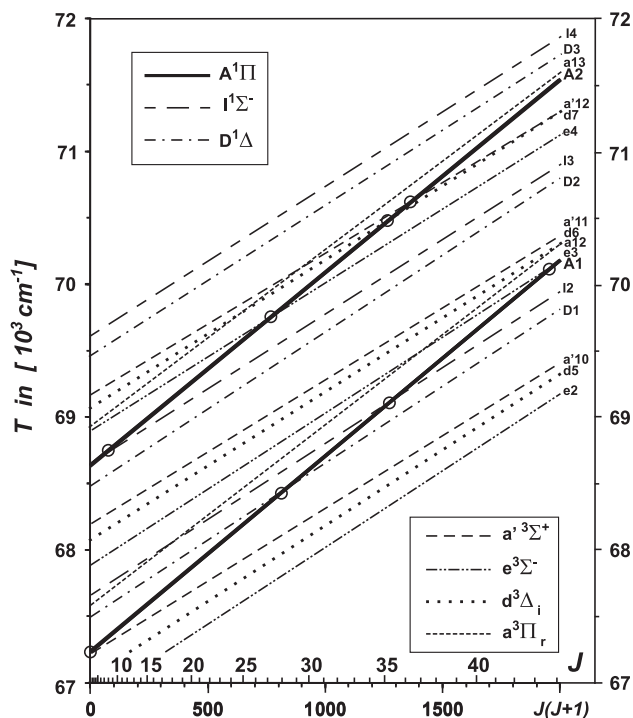
**Fig. 6.** The  $g_x(J)$  functions for the 0–1 band of the  $B^1\Sigma^+-A^1\Pi$  system in the  $^{13}\text{C}^{17}\text{O}$  molecule. The functions were introduced by Kovács [34], where  $x = Q$  or  $\overline{PR}$ . The ordinate values of the points indicated by arrows go beyond the range established for the charts.



**Fig. 5.** The  $f_x(J)$  functions for the 0–2 band of the  $B^1\Sigma^+-A^1\Pi$  system in the  $^{13}\text{C}^{17}\text{O}$  molecule. The functions were introduced by Kovács [34], where  $x = Q$  or  $\overline{PR}$ . The ordinate values of the points indicated by arrows go beyond the range established for the charts.



**Fig. 7.** The  $g_x(J)$  functions for the 0–2 band of the  $B^1\Sigma^+-A^1\Pi$  system in the  $^{13}\text{C}^{17}\text{O}$  molecule. The functions were introduced by Kovács [34], where  $x = Q$  or  $\overline{PR}$ . The ordinate values of the points indicated by arrows go beyond the range established for the charts.

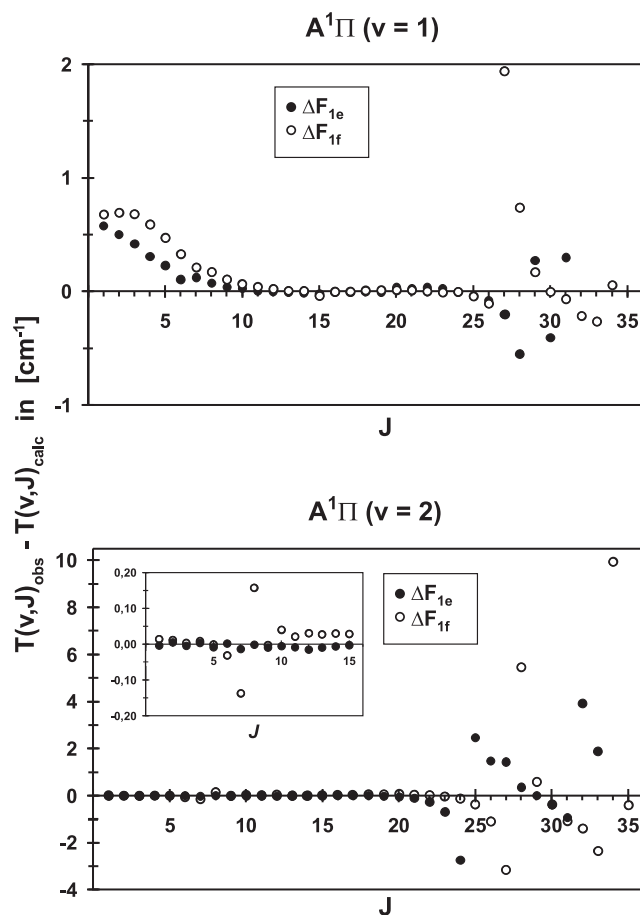


**Fig. 8.** Values of rovibronic terms of the perturbed  $A^1\Pi v = 1$  and 2 levels together with six nearby lying perturbing electronic states in the rare  $^{13}\text{C}^{17}\text{O}$  isotopologue. The origin is the minimum of the ground state. Points of crossing (marked by circles) show the positions of expected interactions. Compare Table 7.

In order to obtain more precise estimates of the magnitudes of the perturbation value the observed (perturbed)  $T(v, J)_{\text{obs}}$  term values of the  $A^1\Pi(v = 1, 2)$  state were compared to those of the calculated (un-perturbed)  $T(v, J)_{\text{calc}}$  ones. The results are presented in Fig. 9. Methods used to obtain these both kinds of the rotational term values were given in Section 3.

## 5. Discussion and conclusions

This paper presents observations and analysis of the high resolution spectrum of the Ångström ( $B^1\Sigma^+ - A^1\Pi$ ) system for the first



**Fig. 9.** Differences between the observed and calculated term values  $[T(v, J)_{\text{obs}} - T(v, J)_{\text{calc}}]$  of the  $A^1\Pi(v = 1, 2)$  rovibrational levels versus  $J$  in  $^{13}\text{C}^{17}\text{O}$ . The small graph is a magnification of the selected region of perturbations.

time in the rare  $^{13}\text{C}^{17}\text{O}$  isotopologue by using a conventional spectroscopic technique.

The applied high precision of the measurements for the 0–1 and 0–2 bands, consisting of 192 emission lines, enabled us to obtain

**Table 7**

Observed and predicted perturbations of the  $A^1\Pi$  state in the rare  $^{13}\text{C}^{17}\text{O}$  isotopologue.<sup>a</sup>

$A^1\Pi(v)$	Level crossing ( $J$ )				Perturbing state	
	$f$ -Parity		$e$ -Parity		Triplet	Vibrational
	Obs.	Calc.	Obs.	Calc.	Component	Level
1	<1	<1	<1	<1	$F(1)$	$a'^3\Sigma^+(v = 10)$
	<1	<1	<1	<1	$F(2)$	
	<1	<1	<1	<1	$F(3)$	
	27–28	27–28	28–29	27–28		$D^1\Delta(v = 1)$
	*	35	*	40–41		$I^1\Sigma^-(v = 2)$
	*	43–44	*	46–47		$e^3\Sigma^-(v = 3)$
2	7–8	7	24–25	24–25	$F(1)$	$I^1\Sigma^-(v = 3)$
	27–28	27–28	31–32	30–31	$F(2)$	$e^3\Sigma^-(v = 4)$
	31–32	31	31	31	$F(3)$	
	34–35	35	*	35	$F(3)$	
	*	39	*	39	$F(2)$	$d^3\Delta_i(v = 7)$
	33–34	33–34	*	36–37	$F(1)$	
	*	39–40	*	36–37	$F(2)$	
	*	39–40	*	36–37	$F(3)$	$a'^3\Sigma^+(v = 12)$
	*	39–40	*	36–37		
	*	39–40	*	36–37		

<sup>a</sup> The spaces marked by asterisks indicate the regions experimentally unverified.

precise information regarding the high lying  $B^1\Sigma^+$  state in the  $^{13}\text{C}^{17}\text{O}$  molecule, which considerably extends our knowledge about the Rydberg states in the carbon monoxide molecule as a whole. Additionally, the experimental data obtained for the extensively perturbed  $A^1\Pi$  state in the  $^{13}\text{C}^{17}\text{O}$  molecule could be used for a more precise characterization of this state.

By means of experiment it has been found that the  $A^1\Pi(v=1)$  level is affected by the  $a^3\Sigma^+(v=10)$  level, as well as by the  $D^1\Delta(v=1)$  level with level crossings occurring at  $J < 1$  and  $J = 27 - 28$ , respectively, for both  $e$ - and  $f$ -parity levels. According to our theoretical calculations the  $A^1\Pi(v=1)$  level should be affected also by the  $I^1\Sigma^-(v=2)$  with level crossing occurring at  $J = 35$  for the  $f$ -parity levels as well as by the  $e^3\Sigma^-(v=3)$  state at  $J = 43-44$  and at  $J = 40-41, 46-47$  for the  $f$ - and  $e$ -parity level, respectively. All of the observed perturbations in the  $A^1\Pi(v=1)$  state are completely in accordance with the theoretical predictions in the frame of this work except crossing level at  $J = 28-29$  for the  $e$ -parity of the  $A^1\Pi(v=1)$  level. All results are collected in Table 7.

We have also shown experimentally that the  $A^1\Pi(v=2)$  level has a strong interaction with the  $I^1\Sigma^-(v=3)$  state with level crossing occurring at  $J = 7-8$  for the  $f$ -parity levels and with the  $e^3\Sigma^-(v=4)$  state at  $J = 27-28$  for the  $f$ -parity levels and at  $J = 24-25, 31-32$  for the  $e$ -parity levels, as well as with the  $d^3\Delta(v=7)$  state with level crossing occurring at  $J = 31$  and  $J = 31-32, 34-35$  for the  $e$ - and  $f$ -parity levels, respectively. It has also been found that there is a strong interaction between the  $A^1\Pi(v=2)$  and  $a^3\Sigma^+(v=12)$  states, with level crossing occurring at  $J = 33-34$  for the  $f$ -parity level. According to our theoretical calculations, the subsequent perturbations of the  $A^1\Pi(v=2)$  should be caused by level crossing with the  $d^3\Delta(v=7)$  state at  $J = 35, 39$  for the  $e$ -parity and at  $J = 39$  for the  $f$ -parity levels as well as with the  $a^3\Sigma^+(v=12)$  level at  $36-37$  and  $39-40$  for the  $e$ - and  $f$ -parity levels, respectively. All of the observed in the  $A^1\Pi(v=2)$  state perturbations are completely in accordance with the theoretical predictions in the frame of this work (see Table 7).

The more precise estimates of the magnitudes of the perturbations values that appeared in the  $A^1\Pi(v=1, 2)$  state for both  $e$ - and  $f$ -parity levels of the  $^{13}\text{C}^{17}\text{O}$  molecule have been presented by means of the differences between the observed and calculated relative term values  $[T(v, J)_{\text{obs}} - T(v, J)_{\text{calc}}]$  (Fig. 9). It appears that the magnitude of the rotational terms shifts of the  $v=1$  level of the  $A^1\Pi$  state caused by interaction with the  $a^3\Sigma^+(v=10)$  at the beginning values of  $J$  equal to approximately  $0.5 - 0.7 \text{ cm}^{-1}$ , while the level crossing with the  $D^1\Delta(v=1)$  state at  $J = 27-28$  generates rotational term shifts of magnitude about  $2 \text{ cm}^{-1}$ . For the higher  $J$  values ( $J > 28$ ) we can see an anomalous course of the deviations of the terms shifts. It is caused by multi-state perturbation in this region.

Subsequently, the term shifts of the  $v=2$  level of the  $A^1\Pi$  state at  $J = 7-8$  are caused by the influence of the  $I^1\Sigma^-(v=3)$ , the maximum of which is revealed, and is quite small, equaling approxi-

mately  $0.15 \text{ cm}^{-1}$ . Incomparably, the largest magnitude of the term shifts occur at  $J > 22$  and equal on average approximately  $3-5 \text{ cm}^{-1}$ , but can reach even approximately  $10 \text{ cm}^{-1}$  for the  $F_1(34)$  term. This substantial shift is caused by multi-state interactions with the  $d^3\Delta(v=7)$ ,  $a^3\Sigma^+(v=12)$ , and  $e^3\Sigma^-(v=4)$  states. The simultaneous interaction of a several states in this area causes a non-characteristic course of rovibrational term shifts, with corresponding effects on the  $f_x(J)$  and  $g_x(J)$  functions, especially for the  $0-2$  band of the  $B^1\Sigma^+-A^1\Pi$  system in the  $^{13}\text{C}^{17}\text{O}$  molecule.

In conclusion, we believe that the present results, where we have analyzed the Ångström ( $B^1\Sigma^+-A^1\Pi$ ) system in the rare  $^{13}\text{C}^{17}\text{O}$  isotopologue for the first time, significantly extend and improve the spectroscopic and quantum-mechanical data about the energetic structure of the CO molecule.

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